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Mono- and binuclear complexes of group 5 metals with diimine ligands: synthesis, reactivity and prospects for application

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Published data on the coordination compounds of group 5 metals with diimine type ligands are surveyed. Methods of synthesis, structural types, reactivity and properties of these compounds are summarized and systematized. Particular attention is paid to the redox, magnetic and catalytic properties and to biological activities of these complexes, which is important for understanding the areas of their potential application.
The bibliography includes 177 references.

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1. Introduction

The coordination chemistry of group 5 metals — vanadium, niobium and tantalum — is an actively developing area of modern chemistry and is closely connected with other areas such as materials science, catalysis, biology and medicine.[1–4] Coordination compounds of vanadium attract considerable attention, which is due, first of all, to their catalytic properties in diverse organic reactions[5–14] and biological activity (insulin-enhancing effect, antidiabetic and antitumour activities).[15–19] These aspects of vanadium chemistry are addressed in quite a few reviews and book chapters that appeared in the last 20 years. One of the latest reviews published by American scientists[20] surveys the papers of the period from 2008 to 2018 devoted to homogeneous and heterogeneous catalysts based on vanadium compounds. On the other hand, paramagnetic vanadium(III and IV) complexes are used as building blocks for the design of bi- and polynuclear structures exhibiting ferro- and antiferromagnetic exchange interactions, which is promising for the development of new magnetic materials.[21,22]

Niobium and tantalum complexes attract much less attention than vanadium complexes, although an obvious interest in the coordination chemistry of these metals has appeared in recent years.[23–25] This is indicated by recent reviews concerning applications of these compounds in catalysis[26,27] and for activation of small molecules, including dinitrogen,[28] white phosphorus[29] and carbon dioxide.[30]

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Being class A elements (Pearson's hard Lewis acids), group 5 metals form stable coordination compounds, mainly with O- and N-donor ligands. In this respect, noteworthy is the pronounced proneness of vanadium to form oxo derivatives. More than 5000 structures containing a V=O group are available in the Cambridge Crystallographic Data Centre alone. Vanadium is highly prone to form complexes with O,N-donor chelating Schiff bases. These complexes mimic the active sites of vanadium-dependent haloperoxidases and nitrogenases and catalyze reactions accompanied by oxygen transfer and C–H activation.[31–36] Niobium and tantalum complexes containing N-donor ligands (amides, imides, *etc.*) attract attention as precursors of NbN and TaN thin films, which are used in various types of detectors.[25,37–43]

Vanadium, niobium and tantalum complexes with N-donor diimine ligands are also widely used. A distinctive feature of these ligands is their redox-active nature, *i.e.*, they can occur in different oxidation states within a complex. Therefore, they are often used to stimulate the redox reactivity of metal complexes.[44–56] Group 5 metals can also exist in different oxidation states: for vanadium, oxidation states from +3 to +5 are rather common, but lower oxidation states down to −1 are also possible; niobium and tantalum usually exist in the high oxidation state (+5), but can also exist in +3 and +4 oxidation states. Therefore, combinations of group 5 metal ions and redox-active diimine ligands are highly demanded for catalytic processes involving electron transfer.[57–72] Currently, there are no integrating publications devoted to diimine complexes of group 5 metals; only niobium and tantalum complexes with 1,4-diazabuta-1,3-dienes are mentioned in a review[73] of 2001, dealing with half-sandwich complexes of early transition metals. The present review summarizes all currently known data on the coordination compounds of vanadium, niobium and tantalum with diimine type redox-active ligands, particularly, 1,4-diazabuta-1,3-dienes (DAD) and acenaphthenequinone-1,2-diimines (acenaphthene-1,2-diimines, bian), and with heterocyclic compounds — 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen) and their derivatives. The information is arranged according to the class of ligands (α-diimines and heterocyclic compounds), the type of metal, nuclearity (mono- and binuclear complexes) and to the presence of the M=O oxo group. Polynuclear compounds are beyond the scope of this review. The emphasis is placed on the properties (redox, magnetic, catalytic) and biological activities of these complexes.

The following designations and abbreviations are used:

Ad — 1-adamantyl,
AIBN — azobis(isobutyronitrile),
Ar-bian — bis(aryl)acenaphthenequinone-1,2-diimine,
bian — acenaphthenequinone-1,2-diimine,
bpy — 2,2′-bipyridine,
Cat — catalyst,
C.N. — coordination number,
Cp — cyclopentadienyl,
Cp* — pentamethylcyclopentadienyl,
cur — curcumin,
Cy — cyclohexyl,
DAD — 1,4-diazabuta-1,3-diene,
dbbpy — 4,4′-di-*tert*-butyl-2,2′-bipyridine,
dcbpy — 2,2′-bipyridine-3,4-dicarboxylic acid,
DFT — density functional theory,
dmbpy — 4,4′-dimethyl 2,2′-bipyridine,
DME — 1,2-dimethoxyethane,
dmphen — 4,7-dimethyl-1,10-phenanthroline,
dnbpy — 4,4′-di(non-5-yl)-2,2′-bipyridine,
dpp — 2,6-diisopropylphenyl,
DPPH — 1,1-diphenyl-2-picrylhydrazyl,
dppz — dipyrido[3,2-*a*:2′,3′-*c*]phenazine,
dpq — dipyrido[3,2-*d*:2′,3′-*f*]quinoxaline,
EAS — electronic absorption spectrum,
EG — ethylene glycol,
esv — (2*R*,4*R*,9*R*,11R)-3,3,10,10-tetramethyl-1,2,3,4,6,7,9,10,11,12-decahydro-2,4,9,11-dimethanodibenzo [*b*,*j*][1,10]phenanthroline,
Fc — ferrocene,
GSSG — glutathione,
Hacac — acetylacetone,
Hbmp — bis(4-methoxyphenyl)phosphinic acid,
H_4bta — benzene-1,2,4,5-tetracarboxylic acid,
H_2ca — chloranilic acid,
H_3cht — *cis*,*cis*-cyclohexane-1,3,5-triol,
Hdppa — diphenylphosphinic acid,
H_2dtbc – 3,5-di-*tert*-butylcatechol,
HER — hydrogen evolution reaction,
HFS — hyperfine structure,
H_2fum — fumaric acid,
Hglyc — glycolic acid,
Hlact — lactic acid,
HMDSO — hexamethyldisiloxane,
HOMO — highest occupied molecular orbital,
Hpbz — 2-(2-pyridyl)benzimidazole,
H_4peol — 2,2-bis(hydroxymethyl)propane-1,3-diol (pentaerythritol),
Hpiv — pivalic acid,
HTcac — trichloroacetic acid,
HTCSQ — tetrachlorosemiquinone,
HTfac — trifluoroacetic acid,
H_3thme — 1,1,1-tris(hydroxymethyl)ethane,
H_3tmp — 1,1,1-tris(hydroxymethyl)propane,
IDA — iminodiacetate,
MAO — methylaluminoxane,
MMA — methyl methacrylate,
PCA — pyrazine-2-carboxylic acid,
PDT — photodynamic therapy,
phen — 1,10-phenanthroline,
Ph_2phen — 4,7-diphenyl-1,10-phenanthroline,
Si-Me-CHD — 1-methyl-3,6-bis(trimethylsilyl)cyclohexa-1,4-diene,
TBHP — *tert*-butyl hydroperoxide,
TEMPO — (2,2,6,6-tetramethylpiperidin-1-yl)oxyl,
TfO — trifluoromethanesulfonate (triflate),
UE — unpaired electron,
VHPO — vanadium-dependent haloperoxidase,
A_{iso} — isotropic hyperfine coupling constant,
A_{xx}, A_{yy}, A_{zz} — hyperfine splitting constants,
B — magnetic field induction,
E — electrode potential,
$E^{Red}_{1/2}$ — half-wave reduction potential,
$E^{Ox}_{1/2}$ — half-wave oxidation potential,
ε — molar absorption coefficient,
g_{iso} — isotropic g-factor,
g_{xx}, g_{yy}, g_{zz} — g-factors along the x, y, z axes, respectively,
I — nuclear spin of the metal,
μ_{eff} — effective magnetic moment,
μ_B — Bohr magneton,
χ_m — molar magnetic susceptibility,
θ — Weiss constant.

2. Metal complexes with 1,4-diazabuta-1,3-dienes and acenaphthene-1,2-diimines

Unique redox properties of diimine ligands are key parameters determining their high utility in coordination chemistry.[74–85] When incorporated in metal complexes, they can occur in three main redox states: neutral, radical anion and dianion states.[52, 86, 87] Furthermore, some metal complexes tend to undergo reversible intramolecular electron transfer (redox isomerism),[77, 82, 84, 85, 88, 89] which opens up prospects for the design of new magnetic materials based on these complexes.

2.1. Vanadium

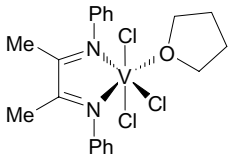
Vanadium complexes with ligands of this type are not abundant. The two known vanadium(III) complexes, [V(Me-Ph-DAD)(THF)Cl_3] (**1**) and [V(H-dpp-DAD)Cl_3] (**2**) [Me-Ph-DAD† is 2,3-dimethyl-1,4-diphenyl-1,4-diazabuta-1,3-diene, dpp is 2,6-diisopropylphenyl, H-dpp-DAD is 1,4-bis(2,6-diisopropylphenyl)-1,4-diazabuta-1,3-diene] were prepared from [V(THF)$_3$$Cl_3$] in 68% and 59% yields, respectively.[90] In complex **2**, the H-dpp-DAD ligand with bulky substituents at the nitrogen atoms stabilizes the coordination number (C.N.) equal to five for the metal. In this case, the vanadium atom has a trigonal-bipyramidal environment, instead of the octahedral one present in complex **1**. In both complexes, the DAD ligands occur in the neutral form.

Complexes **1** and **2** exhibit catalytic properties towards ethylene polymerization after methylaluminoxane (MAO) or $AlEt_2Cl$ activation. They show relatively high activity when used in combination with $AlEt_2Cl$ in toluene at −40 °C. The catalyst efficiency increases with temperature rise and with increasing concentration of the aluminium co-catalyst.

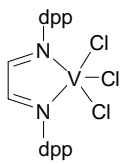
Danish researchers[85] reported the synthesis of octahedral tris-chelates with the acenaphthene-1,2-diimine derivative Ar-bian (Ar is 3,5-dimethylphenyl): [V(Ar-bian)$_3$] (**3**) and [V(Ar-bian)$_3$](PF_6) (**4**). Complex **3** was synthesized by the reaction of [V(THF)$_3$$Cl_3$] with Li(Ar-bian) taken in a 3 equiv. amount, while compound **4** was formed upon the one-electron oxidation of complex **3** with $FcPF_6$ (Fc^+ is ferrocenium) (Scheme 1).

† In the acronyms of symmetrical diazabutadienes, the first substituent is attached to carbon atoms and the second one is attached to nitrogen atoms.

Structures 1, 2



1



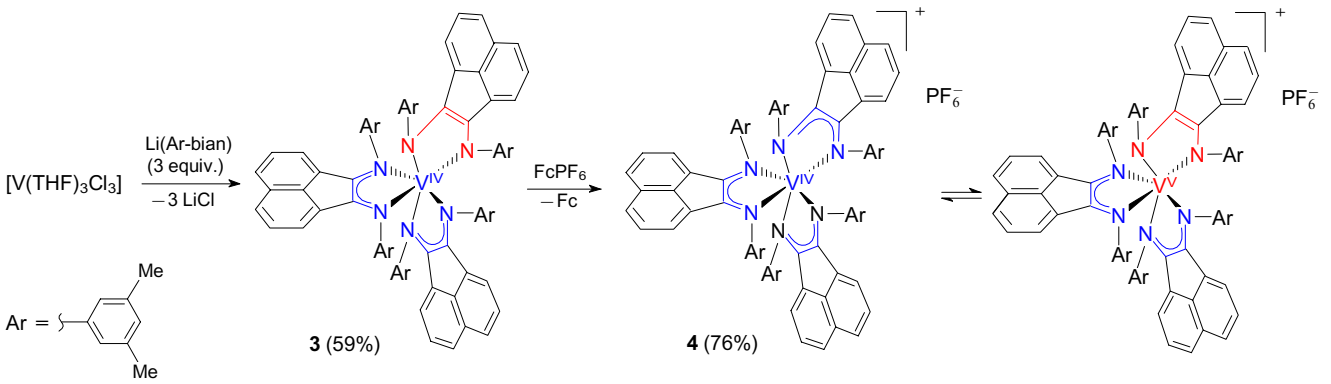
2

Figure 1 shows the cyclic voltammograms of solutions of complexes **3** and **4** in THF.[85] The complexes demonstrate similar redox behaviours, including four quasi-reversible one-electron processes. Nevertheless, two additional quasi-reversible processes were detected for the latter complex in a wider potential range, at −3.62, −2.65, −1.97, −1.07, −0.68 and +0.46 V (*versus* an Fc^+/Fc electrode). The observed pattern of redox transitions for compounds **3** and **4** is very similar to that for the analogous titanium complex [Ti(Ar-bian)$_3$] (Ar is 3,5-dimethylphenyl).[85] This means that these redox processes are mainly ligand-centred. However, the moderate positive shift of potentials observed for vanadium complexes implies that the energy of the highest occupied molecular orbital (HOMO) is lower for complexes **3** and **4** than for the analogous titanium complex. The processes at −0.68 and +0.46 V refer to the $[VL_3]^{2+}$/$[VL_3]^+$ and $[VL_3]^{3+}$/$[VL_3]^{2+}$ pairs, respectively, whereas the transitions at −1.07 −1.97, −2.65 and −3.62 V correspond to the $[VL_3]^+$/$[VL_3]^0$, $[VL_3]^0$/$[VL_3]^-$, $[VL_3]^-$/$[VL_3]^{2-}$ and $[VL_3]^{2-}$/$[VL_3]^{3-}$ pairs, respectively (L means a ligand).

The above complexes differ in the magnetic behaviours. Compound **3** shows temperature-independent paramagnetism (see curve *1* in Fig. 1), while compound **4** demonstrated a wide spin transition at a temperature of ~150 K. The effective magnetic moment (μ_{eff}) at 5 K is 1.33 μ_B (μ_B is the Bohr magneton), indicating the presence of antiferromagnetic exchange. Upon spin transition, the μ_{eff} value increases to approximately 3.41 μ_B. This is due to the fact that complex **4** exists as two valence tautomers depending on temperature: at < 150 K, complex **4** can be described by the formula $[V^V(Ar\text{-}bian^{2-})(Ar\text{-}bian^{\bullet-})_2]^+$, while at > 150 K, it is described as $[V^{IV}(Ar\text{-}bian^{\bullet-})_3]^+$. This phenomenon is called valence tautomerism (or redox isomerism) and has been considered in detail by Bendix and Clark.[85]

A recently reported series of isostructural mononuclear vanadium(III) complexes **5**–**10** has the general formula [V(Ar-bian)(THF)Cl_3], where Ar = 2,6-$Me_2C_6H_3$ (**5**),

Scheme 1



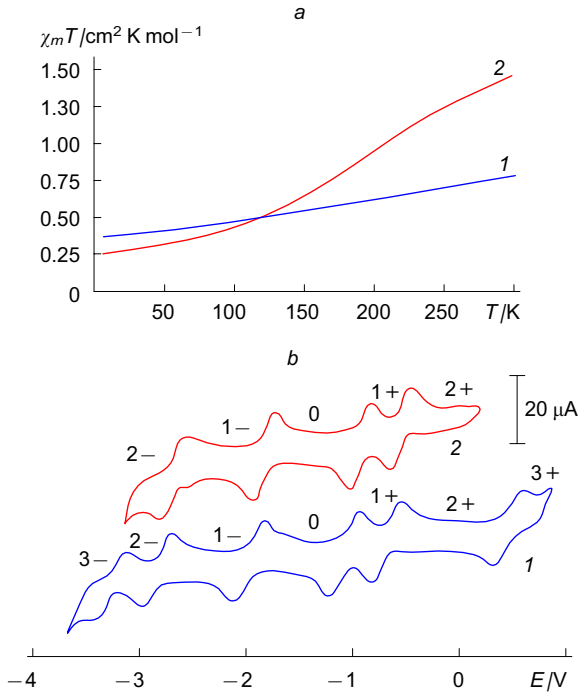
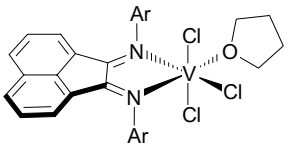


Figure 1. Temperature dependences of $\chi_m T$ (χ_m is the molar magnetic susceptibility) (*a*) and cyclic voltammograms of THF solutions *versus* Fc^+/Fc (*b*) for complexes **3** (*1*) and **4** (*2*).[85] The concentration of $(Bu^n_4N)PF_6$ is 0.1 mol L^{-1}, the sweep rate is 200 mV s^{-1}. *E* is the electrode potential.

2,6-$Et_2C_6H_3$ (**6**), 2,6-$Pr^i_2C_6H_3$ (**7**), 3,5-$(F_3C)_2C_6H_3$ (**8**), 4-$MeOC_6H_4$ (**9**), 2,6-$(Ph_2CH)_2$-4-$MeOC_6H_2$ (**10**). All complexes were synthesized by a procedure that included the reaction of $[V(THF)_3Cl_3]$ with the appropriate diimine. In these compounds, the vanadium atom has a distorted octahedral geometry formed by two diimine nitrogen atoms, the oxygen atom of the solvent molecule and three chlorine atoms in the *mer*-orientation.[91] Complexes **5**–**10** are structurally similar to the compound *mer*-$[V(L_{NN})(MeCN)Cl_3]$, where L_{NN} is 2,2′-bipyridine or 1,10-phenanthroline (see Section 4.1.1).

Structures 5–10

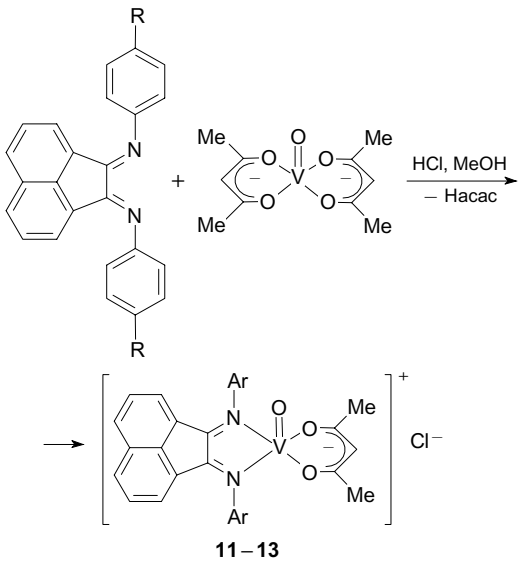


Ar = 2,6-$Me_2C_6H_3$ (**5**, 82%),
2,6-$Et_2C_6H_3$ (**6**, 81%),
2,6-$Pr^i_2C_6H_3$ (**7**, 87%),
3,5-$(F_3C)_2C_6H_3$ (**8**, 76%),
4-$MeOC_6H_4$ (**9**, 78%),
2,6-$(Ph_2CH)_2$-4-$MeOC_6H_2$ (**10**, 82%)

These vanadium(III) complexes catalyze the polymerization of ethylene in the presence of $AlEt_2Cl$ to give linear polymers with high molecular mass. Complex **7** with 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-bian) proved to be a more active catalyst than other compounds.[91]

There are four oxovanadium complexes with bian type ligands. Three similar complexes, [VO(Ar-bian)(acac)]Cl [Ar = Ph (**11**), 4-MeC_6H_4 (**12**) and 4-ClC_6H_4 (**13**); Hacac is acetylacetone], were not structurally characterized (Scheme 2). They catalyze the oxidation of alkenes such as cyclohexene, *cis*-cyclooctene, styrene, (*S*)-(−)- and (*R*)-(+)-

Scheme 2



11–**13**

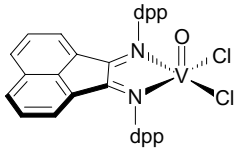
Ar = Ph (**11**, 88%), 4-MeC_6H_4 (**12**, 86%), 4-ClC_6H_4 (**13**, 90%)

pinenes and (*S*)-(−)- and (*R*)-(+)-limonenes with *tert*-butyl hydroperoxide (TBHP) or H_2O_2. In the case of enantiopure alkenes, the reaction proceeds selectively to give the corresponding epoxides. Complex **13** with Ar = 4-ClC_6H_4 proved to be most active in the styrene epoxidation on treatment with H_2O_2, while its analogue **12** with Ar = 4-MeC_6H_4 showed the highest activity in the epoxidation of *cis*-cyclooctene with TBHP. Kinetic data indicate that the first step (reaction of the catalyst with the oxidant) follows an associative pathway, and in the case of complex **11**, the product of this reaction $[VO(Ph\text{-}bian)(acac)(TBHP)]^+$ was isolated. Acording to density functional theory (DFT) calculations, the vanadium(IV) complex $[VO(Ph\text{-}bian)(MeOO)]^+$ is the most likely active species of this process. Two competing pathways are possible, one involving the reaction of the alkene with the coordinated peroxide and another one involving the reaction of the peroxide with the coordinated alkene.[92]

One more example of oxovanadium diimine complexes is $[VO(dpp\text{-}bian)Cl_2]$ (**14**), prepared recently by the reaction of VCl_3 with dpp-bian in acetonitrile in air. Unlike complexes **11**–**13**, this compound was studied by X-ray diffraction. The coordination environment of vanadium is a distorted square pyramid, in which two N atoms and two Cl atoms are located in the equatorial plane, while the terminal oxygen atom occupies the axial position.[63]

Complex **14** is paramagnetic and has a typical EPR spectrum consisting of eight lines, which is usual for vanadium(IV) complexes. At 300 K, the efficient magnetic moment is 1.67 μ_B; this value does not change as the temperature decreases down to 2 K, which attests to the absence of considerable exchange interactions and to separation of paramagnetic centres.[63]

Structure 14

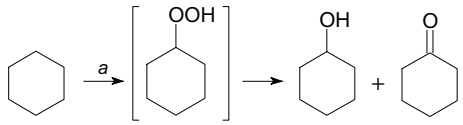


14

The cyclic voltammogram of complex **14** in CH_2Cl_2 exhibits two quasi-reversible reduction steps at −0.32 and −1.05 V (*versus* Ag/AgCl); presumably, these reactions are ligand-centred and can be assigned to the bian/bian$^{\bullet-}$ and bian$^{\bullet-}$/bian^{2-} pairs in view of the ability of the acenaphthene diimine moiety to successively accept two electrons to give the acenaphthylene diamide dianion.[63]

Complex **14**, when used in combination with pyrazine-2-carboxylic acid (PCA) as a co-catalyst, shows a high catalytic activity towards the oxidation of cyclohexane with hydrogen peroxide at moderately elevated temperature (40–50 °C) (Scheme 3). The yields of the resulting cyclohexanol and cyclohexanone are 28.2% and 8.7%, respectively;[63] this is comparable with the catalytic activity of the complexes $[VO(L_{NN})X_2]$ (L_{NN} = bpy, phen; X = Cl, Br)[64] discussed in Section 4.1.4.

Scheme 3

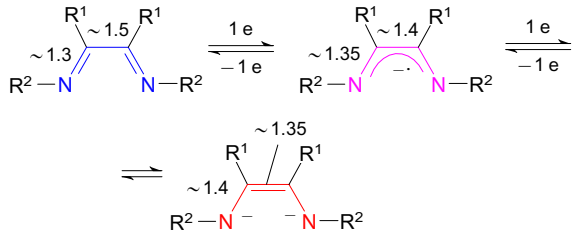


(*a*) H_2O_2, Cat, MeCN, 40 °C, 6 h; Cat is the catalyst

2.2. Niobium and tantalum

Niobium and tantalum are more prone to form complexes with 1,4-diazabuta-1,3-diene ligands than vanadium. As noted above, these ligands are redox active and can occur in coordination compounds in neutral, radical anion and dianion states. Each state is characterized by particular bond lengths of the diimine moiety (Scheme 4; the bond lengths are given in nm). For this reason, metal complexes with DAD ligands are actively used as catalysts in various redox reactions.

Scheme 4



Apart from the unique redox properties, the DAD ligands can be coordinated to the metal in a great variety of modes, as shown by structures **A**–**F** (Fig. 2). The neutral diimine form can be coordinated in the η^2(N,N) (**C**) and η^2(C,N) (**E**) modes. Structure **C** exists in the complexes [V(Me-Ph-DAD)(THF)Cl_3] and [V(H-dpp-DAD)Cl_3], which have been considered above.[90] The DAD dianion tends to occur in the η^2 (**A**) and $\eta^4(\sigma,\pi)$ (**B**) coordination modes, and in rare cases, the μ-η^1,η^1 bridging coordination is possible (**F**). In the case of the radical anion form, structure **D** with η^2(N,N) coordination mode is formed.

For early transition metal complexes, structure **B**, characterized by additional π-interaction between the metal and the C=C bond, is formed most frequently. This interaction makes the DAD ligand non-planar (the C, N and metal atoms do not lie in one plane). This gives rise to different possible orientations for the non-planar DAD ligand, *supine* (facing upwards) or *prone* (facing downwards). The *supine* and *prone* orientations are mainly typical of half-sandwich cyclopentadienyl complexes (see Section 2.3). In the case of *supine* conformation, the substituents R at the nitrogen atoms point upwards, towards the cyclopentadienyl (Cp) ligand. Conversely, the *prone* conformation implies that the groups R point away from this ligand (Fig. 3).

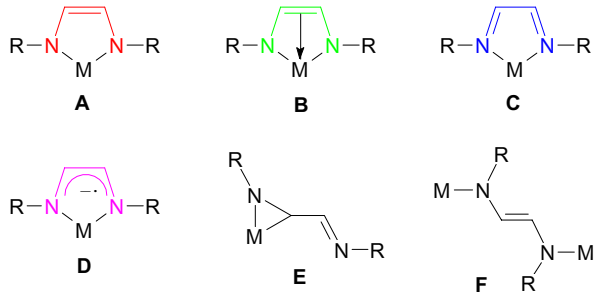


Figure 2. Coordination modes of the DAD ligand to the metal (M).

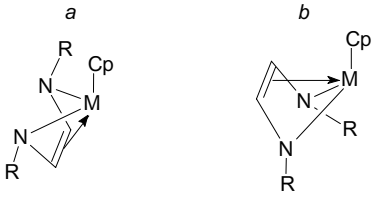
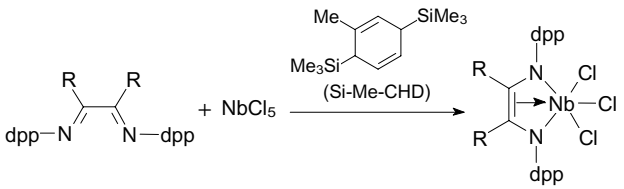


Figure 3. *Supine* (*a*) and *prone* orientations (*b*) of the DAD ligand.

The niobium complex [Nb(DAD)X_n] (n = 3, 4) is prepared from niobium(V) halides NbX_5 (X = F, Cl, Br) by ligand exchange reactions. Thr complexes [Nb(η^4-*supine*-R-dpp-DAD)Cl_3] [R = Me (**15**), H (**16**)] were obtained by reactions of $NbCl_5$ with substituted DAD in 1 : 1 ratio in the presence of 1-methyl-3,6-bis(trimethylsilyl)cyclohexa-1,4-diene (Si-Me-CHD) in toluene (Scheme 5). The diimine ligand is coordinated to niobium in the dianion form to form structure **B**.[93]

Scheme 5

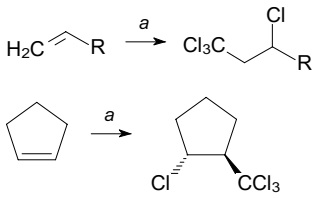


R = Me (**15**, 65%), H (**16**, 91%)

15, **16**

Complex **15** catalyzes the radical addition of CCl_4 to various alkenes in toluene at 100 °C (Scheme 6). The product yield and the degree of substrate conversion considerably depend on the nature of substituent. In the case of R = n-C_6H_{13}, these values approach 100%. High activity (the yield and conversion of >90%) is also observed for R = 4-MeC_6H_4, 4-ClC_6 H_4 and 3-MeC_6H_4; in other cases, these characteristics are <85%. The reaction involving cyclopentene has a high stereoselectivity giving only *trans*-1-chloro-2-(trichloromethyl)cyclopentane in 62% yield.

Scheme 6

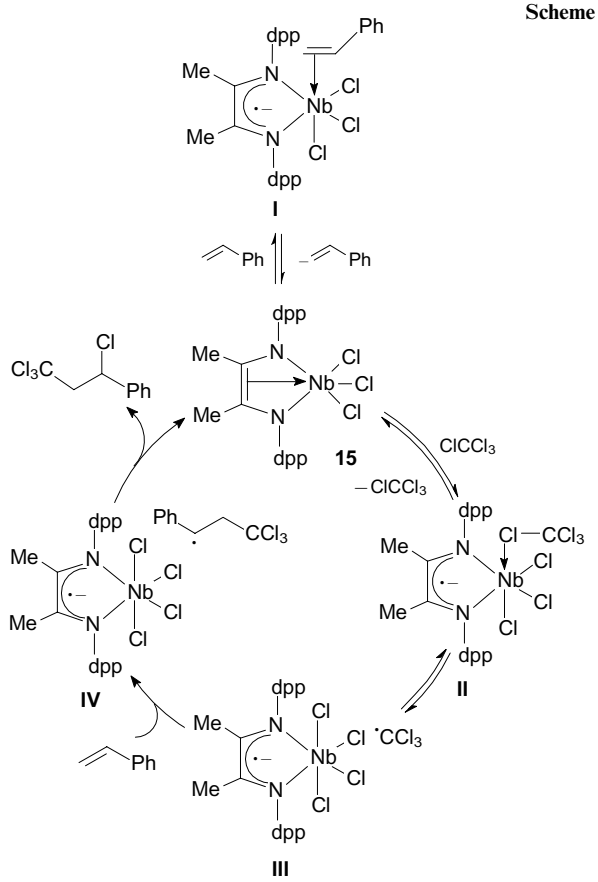


(*a*) CCl_4, Cat, 100 °C; R = 4-MeC_6H_4, 4-ClC_6H_4, 4-$F_3CC_6H_4$, 3-MeC_6H_4, 2-MeC_6H_4, n-C_6H_{13}, Cy, Bn; Cy is cyclohexyl

Therefore, the authors suggest that the reaction occurs within the niobium coordination sphere. For comparison, when [Nb(DME)Cl_3] (DME is 1,2-dimethoxyethane) is used as the catalyst, this reaction affords a mixture of *cis*- and *trans*-isomers in 1 : 5 ratio.[93]

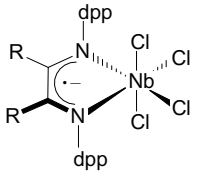
A mechanism has been proposed for this reaction; this mechanism, typical of niobium complexes with DAD ligands, is considered in relation to the reaction of styrene with CCl_4 (Scheme 7). It is noteworthy that styrene can react with initial complex **15** to give π-complex **I**. The coordination of styrene stimulates the electron transfer from the DAD^{2-} ligand to the metal, which changes the coordination of the DAD ligand from mode **B** to mode **D** (see Fig. 2). Nevertheless, complex **I** is not involved in the catalytic cycle; upon the addition of CCl_4, the initial complex is regenerated. First, CCl_4 reacts with [Nb(Me-dpp-DAD)Cl_3] to give niobium(IV) complex **II** containing the DAD ligand in the radical anion form, which is followed by reductive cleavage of the C–Cl bond to give niobium(V) derivative **III** and the $^{\bullet}CCl_3$ radical. The latter reacts with styrene within the coordination sphere of complex **III** to form structure **IV** and the $^{\bullet}CHPhCH_2$ CCl_3 radical. Then the organic radical abstracts a chloride ion from the metal centre of complex **IV**, which gives the reaction product and regenerates the initial complex. The key role in the generation of organic radicals is played by the redox-active DAD ligand, which facilitates the electron transfer from DAD to the substrate *via* the metal centre.[93]

Scheme 7



The formation of the intermediate complexes [Nb(η^2-R-dpp-DAD)Cl_4] [R = Me (**17**), H (**18**)], which correspond to intermediates **III** and **IV** in Scheme 7, was confirmed experimentally. Moreover, these complexes were isolated and structurally characterized in the reactions of $NbCl_5$ with R-dpp-DAD (R = Me, H) in the presence of Si-Me-CHD (0.5 equiv.).[93]

Structures 17, 18



17, **18**

R = Me (**17**, 59%), H (**18**, 65%)

Despite the similar composition and structure, these complexes have different EPR spectra (Fig. 4). The spectrum of compound **17** exhibits a signal consisting of 10 lines as a result of hyperfine coupling with the ^{93}Nb nucleus (nuclear spin I = 9/2). The isotropic hyperfine coupling constant (A_{iso}) equal to 105 G indicates that the unpaired electron (UE) is not completely localized on the metal, but has a contribution of the ligand. However, the EPR spectrum of complex **18** consists of 9 lines, and lower A_{iso} value (6.56 G) attests to complete localization of the unpaired

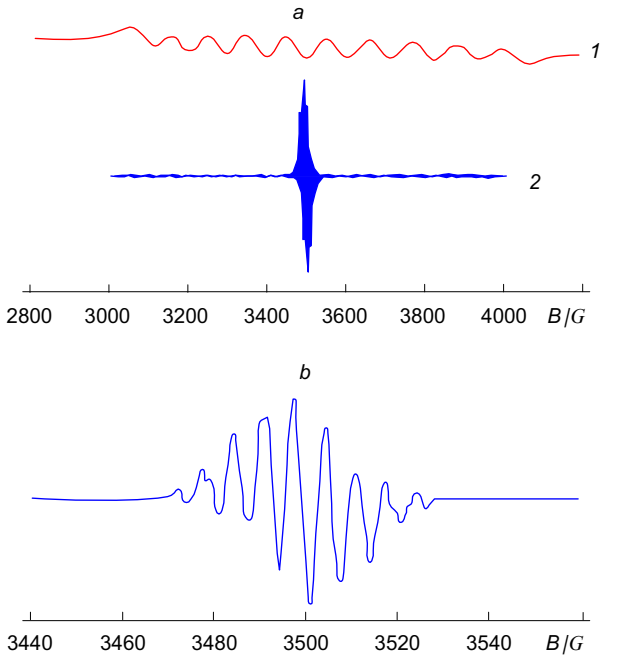
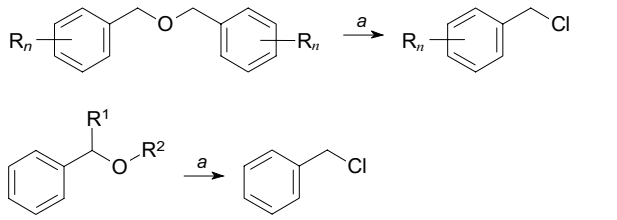


Figure 4. EPR spectra of complexes **17** (*1*) and **18** (*2*) in the 2800–4200 and 3000–4000 G ranges, respectively (*a*), and of complex **18** in the 3440–3560 G range (*b*).[93]
B is the magnetic field induction.

electron on the ligand.[93] A similar difference in the UE localization is also observed for tantalum complexes discussed below.[57]

Complexes of the [Nb(R^1-R^2-DAD)Cl_3] type also activate the C–O and C–Cl bonds. In particular, they catalyze the chlorination of benzyl ethers with silicon tetrachloride to give the corresponding benzyl chloride (Scheme 8). In these reactions, $SiCl_4$ acts simultaneously as an oxygen scavenger and the source of chloride ions. The reaction mechanism includes two successive etherification reactions, the first step giving one benzyl chloride molecule and silyl ether and the second step giving the other benzyl chloride molecule and silicon dioxide, which precipitates. Symmetrical and unsymmetrical substrates with a benzyl group were tested; in the latter case, the yields of products sharply decreased.[94] Analogous tantalum complexes also catalyze this reaction, but they are less efficient.

Scheme 8



(*a*) $SiCl_4$, Cat, $CDCl_3$; R_n = H, 4-Me, 2,4,6-Me_3, 4-OMe, 2-OMe, 4-Ph, 4-Cl, 4-F, *etc.*; R^1 = H, Me, Pr^n, Ph; R^2 = Et, All, n-C_6H_{13}, Ph, CPh_3

The authors note that benzyl groups in the ether molecule play an important role in stabilization of the radicals that are formed in the catalytic reaction. The reaction does not occur for substrates without these groups. The above-mentioned complex [Nb(η^4-*supine*-Me-dpp-DAD)Cl_3] (**15**) was most active in the chlorination of the substrates shown in Fig. 5.[94]

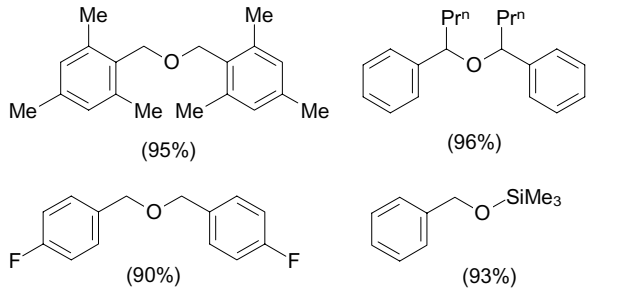
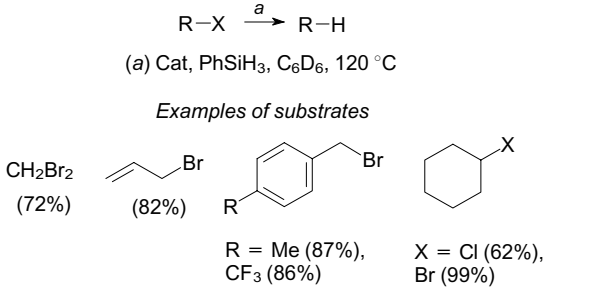


Figure 5. Benzyl type substrates used in the chlorination reactions catalyzed by complex **15** (the values in parentheses are the yields of the chlorination product).

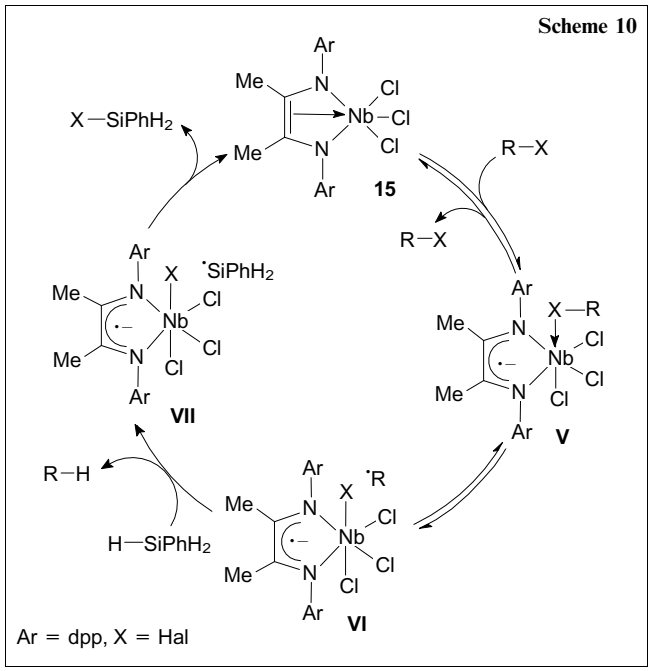
This complex catalyzes hydrodehalogenation of cyclic and acyclic halohydrocarbons in the presence of $PhSiH_3$ (Scheme 9; the values in parentheses are product yields).[95]

The putative mechanism of hydrodehalogenation is depicted in Scheme 10. The key role in the formation of hydrocarbon radicals is played by the redox-active DAD ligand. The first step is coordination of halohydrocarbon to the metal centre to give Nb^V complex **V** upon the transfer of one electron from the DAD ligand to the metal. The ligand

Scheme 9



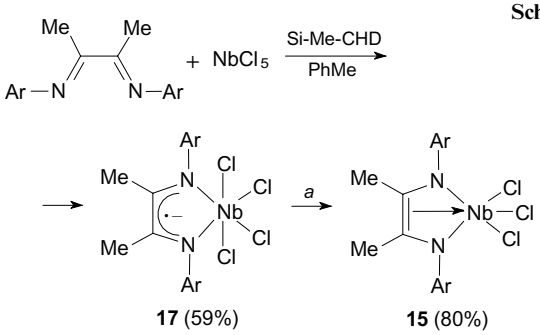
Scheme 10



is thus converted to the radical anion with a planar type of coordination (mode **D**, see Fig. 2). This is followed by electron transfer from Nb^{IV} to halohydrocarbon to give Nb^V complex **VI**, cleavage of the C–X bond and formation of the hydrocarbon radical. In the next step, the hydrocarbon radical reacts with $PhSiH_3$ to give the product RH and the $PhSiH_2^{\bullet}$ radical. In the last step, intermediate **VII** disproportionates to give $PhSiH_2$ and complex **15**.[95]

As noted above, the complex [Nb(η^2-Me-dpp-DAD)Cl_4] (**17**), corresponding to intermediate **VII**, was obtained by the reaction of $NbCl_5$ with Me-dpp-DAD in the presence of Si-Me-CHD (Scheme 11).[95] The reaction of compound **17** with $PhSiH_3$ affords [Nb(η^4-*supine*-Me-dpp-DAD)Cl_3] (**15**)

Scheme 11



(*a*) $PhSiH_3$, C_6D_6 (–$PhSiH_2Cl$); Ar = dpp

in high yield (80%). Thus, $PhSiH_3$ serves as not only the source of an H atom, but also as the reducing agent needed for reduction of intermediate **VII** to complex **15**.

The hydrodehalogenation reactions catalyzed by complex **15** can be used to convert toxic organic compounds, which have low reactivity by themselves, to less toxic products under mild conditions.[95]

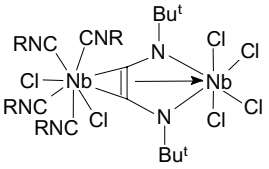
Professor Scholz's research team published a series of studies on niobium and tantalum complexes with DAD ligands. The reaction of $NbCl_5$ with Li_2(H-Bu^t-DAD)$(THF)_4$ gave complexes with different compositions and structures depending on the reactant ratio (Scheme 12). When the ratio was 1 : 3 and 1 : 2.5, binuclear complexes **19** and **20** were isolated. Compound **19** is a heterometallic complex where the Nb and Li atoms are connected by two bridging DAD ligands. They are coordinated to niobium in the η^2(C,N) mode (see structure E in Fig. 2) and to lithium in the η^2(N,N) mode (structure **A**). The third DAD ligand completes the octahedral environment of niobium, being coordinated in the $\eta^4(\sigma,\pi)$ mode (**B**).[96] Three different coordination modes of the H-Bu^t-DAD ligand are present simultaneously in binuclear complex **20**, in particular, $\eta^4(\sigma,\pi)$ (**B**), η^2(C,N) (**E**) and μ-η^1,η^1 (**F**).[96]

The mononuclear complexes *mer*-[Nb(H-Bu^t-DAD)$(THF)Cl_3$] (**21**) and [Nb(H-Bu^t-DAD)$_2$Cl] (**22**) are formed if the reactants are taken in 1 : 1 and 1 : 2 ratios, respectively. In addition, the complex (Bu^{t}NH$_3$)[Nb(H-Bu^t-DAD)Cl_4] (**23**) was isolated as a by-product in the synthesis of compound **21**. In these complexes, the ligand is coordinated in a mode **B** (see Scheme 12).[97]

Later, a similar procedure was applied to prepare complexes *fac*-[Nb(H-R-DAD)$(THF)Cl_3$] [R = Pr^i (**24**), Cy (**25**)] (Scheme 12) with strong C–H···X hydrogen bonds (~2.7 Å distance), retained in solution, between the chloride ligand and hydrogen at the α-carbon atom of the Pr^i or Cy substituent.[98] This gives rise to facial isomers instead of *mer*-forms, which are produced for compound **21**. One more distinction is that no additional π-interaction between the metal and the ligand is present in complexes **24** and **25**, and the Nb, C and N atoms are located nearly in the same plane (coordination mode **A**) (see Scheme 12).

A series of binuclear niobium and tantalum complexes [$M_2Cl_6(RNC)_4$(RNC═CNR)] [M = Nb, R = Bu^t (**26**), Cy (**27**); M = Ta, R = Pr^i (**28**)] were obtained in 60% or higher yields by reactions of $[M_2Cl_6(SMe_2)_3]$ with RNC in 1 : 10 ratio in toluene.[65, 99] This is a rare example of mixed-valence binuclear complexes containing M^{III} and M^V centres.

Structures 26, 27



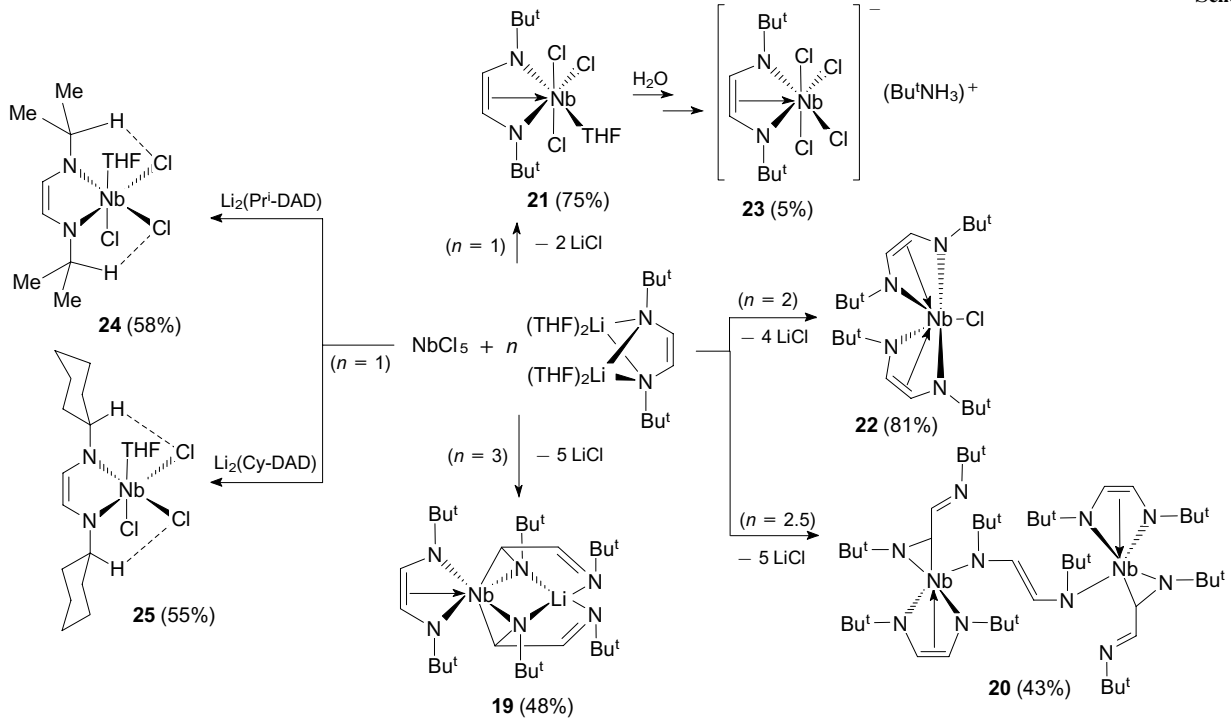
26, **27**

R = Bu^t (**26**), Cy (**27**)

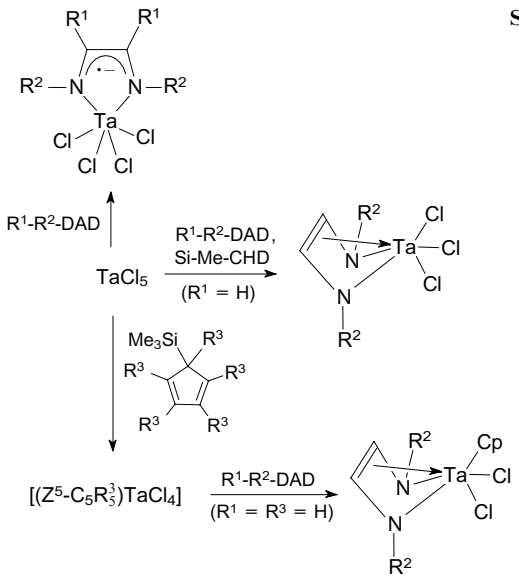
For [Nb_2Cl_6(Bu^{t}NC)$_4$(Bu^{t}NC═CNBu^t)] (**26**), the crystal structure was determined. The RNC═CNR ligand formed upon isocyanide dimerization is coordinated to the {$NbCl_2(RCN)_4$} moiety *via* two central carbon atoms and to the {$NbCl_4$} moiety *via* nitrogen atoms. In the {$NbCl_2(RCN)_4$} moiety, niobium has a distorted pentagonal-bipyramidal environment, whereas the niobium environment in {$NbCl_4$} is a distorted octahedron.[65, 99]

The chemistry of tantalum complexes with 1,4-diaza-1,3-butadiene ligands is similar to that of the niobium complexes. Tantalum also tends to form compounds of type [Ta(η^4-R^1-R^2-DAD)Cl_3], in which DAD ligands are bound to the metal in amode **B** (see Fig. 2). They are prepared by reactions of $TaCl_5$ with R^1-R^2-DAD in the presence of excess reducing agent. If the reducing agent is taken in deficiency, the reaction may give the complexes [Ta(η^2-R^1-R^2-DAD)Cl_4] with the DAD ligand in the radical

Scheme 12



Scheme 13

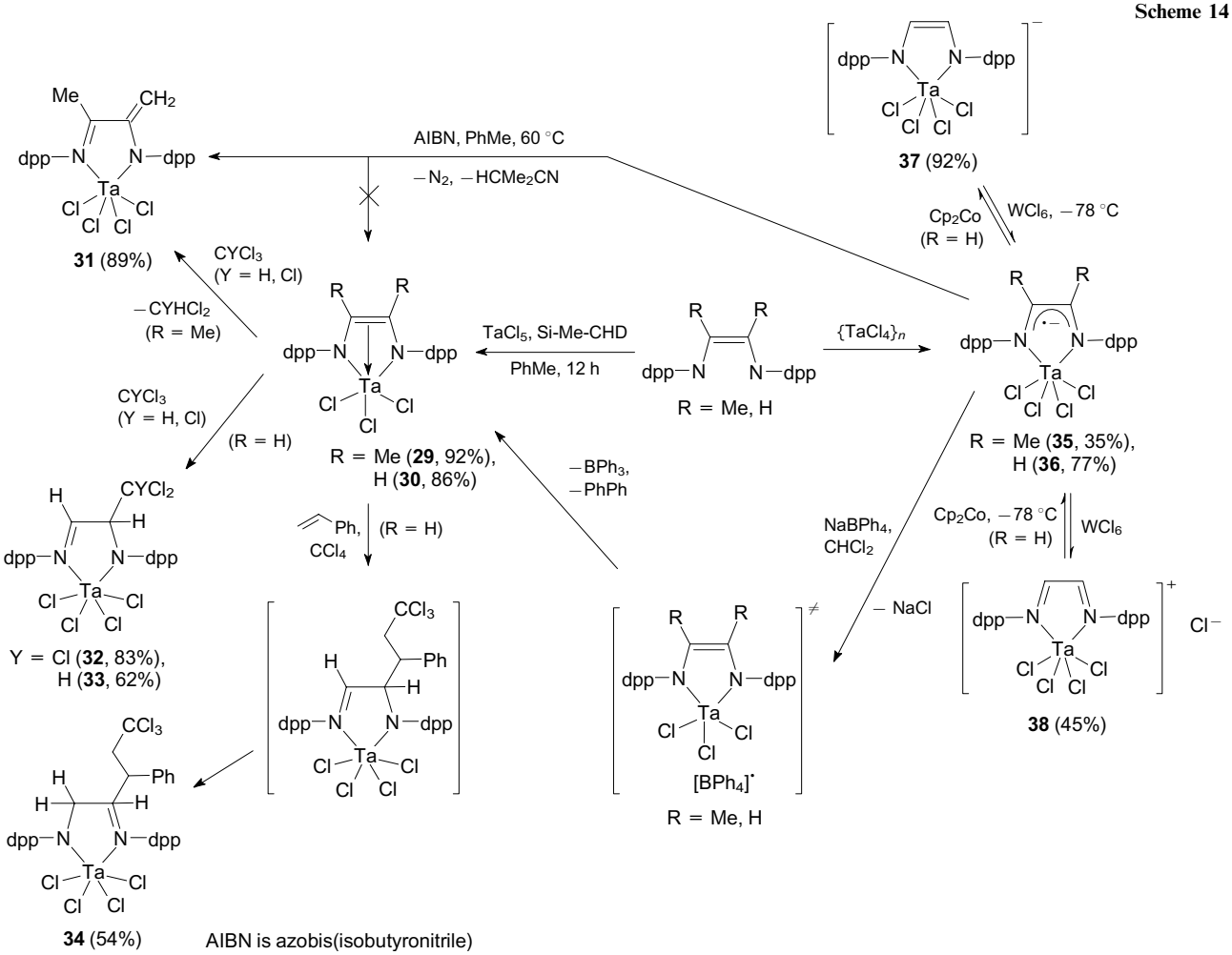


anion form (mode **D**). In addition, half-sandwich complexes $[(\eta^5\text{-}C_5R_5)Ta(\eta^4\text{-}R^1\text{-}R^2\text{-}DAD)Cl_2]$, which are prepared most often by displacement of chloride ligands from $[(\eta^5\text{-}C_5R_5)TaCl_4]$, are often encountered in the chemistry of tantalum (Scheme 13). For niobium, such complexes are less frequent and will be considered in more detail in Section 3.2.

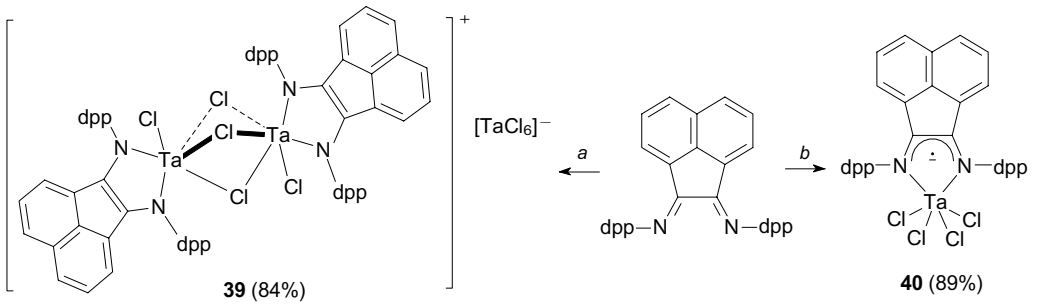
Systematic research in this field is carried out by Professor Mashima's group in Japan.[57] The authors prepared a wide range of high-valent tantalum complexes $[Ta(L_{NN})Cl_n]$ [L_{NN} = R-dpp-DAD (R = Me, H) and dpp-bian] (Scheme 14). The reactions of Me-dpp-DAD and H-dpp-DAD diimines with $TaCl_5$ in toluene in the presence of 1-methyl-3,6-bis(trimethylsilyl)cyclohexa-1,4-diene as a reducing agent give the complexes [Ta(η^4-*supine*-R-dpp-DAD)Cl_3] [R = Me (**29**), H (**30**)] in high yields. During the reaction, diimine is reduced and coordinated to the metal in the ene-diamide dianion form (see Scheme 14).[57]

Complexes **29** and **30** activate the C–Cl bond in reactions with alkyl halides ($CHCl_3$, CCl_4) giving compounds **31** (for R = Me) or **32** and **33** (for R = H). The formation of complex **31** is accompanied by insertion of methyl halide into the C–N bond followed by elimination and formation of the vinylidene group. In the case of complexes **32** and **33**, the insertion into the C–C bond can also take place, resulting in the formation of amide imine complexes. The authors suggest that the reaction starts with the electron transfer from the ene-diamide dianion ligand to $CYCl_3$ (Y = H, Cl), resulting in generation of $\{TaCl_4\}$ complexes with the DAD ligand in the radical anion form and also $^{\bullet}CYCl_2$ radicals followed by their into the C–C bond.[57] In addition, [Ta(η^4-*supine*-R-dpp-DAD)Cl_3] [R = Me (**29**), H (**30**)] catalyze the radical polymerization of styrene in the presence of chloroalkanes to give polystyrene in a yield of 26% and a polydispersity [the ratio of

Scheme 14



Scheme 15



39 (84%) **40** (89%)

(*a*) $TaCl_5$, Si-Me-CHD, PhMe, 12 h; (*b*) $\{TaCl_4\}_n$, PhMe, 15 h

weight-average to number-average molecular masses (M_w/M_n)] of 1.3 in the case of compound **29**. When homologue **30** was used in a similar reaction, only complex **34** was isolated (see Scheme 14).[57]

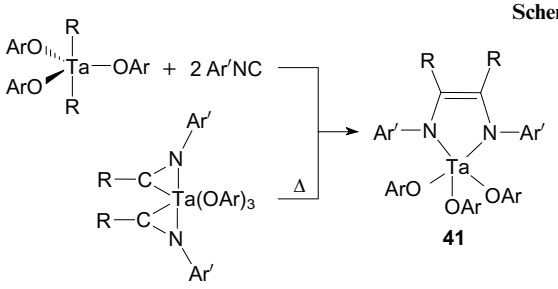
The reaction of $\{TaCl_4\}_n$ (obtained by the reaction of $TaCl_5$ with Si-Me-CHD in 2 : 1 ratio) with Me-dpp-DAD and H-dpp-DAD affords the complexes [Ta(η^2-R-dpp-DAD)Cl_4] [R = Me (**35**), H (**36**)], in which DAD occurs in the radical anion form (mode **D** in Fig. 2) (see Scheme 14). The cyclic voltammograms of these complexes exhibit two reversible one-electron redox processes: the reduction of [Ta(DAD)Cl_4]/[Ta(DAD)Cl_4]$^-$ [half-wave reduction potentials $E_{1/2}^{Red} = -0.47$ (**35**), -0.39 V (**36**)] and the oxidation of [Ta(DAD)Cl_4]/[Ta(DAD)Cl_4]$^+$ [half-wave oxidation potentials $E_{1/2}^{Ox} = -0.01$ (**35**), 0.11 V (**36**)]. Therefore, the complexes can be reduced with Cp_2Co; for example, complex **37** was prepared and then converted back to compound **36** *via* the reaction with WCl_6. Further oxidation of **36** with WCl_6 gives complex **38**, which can be reduced back to compound **36** on treatment with Cp_2Co.[57] Complexes **35** and **36** react with $NaBPh_4$ to be converted to compounds **29** and **30**, respectively (see Scheme 14). During this reaction, the DAD ligand accepts an electron from the BPh_4^- anion, generating the ene-diamide dianion form of the ligand (coordination mode **B** in Fig. 2) with the *supine* orientation. In addition, complex **35** reacts with AIBN to afford compound **31**.[57]

It is noteworthy that the use of acenaphthene-1,2-diimine (dpp-bian) instead of DAD does not give [Ta(dpp-bian)Cl_3] under similar conditions, but affords instead the binuclear complex [{Ta(dpp-bian)Cl}$_2$(μ-Cl)$_3$][$TaCl_6$] (**39**) (Scheme 15). This compound contains the [{Ta(dpp-bian)Cl}$_2$(μ-Cl)$_3$]$^+$ cation in which each tantalum atom has a distorted octahedral geometry, with the ligand being in the dianion form. No formation of binuclear complexes was detected in the case of DAD ligands. Similarly to the synthesis of [Ta(η^2-R-dpp-DAD)Cl_4] [R = Me (**35**), H (**36**)], the reaction of $\{TaCl_4\}_n$ with dpp-bian resulted in the isolation of [Ta(dpp-bian)Cl_4] (**40**).[57]

The diimine complex [Ta(Ar′NC(R)=C(R)NAr′)(OAr)$_3$] (Ar′ = 2,6-dimethylphenyl, R = Bn) (**41**) is obtained by reactions of [Ta(OAr)$_3$R$_2$] with aryl isocyanide 2,6-$Me_2C_6H_3NC$ (Scheme 16).[58] The same complex is also formed upon thermolysis of the bis(iminoacyl) derivative [Ta(OAr)$_3$(Ar′NCR)$_2$] in toluene.[100]

The coordination environment of tantalum in complex **41** can be described as a trigonal bipyramid. The nitrogen atoms of the ene-diamide ligand occupy one axial and one equatorial positions. The TaN_2C_2 metallacycle has a nearly planar orientation (mode **A** in Fig. 2). Niobium complexes

Scheme 16



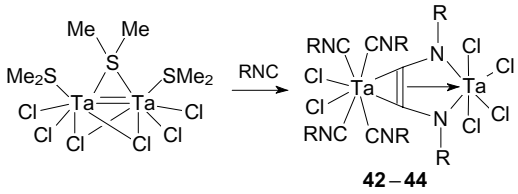
41

Ar′ = 2,6-$Me_2C_6H_3$, R = Bn

of this type are rather prone to nonplanar ligand coordination due to additional π-interaction between the metal and the C=C bond.[100]

The reactions of the binuclear complex [$Ta_2C1_6(SMe_2)_3$] with the isocyanides RNC (R = Bu^t, Pr^i and Cy), like these reactions of niobium, are accompanied by dimerization of isocyanide to give binuclear the complexes [Ta_2Cl_6(RNC)$_4$(μ-RNC=CNR)] (**42**–**44**) (Scheme 17).[99]

Scheme 17

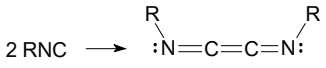


42–**44**

R = Bu^t (**42**), Pr^i (**43**), Cy (**44**)

The mechanism of formation of the bridging pseudo-diimine ligand in these compounds is not entirely clear. The authors suggest that the reaction starts with the binding of two isonitrile molecules to give a linear heterocumulene molecule (Scheme 18).[99]

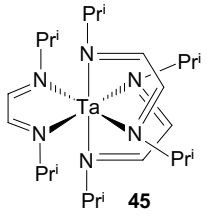
Scheme 18



In this molecule, the π-orbital of the C=N bond should be perpendicular to the plane of the drawing, while the π-orbital of the C=C bond should lie in this plane. Upon interaction with a Lewis acid (in this case, the metal centre), it is coordinated to the C=C bond. As this takes place, the ligand conformation changes to enable interaction with one more metal ion *via* nitrogen.[99]

The formally zerovalent 17-electron complex [Ta(H-Pr^i-DAD)$_3$] (**45**) is formed in the reaction of $TaCl_5$ with 5 equiv. of sodium naphthalenide and 3.5 equiv. of H-Pr^i-DAD in dimethoxyethane. (In the case of niobium, the reaction proceeds in a similar way.) Tantalum complex **45** was structurally characterized. All DAD ligands incorporated in the complex have a planar conformation and are coordinated to the metal in the η^2(N,N) mode (see structure **C** in Fig. 2). This compound is paramagnetic (μ_{eff} = 1.66 μ_B at 11 K) and has one unpaired electron (d^5 electron configuration).[101]

Structure 45



45

The oxidation of complex **45** on treatment with $AgBPh_4$ gives rise to the diamagnetic 16-electron complex [M(H-Pr^i-DAD)$_3$][BPh_4] (**46**) (d^4 electron configuration).[101]

3. Mixed-ligand metal complexes containing the {(η^5-C_5R_5)M(DAD)} moiety (M = Nb, Ta)

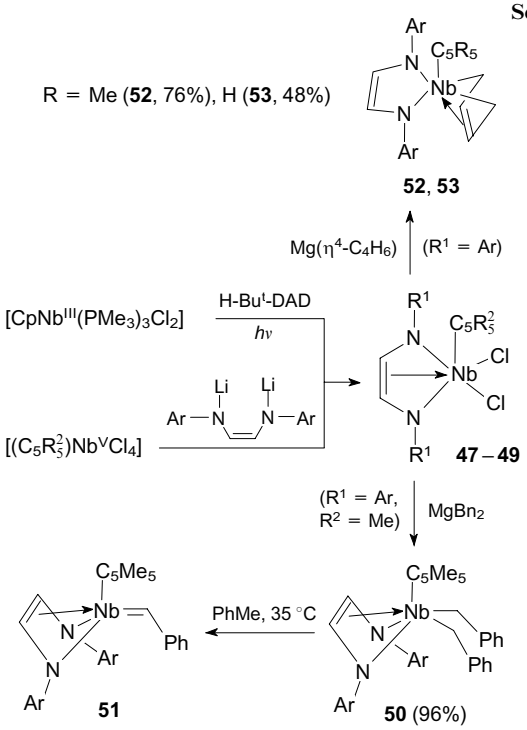
Cyclopentadienyl complexes of transition metals are extensively studied in relation to their high catalytic activity, in particular in polymerization reactions. The presence of 1,4-diazabuta-1,3-diene as an additional ligand in these complexes improves their catalytic characteristics because of redox-active nature of the DAD ligand and the possibility of varying the nature of substituents at nitrogen and carbon atoms. Niobium and tantalum, unlike vanadium, tend to form mixed-ligand half-sandwich high-valent complexes. Usually, the structures of these complexes have a 'piano stool' geometry, which is typical of half-sandwich cyclopentadienyl complexes. Furthermore, as noted above, DAD ligands can occur in different conformations, *supine* and *prone* (see Fig. 3).

3.1. Niobium

The complex [(Cp)Nb^V(H-Bu^t-DAD)Cl$_2$] (**47**) was prepared in 45% yield by the reaction of [(Cp)Nb^{III}(PMe$_3$)$_3$Cl$_2$] with H-Bu^t-DAD in 1 : 1.5 ratio in toluene under light irradiation with a power of 125 W (Scheme 19). The DAD moiety is η^4(σ,π)-coordinated to niobium (see structure **B** in Fig. 2) in the *supine* orientation relative to the Cp ligand. The back π-donation from the ligand to the metal is necessary to counterbalance the electron density deficit on pentavalent niobium.[102]

One more method for the preparation of half-sandwich niobium(V) complexes is based on reactions of an appropriate compound of pentavalent metal with the DAD ligand reduced to the dianion taken as the lithium salt. For example, the complexes [(η^5-C_5R_5)Nb(η^4(σ_2,π)-*supine*-H-Ar-DAD)Cl$_2$] [Ar = 4-MeOC$_6$H$_4$; R = Me (**48**), H (**49**)] are formed in reactions of [(η_5-C_5R_5)Nb^{V}Cl$_4$] with 1 equiv. of Li$_2$[H-(4-MeOC$_6$H$_4$)-DAD] in 32% and 18% yields, respectively (see Scheme 19).[103] Dialkylation of compound **48** with $MgBn_2$ affords [Cp*Nb(η^4-*prone*-H-Ar-DAD)(CH$_2$Ph)$_2$] (Cp* = η^5-C$_5$Me$_5$, Ar = 4-MeOC$_6$H$_4$) (**50**), while the orientation of the DAD ligand changes from *supine* to *prone*. This complex is unstable in solution and decomposes to the benzylidene complex [Cp*Nb(=CHPh)(η^4-*prone*-H-Ar-DAD)] (Ar = 4-MeOC$_6$H$_4$) (**51**).[103] Reactions of this type are also typical of tantalum compounds (see Section 3.2.).

Scheme 19

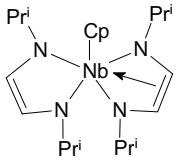


Ar = 4-MeOC$_6$H$_4$; R^1 = Bu^t, R^2 = H (**47**); R^1 = Ar: R^2 = Me (**48**), H (**49**)

The reactions of complexes **48** and **49** with a minor excess of magnesium buta-1,3-dienyl [Mg(C_4H_6)] afford [(η^5-C_5R_5)Nb(η^2-H-Ar-DAD)(η^4-*supine*-buta-1,3-diene)] [Ar = 4-MeOC$_6$H$_4$; R = Me (**52**), H (**53**)] (see Scheme 19). In these compounds, coordination mode **A** is implemented.[103]

The complex [CpNb(H-Pr^i-DAD)$_2$] (**54**) was prepared in 63% yield by the reaction of $CpNbCl_4$, H-Pr^i-DAD ligand and sodium amalgam in THF at −40 °C. Both DAD ligands occur as dianions, but they are coordinated to niobium in different modes. One ligand is coordinated in a mode **B** in the *supine* orientation, while the other is virtually planar and is coordinated in a mode **A**.[104]

Structure 54

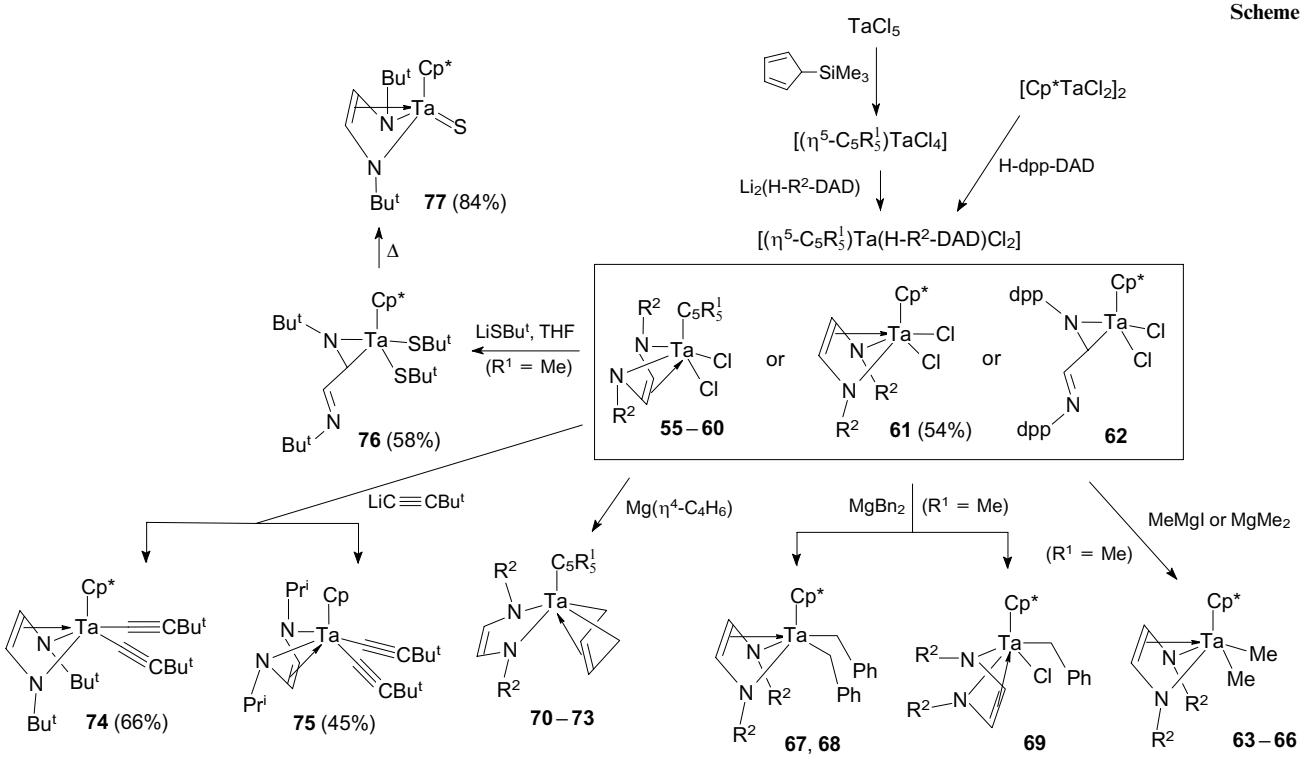


54

3.2. Tantalum

The reaction of [(η^5-$C_5R^1_5$)Ta^{V}Cl$_4$] (R = H, Me) with 1 equiv. of Li$_2$(H-R^2-DAD) in THF gives the complexes [(η^5-$C_5R^1_5$)Ta^V(η^4-*supine*-H-R^2-DAD)Cl$_2$] [R^1 = H, R^2 = 4-MeOC$_6$H$_4$ (**55**); R^1 = Me, R^2 = 4-MeOC$_6$H$_4$ (**56**), 4-MeC$_6$H$_4$ (**57**), 2-MeC$_6$H$_4$ (**58**), Cy (**59**), Pr^i (**60**)] and

Scheme 20



R^1 = H, R^2 = 4-MeOC$_6$H$_4$ (**55**; **70**, 56%); R^1 = Me: R^2 = 4-MeOC$_6$H$_4$ (**56**; **63**, 81%; **67**, 91%; **71**, 52%), 4-MeC$_6$H$_4$ (**57**; **72**, 60%), 2-MeC$_6$H$_4$ (**58**; **64**, 76%; **69**, 43%), Cy (**59**; **68**, 83%; **73**, 59%), Pr^i (**60**; **65**, 40%), Bu^t (**61**; **66**, 28%)

[Cp*Ta^V(η^4-*prone*-H-Bu^t-DAD)Cl$_2$] (**61**). The complex [Cp*Ta^{III}(η^2-H-dpp-DAD)Cl$_2$] (**62**) results from the oxidation of the binuclear tantalum(III) complex [Cp*TaCl$_2$]$_2$ in the presence of dpp-DAD (Scheme 20).[103, 105]

In complexes **55** – **61**, DAD ligands exist in the ene-diamide dianion form and are η^4-coordinated to the metal centre by two nitrogen atoms and two carbon atoms *via* additional π-interaction (mode **B** in Fig. 2), but have different conformations. In compounds **55** – **60**, the R-DAD ligands adopt a *supine* conformation relative to the cyclopentadienyl ligand. Conversely, the *prone* conformation is observed in [Cp*Ta(H-Bu^t-DAD)Cl$_2$] (**61**) because of steric crowding (the Bu^t groups point away from Cp*). In the complex [Cp*Ta(H-dpp-DAD)Cl$_2$] (**62**), rare η^2(C,N) coordination mode is implemented (see structure **E** in Fig. 2); the same coordination mode was found in [Nb$_2$(H-Bu^t-DAD)$_5$] (**20**).[96, 103, 105]

The halogen atoms in [(η^5-C$_5$R$^1_5$)Ta^V(H-R^2-DAD)Cl$_2$] can be replaced by other ligands *via* reactions depicted in Scheme 20. Dialkylation reactions give coordination compounds [Cp*TaMe$_2$(η^4-*prone*-H-R-DAD)] [R = 4-MeOC$_6$H$_4$ (**63**), 2-MeC$_6$H$_4$ (**64**), Pr^i (**65**), Bu^t (**66**)] and [Cp*Ta(CH$_2$Ph)$_2$(η^4-*prone*-H-R-DAD)] [R = 4-MeOC$_6$H$_4$ (**67**), Cy (**68**)], while the orientation of DAD ligands changes from *supine* to *prone*. The replacement of one chlorine atom by the benzyl group gives the derivative [Cp*Ta(CH$_2$Ph)(η^4-*supine*-H-(2-MeC$_6$H$_4$)-DAD)Cl] (**69**), in which the *supine* orientation is retained. The complexes [Cp*Ta(CH$_2$Ph)$_2$(η^4-*prone*-H-R-DAD)] decompose in a toluene solution to give the benzylidene complexes [Cp*Ta(=CHPh)(R-DAD), which are considered below in more detail.[103]

The butadiene complexes [(η^5-C$_5$R$^1_5$)Ta(η^2-H-R^2-DAD)(η^4-buta-1,3-diene)] [R^1 = H, R^2 = 4-MeOC$_6$H$_4$ (**70**); R^1 = Me, R^2 = 4-MeOC$_6$H$_4$ (**71**), 4-MeC$_6$H$_4$ (**72**), Cy (**73**)] were obtained by reactions of [(η^5-C$_5$R$^1_5$)Ta^V(H-R^2-DAD)Cl$_2$] (**55** – **57**, **59**) with Mg(C$_4$H$_8$)$_2$. In this case, the coordination of the DAD ligand changes from η^4-*supine* to the virtually planar η^2-(N,N) (mode **A**), while the butadiene ligand is coordinated in the η^4-mode with *supine* orientation (similarly to mode **B** in the case of DAD ligands) (see Scheme 20).[103, 106]

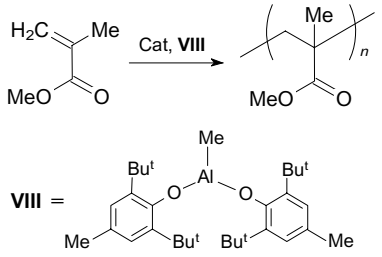
The reactions between [Cp*Ta(H-Bu^t-DAD)Cl$_2$] (**61**) and LiC≡CBu^t generate the acetylide complexes [(η^5-C$_5$R$^1_5$)Ta(η^4-H-R^2-DAD)(C≡CBu^t)$_2$] [R^1 = Me, R^2 = Bu^t (**74**); R^1 = H, R^2 = Pr^i (**75**)]. In both complexes, the DAD ligand exists in the ene-diamide form, follows coordination mode **B**, and has the *prone*-orientation in complex **74** and *supine* orientation in complex **75** (see Scheme 20).[105]

Compound **61** reacts with LiSBu^t to give the complex [Cp*Ta(H-Bu^t-DAD)(SBu^t)$_2$] (**76**), in which DAD is η^2(C,N)-coordinated (mode **E** in Fig. 2). Heating of derivative **76** in toluene induces C – S bond cleavage to afford [Cp*TaS(H-Bu^t-DAD)] (**77**), in which the DAD ligand has a η^4(σ$_2$,π) conformation (mode **B**) with the *prone* orientation, like in the initial complex **61** (see Scheme 20).[105]

Complexes **71** and **73** catalyze polymerization of methyl methacrylate (MMA) in the presence of aluminium-based co-catalyst **VIII** (Scheme 21). The **73** – **VIII** – MMA system (1 : 10 : 100) showed the best results in this reaction, providing a quantitative product yield and low polydispersity (M_w/M_n = 1.4).[107]

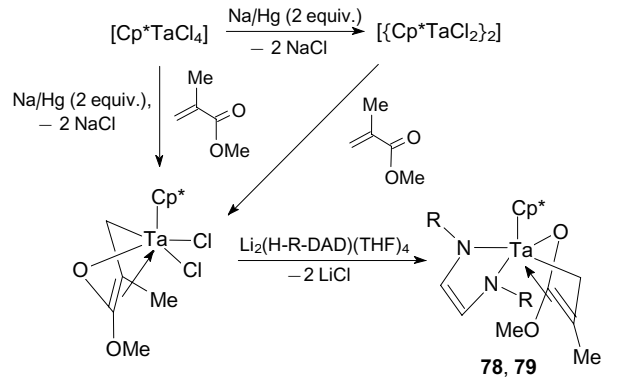
A similar polymerization reaction is also catalyzed by the complexes [Cp*Ta(η^2-H-R-DAD)(η^4-*supine*-MMA)]

Scheme 21



[R = 4-MeOC$_6$H$_4$ (**78**), Cy (**79**)], which are formed upon the reaction of [Cp*Ta(η^4-*supine*-MMA)Cl$_2$] with Li$_2$(R-DAD)(THF)$_4$. The complex [Cp*Ta(η^4-*supine*-MMA)Cl$_2$] can be prepared in two different ways, as shown in Scheme 22. Compounds AlR$_3$ (R = Me, Et) or AlEt$_2$Cl were used as co-catalysts. The authors note that without a co-catalyst, the complexes do not exhibit catalytic activity. The best results were shown for the **78**–AlMe$_3$–MMA system (1 : 1 : 100); the quantitative product yield was attained in 10 min and the polydispersity index was relatively low (M_w/M_n = 1.1).[108]

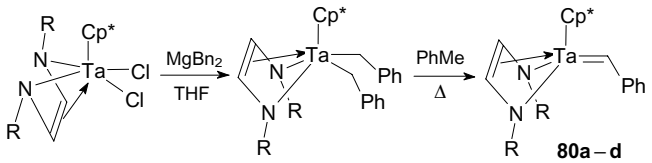
Scheme 22



R = 4-MeOC$_6$H$_4$ (**78**), Cy (**79**)

As noted above, the bis-benzyl complexes [Cp*Ta(CH$_2$Ph)$_2$(η^4-*prone*-DAD)] are converted to the benzylidene complexes [Cp*Ta(=CHPh)(η^4-DAD)].[103] Subsequently, the same group of authors extended the range of benzylidene complexes of tantalum and obtained products [Cp*Ta(=CHPh)(η^4-*prone*-H-R-DAD)] (**80a**–**d**) (Scheme 23).[109]

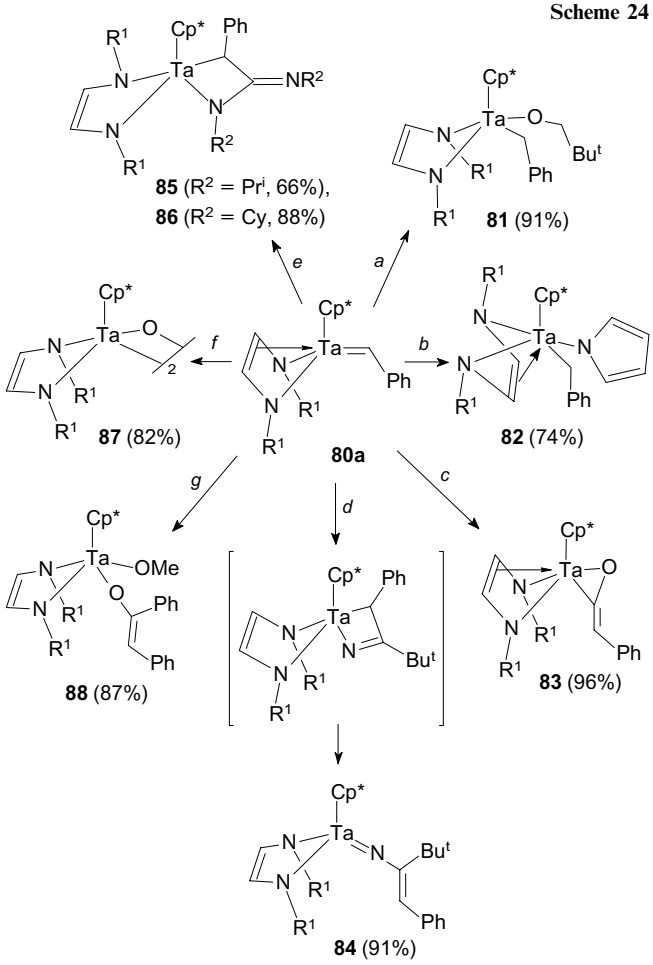
Scheme 23



R = 4-MeOC$_6$H$_4$ (**a**, 83%), 4-MeC$_6$H$_4$ (**b**, 75%), 4-FC$_6$H$_4$ (**c**, 80%), 4-ClC$_6$H$_4$ (**d**, 81%)

These complexes proved to be fairly reactive. Their characteristic reactions are summarized in Scheme 24 in relation to [Cp*Ta(=CHPh)(η^4-*prone*-H-(4-MeOC$_6$H$_4$)-DAD)] (**80a**).[109] The reaction of compound **80a** with neopentyl alcohol in toluene at −78 °C includes protonation of the benzylidene group, resulting in the formation of [Cp*Ta(OCH$_2$Bu^t)(CH$_2$Ph)(η^2-N,N′-*prone*-H-(4-MeOC$_6$H$_4$)-DAD)] (**81**). In complex **81**, the DAD ligand is coordinated in the η^2-N,N′ mode with a partial contribution of the η^4-*prone* coordination.

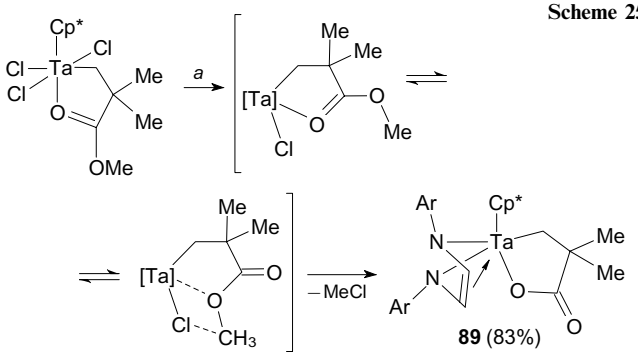
Scheme 24



(*a*) Bu^{t}CH$_2$OH, PhMe, −78 °C; (*b*) pyrrole, PhMe, 80 °C; (*c*) CO (1 atm), PhMe; (*d*) Bu^{t}CN, PhMe, −78 °C; (*e*) R^{2}N=C=NR^2; (*f*) PhC(O)Me, PhMe, −78 °C; (*g*) PhCO$_2$Me, hexane, 50 °C; R^1 = 4-MeOC$_6$H$_4$

Similarly, compound **80** reacts with pyrrole in toluene to give the complex [Cp*Ta(η^1-NC$_4$H$_4$)(CH$_2$Ph)(η^4-*supine*-H-(4-MeOC$_6$H$_4$)-DAD)] (**82**) in a moderate yield. In this case, the DAD ligand orientation changes from *prone* to *supine*. The reaction with CO affords [Cp*Ta(η^2-OC=CHPh)(η^4-*supine*-H-(4-MeOC$_6$H$_4$)-DAD)] (**83**) in a quantitative yield, while the reactions with Bu^{t}CN and carbodiimides (Pr^{i}N=C=NPr^i and CyN=C=NCy) give the imide complex {Cp*Ta[=NC(Bu^t)=CHPh](η^2-*prone*-H-(4-MeOC$_6$H$_4$)-DAD)} (**84**) and the azametallacyclobutane complexes {Cp*Ta[NR^{2}C(=NR^2)CHPh](η^2-*supine*-H-(4-MeOC$_6$H$_4$)-DAD)} [R = Pr^i (**85**), Cy (**86**)]. In addition, compound **80** reacts with acetophenone and methyl benzoate. In the former case, the binuclear complex [Cp*Ta(μ-O)(η^2-*prone*-H-(4-MeOC$_6$H$_4$)-DAD)]$_2$ (**87**) is formed, while in the latter case, the complex [Cp*Ta(OMe)(OC(Ph)=CHPh)(η^2-*prone*-H-(4-MeOC$_6$H$_4$)-DAD)] (**88**) is produced as a result of C–O bond cleavage in the ether (see Scheme 24).

Scheme 25

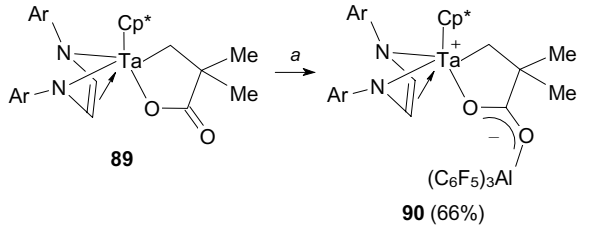


(*a*) Li_2(H-(4-$MeOC_6H_4$)-DAD), THF, −78 °C;
[Ta] = Cp*Ta(H-(4-$MeOC_6H_4$)-DAD), Ar = 4-$MeOC_6H_4$

One more half-sandwich tantalum complex [Cp*Ta(η⁴-H-(4-$MeOC_6H_4$)-DAD)($CH_2CMe_2CO_2$)] (**89**) was obtained by the reaction of [Cp*Ta($CH_2CMe_2CO_2Me$)Cl_3] with 1 equiv. of Li_2[H-(4-$MeOC_6H_4$)-DAD] in THF at −78 °C (Scheme 25).[110]

This reaction starts with the transformation of the homoenolate moiety into the lactone one *via* C–O bond cleavage of the ether group, which is followed by chloroform elimination to give complex **89**. This product is a rare example of metallalactone complexes of early transition metals. The crystal structure of [Cp*Ta(η⁴-*supine*-H-(4-$MeOC_6H_4$)-DAD)($CH_2CMe_2CO_2Al(C_6F_5)_3$)] (**90**), resulting from the reaction of compound **89** with $Al(C_6F_5)_3$, was determined by X-ray diffraction (Scheme 26).[110]

Scheme 26



(*a*) $Al(C_6F_5)_3$, C_6D_6; Ar = 4-$MeOC_6H_4$

4. Complexes with 2,2-bipyridine, 1,10-phenanthroline and their derivatives

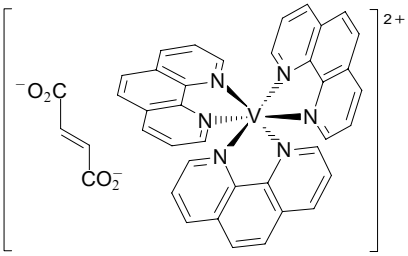
4.1. Vanadium

4.1.1. Complexes without an oxovanadium group

Octahedral vanadium tris-chelates $[V(L_{NN})_3]^n$ (L_{NN} are 2,2′-bipyridine and 1,10-phenanthroline derivatives) have been studied more extensively than their α-diimine or acenaphthene-1,2-diimine analogues. The complexes $[V(bpy)_3]^n$ ($n = -3, -1, 0, +1, +2$) synthesized under supervision of Professor Herzog in Germany have been known since the 1950s. Much later, the vanadium(IV) complex {[V(phen)$_3$](fum)}$(OH)_2 \cdot 10\,H_2O$ (**91**) (H_2fum is fumaric acid) was synthesized in 23% yield by the reaction of sodium orthovanadate, malic acid and 1,10-phenanthroline in the presence of hydrazine under hydrothermal conditions.[111] In air, this compound rapidly loses water molecules of solvation. Under the reaction conditions, the malate anion is dehydrated to fumarate.

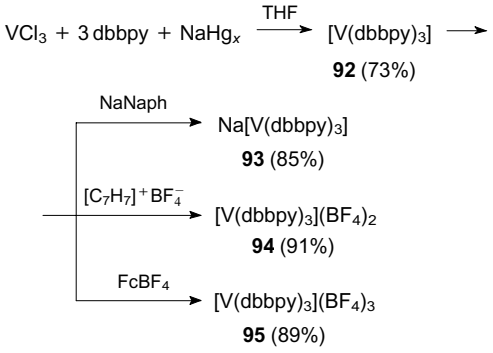
In addition, several vanadium complexes with 4,4′-di-*tert*-butyl-2,2′-bipyridine (dbbpy) with the composition $[V(dbbpy)_3]^n$, where $n = 0$ (**92**), −1 (**93**), + 2 (**94**), + 3 (**95**), have been prepared.[112] None of these compounds was structurally characterized. The neutral complex $[V(dbbpy)_3]$ (**92**) is formed upon the reaction of vanadium(III) chloride with 3 equiv. of the ligand and sodium amalgam and THF (Scheme 27).

Structure 91



91

Scheme 27



Complex **92** is unstable and is oxidized and hydrolyzed in air. Charged complexes were prepared from the neutral compound. The reduction of $[V(dbbpy)_3]$ with sodium naphthalenide (NaNaph) in THF furnishes the highly unstable anionic complex Na[V(dbbpy)$_3$] (**93**). Complexes with a charge of +2 (**94**) and +3 (**95**) were prepared by the oxidation of the neutral complex with tropylium tetrafluoroborate and $FcBF_4$, respectively (see Scheme 27). Whereas $[V(dbbpy)_3]^{2+}$ is sensitive to oxygen, $[V(dbbpy)_3]^{3+}$ proves to be stable in air. The complex $[V(dbbpy)_3]^+$ is not produced under these conditions, but disproportionates to $[V(dbbpy)_3]$ and $[V(dbbpy)_3]^{2+}$ (Ref. 112).

According to spectral data, vanadium in $[V(dbbpy)_3]^{3+}$ (**95**) is in the trivalent state, *i.e.*, its electron configuration is d^2. The formation of the doubly charged complex $[V^{II}(dbbpy)_3]^{2+}$ can be represented as a result of metal-centred one-electron reduction of $[V^{III}(dbbpy)_3]^{3+}$. The next one-electron reduction is ligand-centred and yields the compound $[V^{II}(dbbpy^{\bullet-})(dbbpy)_2]^+$ with the radical anion form of one of the three diimine ligands. Finally, the neutral complex $[V^{II}(dbbpy^{\bullet-})_2(dbbpy)]$ contains two ligands in the radical anion form. In the negatively charged complex $[V^{II}(dbbpy^{\bullet-})_3]^-$, all three ligands are radical anions, while vanadium is still in +2 oxidation state.[112]

The cyclic voltammogram of $[V(dbbpy)_3]$ in THF exhibits three reversible one-electron oxidation waves at −1.78, −1.66 and −0.09 V (*versus* the Fc^+/Fc pair), which correspond to the +1/0, +2/+1 and +3/+2 redox pairs of vanadium (Fig. 6). In addition, a reversible one-electron

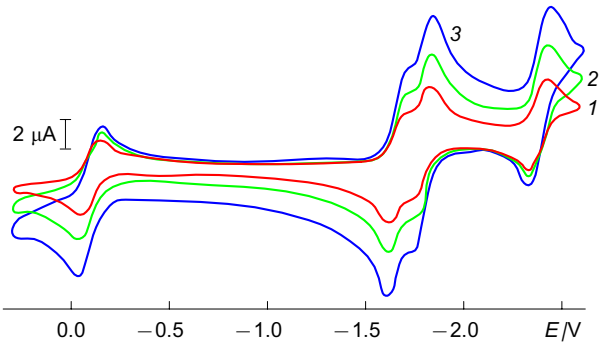


Figure 6. Cyclic voltammogram of $[V(dbbpy)_3]$ (**92**) in THF (0.1 M $Bu^n_4NPF_6$) for sweep rates of 100 (*1*), 200 (*2*) and 400 mV s^{-1} (*3*).[112]

reduction takes place at −2.38 V (corresponds to the 0/−1 pair) and is followed by irreversible reduction at −2.79 V. This reduction is apparently associated with the formation of the $[V(dbbpy)_3]^{2-}$ anion, unstable under these conditions,[112] which is also confirmed by the absence of data on dianionic and trianionic complexes, despite the reported isolation of $Na_3[V(bpy)_3]\cdot 7\,THF$.[113]

For all paramagnetic compounds — $[V(dbbpy)_3]$ (**92**), $[V(dbbpy)_3]^{2+}$ (**94**) and $[V(dbbpy)_3]^{3+}$ (**95**) — the temperature dependence of the magnetic susceptibility was studied in the 4–290 K range. The authors detected that $[V(dbbpy)_3]$ (**93**) is diamagnetic. For neutral complex **92**, the magnetic moment is 1.80 μ_B and does not change in the range of 50–290 K. This is in line with the ground state with the spin S = 1/2, as was shown previously for $[V(bpy)_3]$. The considerable decrease in the magnetic moment at $T < 50$ K is caused by the weak intermolecular antiferromagnetic interaction. The effective magnetic moment of compound **94** amounts to 3.84 μ_B, which corresponds to the ground state with S = 3/2. In the case of complex **95**, the effective magnetic moment is 2.80 μ_B in the range from 50 to 290 K, while at 50 K, the magnetic moment markedly decreases due to large zero-field splitting (Fig. 7).[112]

Complexes **96** and **97** described as $[V(L_{NN})_3]$ with 4,4′-dimethyl-2,2′-bipyridine (dmbpy) and 5,6-dimethylphenanthroline (Me_2phen) ligands, respectively, were prepared in a similar way. Compound **96** was studied by X-ray diffraction. The magnetic moments of these complexes do

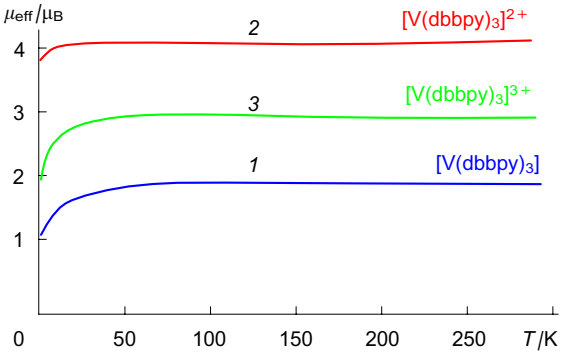


Figure 7. Temperature dependences of the effective magnetic moment for powdered samples of complexes **92** (*1*), **94** (*2*) and **95** (*3*).[112]

not change considerably with temperature and are 1.7 (**96**) and 1.75 μ_B (**97**), which is indicative of the ground state with S = 1/2.[66]

The EPR spectrum of a frozen solution of compound **96** in THF at 30 K (Fig. 8) is typical of $[V(L_{NN})_3]$ (L_{NN} = bpy, dbbpy, Me_2phen). The isotropic g-factor (g_{iso}) is 1.984, while $|A_{iso}| = 78\times10^{-4}$ cm^{-1}. The axial splitting is substantially anisotropic (hyperfine splitting constants $|A_{xx}| \sim |A_{yy}| > |A_{zz}|$), which is characteristic of systems in which the unpaired electron occupies a metal-centred orbital (vanadium d_z^2 orbital). In view of the above, the structure of $[V(Me_2bpy)_3]^0$ (**96**) is best described as $[V^{II}(Me_2bpy^{\bullet-})_2(Me_2bpy^0)]^0$, where the ground state with S = 1/2 appears due to the antiferromagnetic interaction of three unpaired electrons of V^{2+} with two π-radical anions ($Me_2bpy^{\bullet-}$).[66] A similar situation is observed for phenanthroline derivative **97**.[67]

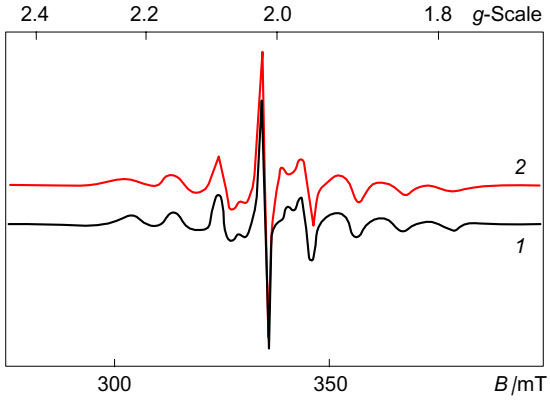
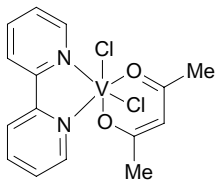


Figure 8. Experimental (*1*) and simulated (*2*) EPR spectra of $[V(dmbpy)_3]$ (**96**) in THF at 30 K.[66]

The synthesis of the mononuclear vanadium(III) complex *cis*-$[V^{III}(bpy)Cl_2(acac)]$ (**98**) was reported; the complex was prepared in 60% yield by the reduction of $[V^{IV}Cl_2(acac)_2]\cdot 0.25\,CH_2Cl_2$ in the presence of bpy in acetonitrile. The diffusion of diethyl ether vapour into an acetonitrile solution containing **98**, together with 3,5-di-*tert*-butylcatechol (H_2dtbc) and Et_3N, induces the oxidation of vanadium to give $[Et_3NH]_2[V^VO_2(\mu\text{-dtbc})]_2$.[114]

Structure 98

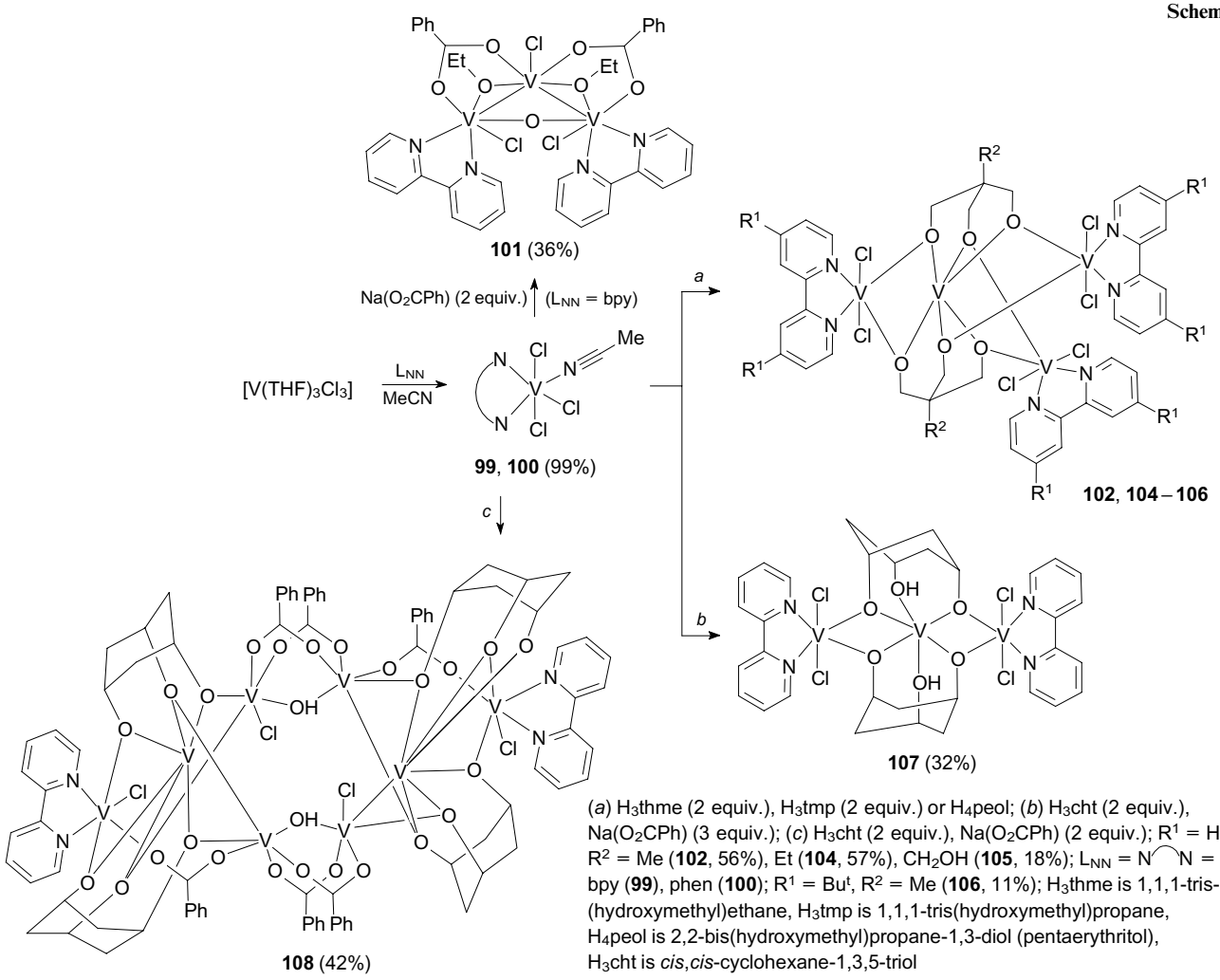


98 (60%)

Two complexes *mer*-$[V^{III}(L_{NN})(MeCN)Cl_3]$ [L_{NN} = bpy (**99**), phen (**100**)] were prepared by the reaction of stoichiometric amounts of $[V(THF)_3Cl_3]$ with bpy and phen ligands in acetonitrile under solvothermal conditions in an argon atmosphere (Scheme 28). In the solid state, the complexes were stable in air for a month.[115]

The presence of labile chloride and nitrile ligands makes these compounds highly attractive for the preparation of polynuclear structures with desired bridging ligands.

Scheme 28



(*a*) H_3thme (2 equiv.), H_3tmp (2 equiv.) or H_4peol; (*b*) H_3cht (2 equiv.), $Na(O_2CPh)$ (3 equiv.); (*c*) H_3cht (2 equiv.), $Na(O_2CPh)$ (2 equiv.); R^1 = H: R^2 = Me (**102**, 56%), Et (**104**, 57%), CH_2OH (**105**, 18%); L_{NN} = N⌒N = bpy (**99**), phen (**100**); R^1 = Bu^t, R^2 = Me (**106**, 11%); H_3thme is 1,1,1-tris-(hydroxymethyl)ethane, H_3tmp is 1,1,1-tris(hydroxymethyl)propane, H_4peol is 2,2-bis(hydroxymethyl)propane-1,3-diol (pentaerythritol), H_3cht is *cis*,*cis*-cyclohexane-1,3,5-triol

Although complexes **99** and **100** are poorly soluble in most organic solvents, this problem was solved by conducting the reactions under solvothermal conditions.[115,116] Polyalcohols and carboxylates were chosen as bridging ligands; the reactions resulted in the synthesis of tri-, tetra- and octanuclear coordination compounds.

The reaction of 3 equiv. of *mer*-[V(bpy)(MeCN)Cl_3] (**99**) with 2 equiv. of $Na(O_2CPh)$ in EtOH at 150 °C furnishes product $[V_3(O)Cl_3(O_2CPh)_2(bpy)_2(OEt)_2]$ (**101**) in 36% yield (see Scheme 28). This product consists of three V^{III} atoms coordinated by bridging benzoate and ethoxide ions and chloride ligands. The vanadium atoms are linked through the μ_3-O atom lying in the $\{V_3\}$ plane, resulting in the formation of a pseudo-T-shaped structure.[115]

The reaction of 1 equiv. of compound **99** with 2 equiv. of 1,1,1-tris(hydroxymethyl)ethane in MeCN at 150 °C gives $[V_4Cl_6(thme)_2(bpy)_3]\cdot 2.5\,MeCN$ (**102**).[115] The double complex salt $[V(bpy)Cl_4][V(bpy)_2Cl_2]$ (**103**) is formed as a by-product.[117] Complex **102** consists of four V^{III} atoms, which form a star-shaped $\{V_4\}$ plane. The central vanadium atom is surrounded by six alkoxide groups of two $thme^{3-}$ anions, one anion being located above the other below the $\{V_4\}$ plane; they bind the central vanadium atom with peripheral atoms. The octahedral coordination of the peripheral vanadium atoms is completed by the coordination of one bpy molecule and two chloride ligands located in the *cis*-positions.[115] Other tetranuclear complexes — $[V_4Cl_6(tmp)_2(bpy)_3]$ (**104**), $[V_4Cl_6(Hpeol)_2(bpy)_3]$ (**105**) and $[V_4Cl_6(thme)_2(dbbpy)_3]$ (**106**) — with identical structure were prepared in a similar way (see Scheme 28).[115]

When two types of bridging ligands are used in the reaction, more complex structures are formed. For example, the reaction of 4 equiv. of *mer*-[V(bpy)(MeCN)Cl_3] (**99**), 2 equiv. of *cis*,*cis*-cyclohexane-1,3,5-triol and 3 equiv. of $Na(O_2CPh)$ in MeCN at 150 °C gave the compound $[V_3Cl_4(Hcht)_2(bpy)_2]Cl\cdot 2\,MeCN$ (**107**) (see Scheme 28). The structure of this compound resembles that of $V_4Cl_6(thme)_2(bpy)_3]$ (**102**) from which one peripheral $\{V(bpy)Cl_2\}$ group was removed.[115] At a different reactant ratio [**99** : H_3cht : $Na(O_2CPh)$ = 1 : 2 : 2], the octanuclear complex $[V_8(OH)_2Cl_4(cht)_4(O_2CPh)_6(bpy)_2]$ (**108**) is formed (see Scheme 28).[115] The structure of complex **108** is a combination of two tetrahedral moieties linked by bridging hydroxyl and benzoate groups.[115]

For $[V_3(O)Cl_3(O_2CPh)_2(bpy)_2(OEt)_2]$ (**101**), the molar magnetic susceptibility sharply decreases with decreasing temperature (Fig. 9). This attests to strong antiferromagnetic interaction between the V^{III} ions. At ~70 K, the plot has a plateau at $\chi_m T$ = 1.08 cm^3 K mol^{-1}, which is indicative of the ground state (S = 1) with a strong antiferromagnetic exchange. In the case of $[V_4Cl_6(thme)_2(bpy)_3]$ (**102**), the situation is markedly different. At room temperature, $\chi_m T$ = 3.38 cm^3 K mol^{-1}, which corresponds to four V^{III} ions with a g-factor of 1.9. It slowly decreases as the

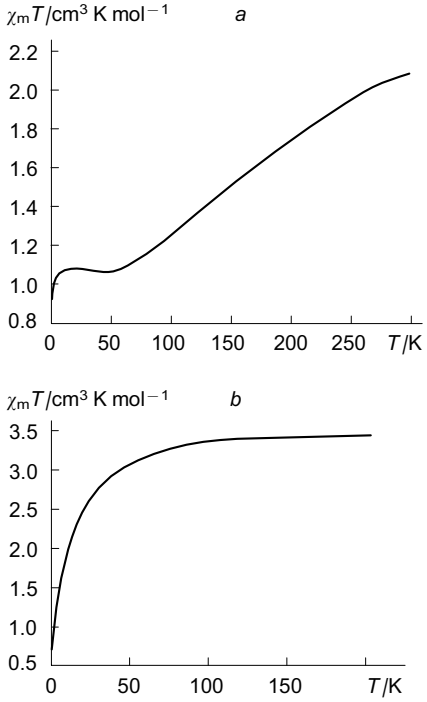


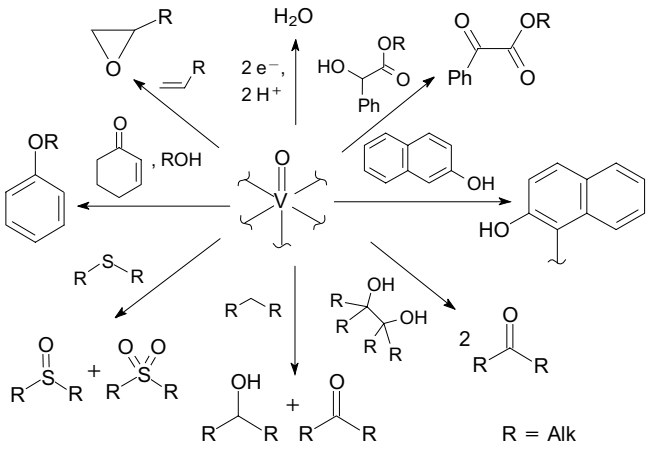
Figure 9. Temperature dependences of χ_mT for $[V_3(O)Cl_3(O_2CPh)_2(bpy)_2(OEt)_2]$ (**101**) (*a*) and $[V_4Cl_6(thme)_2(bpy)_3]$ (**102**) (*b*).[115]

temperature decreases to 100 K. This attests to a weak antiferromagnetic exchange interaction. Further lowering of the temperature induces a more pronounced decrease in χ_mT down to 0.78 cm^3 K mol^{-1} at 2 K (see Fig 9).[115]

4.1.2. Oxovanadium complexes

Currently ever increasing attention is being paid to oxovanadium complexes containing the highly stable V=O group. This is due, first of all, to the fact that they possess important catalytic properties and biological activities. In nature, vanadium-dependent haloperoxidases (VHPO)[118–120] catalyze the oxidation of halides with hydrogen peroxide, while vanadium-dependent nitrogenases[121, 122] are involved in nitrogen fixation. Furthermore, oxovanadium complexes are very important for homo- and heterogeneous catalysis. They behave as oxidants in various transformations: epoxidation of alkenes, aromatization of α,β-unsaturated cyclohexanone derivatives, oxidation of alcohols, C–C bond cleavage in glycols giving the corresponding ketones, oxidation of alkanes, hydroxy esters and amines and so on (Scheme 29).[5–12]

Scheme 29



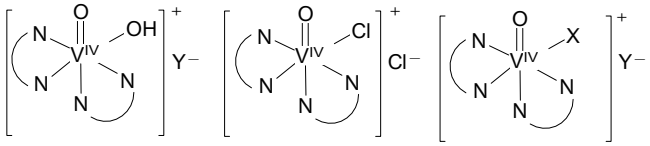
4.1.3. Oxovanadium complexes VOL_2

Oxovanadium complexes described as VOL_2 represent a rather abundant class of compounds with octahedral structures. In these complexes, two diimine ligands occupy four coordination sites, the oxo ligand occupies the fifth site, while the sixth one is occupied most often by a solvent molecule, halide ion, *etc*. The ligands may be either identical, giving rise to the most frequently encountered homoleptic complexes VOL_2, or different, giving rise to heteroleptic complexes VOL^1L^2.

The following compounds of this type have been prepared: *cis*-$[V^{IV}O(L_{NN})_2(OH)]Y$ [Y = BF_4; L_{NN} = bpy (**109**), dbbpy (**110**), dmbpy (**111**), phen (**112**); Y = ClO_4; L_{NN} = bpy (**113**); Y = SbF_6; L_{NN} = dbbpy (**114**)], *cis*-$[V^{IV}O(L_{NN})_2Cl]Cl$ [L_{NN} = bpy (**115**), dbbpy (**116**)], *cis*-$[V^{IV}O(L_{NN})_2(BF_4)](BF_4)$ [L_{NN} = dmbpy (**117**), dbbpy (**118**)], *cis*-$[V^{IV}O(bpy)_2(Tcac)](OTf)$ (**119**), cis-$[V^{IV}O(bpy)_2(SO_4)]$ (**120**) and *cis*-$[V^{IV}O(dbbpy)_2(SbF_6)](SbF_6)$ (**121**).

Complexes **109**–**114** were synthesized by reactions of $[VO(THF)_2Cl_2]$ with 2 equiv. of $AgBF_4$ or $AgSbF_6$ and 2 equiv. of the ligand in water. *cis*-$[V^{IV}O(bpy)_2(OH)](ClO_4)$ (**113**) was also formed upon the reaction of $VOSO_4$ with bpy in the presence of $Ba(ClO_4)_2$. All compounds contain a *cis*-$\{V^{IV}O(OH)\}$ moiety. In non-aqueous media, $[VO(THF)_2Cl_2]$ was converted to *cis*-$[V^{IV}O(L_{NN})_2Cl]Cl$ [L_{NN} = bpy (**115**), dbbpy (**116**)] and *cis*-$[V^{IV}O(L_{NN})_2(Y)]Y$ [Y = BF_4; L_{NN} = dmbpy (**117**), dbbpy (**118**); Y = SbF_6: L_{NN} = dbbpy (**121**)].[123] A complex of a similar composition, $[VO(bpy)_2(Tcac)](OTf)$ (**119**), was synthesized by the reaction of $[VO(H_2O)_5](OTf)_2$ and bpy with LiTcac in 1 : 1 : 2 ratio.[124, 125] Complex **120** was formed in 56% yield upon the reaction of $VOSO_4$ with bpy in 1 : 2 ratio.

Structures 109–121



109–114 **115, 116** **117–121**

Y = BF_4: N⌒N = bpy (**109**, 86%), dbbpy (**110**, 85%), dmbpy (**111**, 76%), phen (**112**); Y = ClO_4, N⌒N = bpy (**113**, 76%); Y = SbF_6, N⌒N = dbbpy (**114**, 78%); N⌒N = bpy (**115**, 80%), dbbpy (**116**, 97%); X = Y = BF_4: N⌒N = dmbpy (**117**, 95%), dbbpy (**118**, 97%); X = Tcac, Y = OTf, N⌒N = bpy (**119**, 20%); X = SO_4, Y is absent, N⌒N = bpy (**120**, 56%); X = Y = SbF_6, N⌒N = dbbpy (**121**, 96%); HTcac is trichloroacetic acid, TfO is trifluoromethanesulfonate (triflate)

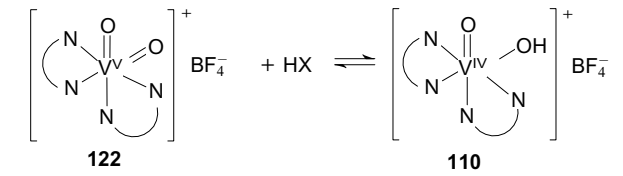
Due to the strong *trans*-effect of the oxo ligand, the diimine ligand is unsymmetrically coordinated to vanadium in all of the complexes. For example, in complex **120**, the length of the V–N bond in the *trans*-position relative to O^{2-} is 2.247 Å, while the V–N bond in the *trans*-position

relative to HO^- is 2.175 Å long. A similar situation is observed for other complexes of this type.[123 – 125]

All complexes are paramagnetic: the magnetic moments vary in the range of 1.66 – 1.75 μ_B, which is close to the spin-only magnetic moment for one unpaired electron (1.73 μ_B). The EPR spectra of the complexes in acetonitrile show a signal composed of eight lines, which is typical of vanadium(IV) complexes with the d^1 configuration and the nuclear spin $I(^{51}V) = 7/2$.[123]

According to another study,[126] $[V^VO_2(dbbpy)_2]BF_4$ (**122**) participates in the $H^\bullet$ transfer from organic substrates HX with activated O – H and C – H bonds, being converted to $[V^{IV}O(dbbpy)_2(OH)]BF_4$ (**110**) (Scheme 30).

Scheme 30



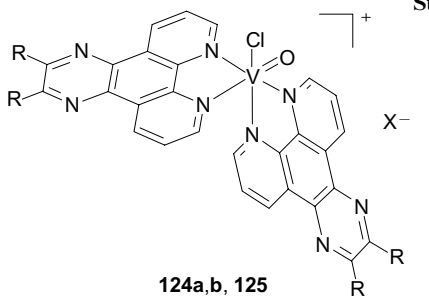
122 **110**

N⌒N = dbbpy

For instance, 2,6-Bu^t_2-4-MeO-C_6H_2OH (ArOH) and 2,2,6,6-tetramethyl-*N*-hydroxypiperidine (TEMPO-H) are converted to the corresponding $ArO^\bullet$ and (2,2,6,6- tetramethylpiperidin-1-yl)oxyl (TEMPO) radicals, hydroquinone is converted to benzoquinone, and dihydroanthracene is transformed into anthracene (Scheme 31). All these reactions are slow and usually proceed for several hours at ambient temperature. It was shown by DFT calculations that the hydrogen atom transfer entails substantial structural changes, which affect the V – O and V – OH bond lengths and the d orbital occupancy, thus giving rise to high activation barriers of such reactions.[126]

The vanadium complexes *cis*-$[VO(L_{NN})_2Cl]Cl$ {L_{NN} = phen (**123**), dipyrido[3,2-*d*:2′,3′-*f*]quinoxaline (dpq, **124a**), dipyrido[3,2-*a*:2′,3′-*c*]phenazine (dppz, **125**)} have been reported.[127] These compounds resemble the complexes described above in the structure and composition, but are formed in the reaction of vanadium trichloride

Structures 124, 125



124a,**b**, **125**

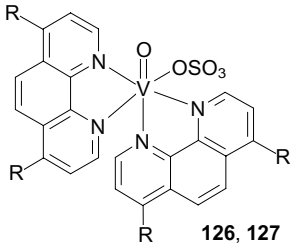
R = H: X = Cl (**124a**), PF_6 (**124b**); R – R is benzo (**125**)

with L_{NN} in methanol. During the reactions, vanadium(III) is oxidized by air oxygen to give the VO^{2+} group. According to X-ray diffraction data, the chloride ligand in $[VO(dpq)_2Cl](PF_6)$ (**124b**) is *cis*-oriented with respect to the oxovanadium oxygen atom.

These complexes are of interest for biomedicine. They show activity in DNA cleavage upon irradiation in the near-IR range (> 750 nm) *via* the formation of hydroxyl radicals and can bind to DNA. The compound $[VO(dppz)_2Cl]Cl$ (**125**) has a pronounced photocytotoxicity in HeLa cells under visible and ultraviolet light, but is not cytotoxic in the dark.[127] Later, the same group of authors published a study[128] describing, apart the above mentioned compounds, a complex of the same composition with the phenanthroline ligand. It was shown that all these complexes can bind to DNA molecules.

The reactions of $VOSO_4$ with phen or dmphen in 1 : 2 ratio in water yield compounds $[VO(L_{NN})_2(SO_4)]$

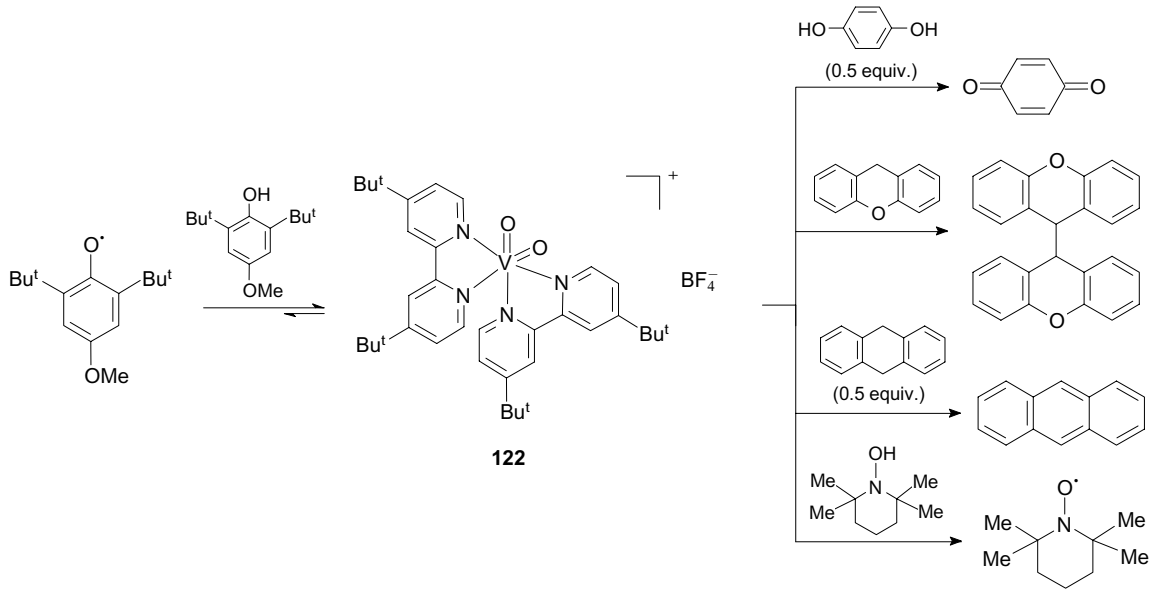
Structures 126, 127



126, **127**

R = H (**126**), Me (**127**)

Scheme 31

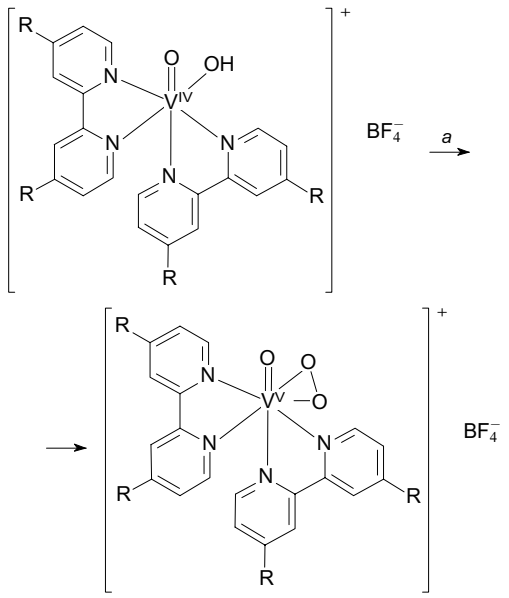


122

[L_{NN} = phen (**126**), 4,7-dimethyl-1,10-phenanthroline (dmphen, **127**)], which are structurally and compositionally similar to complex **120**. It was shown that these compounds have high cytotoxic activities against human acute lymphoblastic leukemia cells. The complex [$VO(dmphen)_2(SO_4)$] (**127**) has a higher cytotoxicity than complex **126**. Presumably, the former can be promising for the therapy of acute lymphoblastic leukemias.[129]

All of the above-described complexes are vanadium(IV) compounds. On the other hand, the complexes $[V^{IV}O(L_{NN})_2(Y)]^+$ are known to be slowly oxidized by air oxygen to give oxo peroxo complexes with the $V^{V}O(O_2)$ moiety. For example, compounds $[V^{V}O(O_2)(L_{NN})_2](BF_4)$ [L_{NN} = bpy (**128**), dmbpy (**129**), dbbpy (**130**)] were prepared by the oxidation of $[V^{IV}O(L_{NN})_2(OH)](BF_4)$ in tetrahydrofuran (Scheme 32). The *cis*-dioxo compound $[V^{V}(O)_2(L_{NN})_2]BF_4$ is an intermediate of this reaction. The reaction is reversible: in the presence of hydrogen donors (hydroquinone, TEMPO-H or triphenylphosphine), the complexes $[V^{V}O(O_2)(L_{NN})_2](BF_4)$ are slowly reduced to $[V^{IV}O(L_{NN})_2(OH)](BF_4)$.[130]

Scheme 32

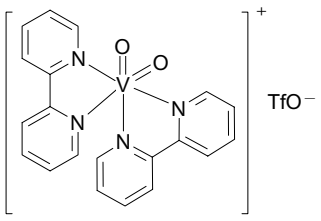


128–130

(*a*) O_2, THF, MeCN; R = H (**128**, 40%), Me (**129**, 60%), Bu^t (**130**, 98%)

The self-oxidation of a mixture of bipyridine and oxovanadium triflate $V^{IV}O(OTf)_2$ in acetonitrile in air affords *cis*-$[V^{V}O_2(bpy)_2](OTf)$ (**131**). The structure of this product comprises two asymmetric units, each consisting of a pair of Δ- and Λ-enantiomers related by an inversion centre. The complex has an octahedral structure and consists of the *cis*-VO_2^+ moiety with an average V–O bond length of 1.622 Å and two *cis*-coordinated bipyridine ligands. The V–N bond lengths, which are trans to each other, are markedly shorter (2.108 Å) than those in the *trans*-position to V=O (2.292 Å) because of the stronger *trans*-effect of the oxo group mentioned above.[131]

Structure 131

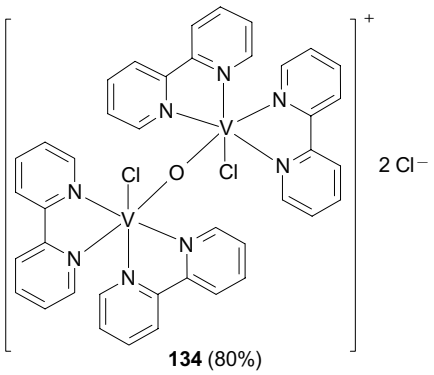


131

The synthesis of analogous compounds, $[V^{IV}O_2(phen)_2]\cdot 6H_2O$ (**132**) and $[V^{V}O_2(bpy)_2](H_2BO_3)\cdot 3H_2O$ (**133**), with *cis*-orientation of the oxo ligands has been reported.[132]

The reaction of VCl_3 with bipyridine in water under inert conditions gives the binuclear complex $[\{V^{III}(bpy)_2Cl\}_2O]Cl_2$ (**134**), in which two $\{V^{III}(bpy)_2Cl\}$ moieties are linked by the bridging O^{2-} ligand.[133] The magnetic moment of this complex is 3.176 μ_B (at 300 K) per vanadium centre, and it does not change with lowering the temperature. This value is close to the spin-only magnetic moment (2.83 μ_B) for the d^2 configuration. The complex is oxidized in air to afford $[V^{V}O_2(bpy)_2]Cl$ (**135**).

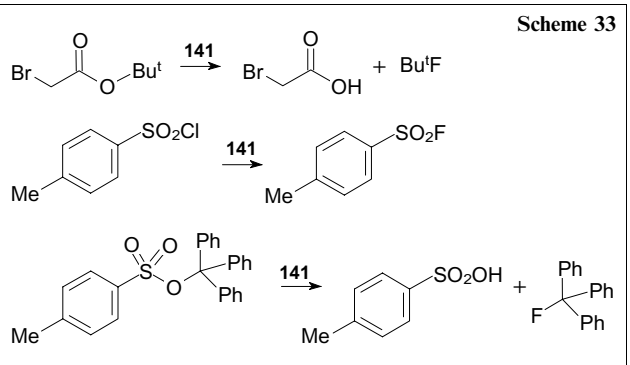
Structure 134



134 (80%)

The isostructural series *cis*-$[V^{IV}O(L_{NN})_2X]^+$ also includes more rare complexes with X = F:[134] *cis*-$[VO(L_{NN})_2F]A$ [A = BF_4; L_{NN} = bpy (**136**), dmbpy (**137**), dbbpy (**138**), phen (**139**); A = ClO_4; L_{NN} = bpy (**140**), dbbpy (**141**); A = SbF_6, L_{NN} = bpy (**142**)]. These compounds are formed in reactions of $VOSO_4$ with the corresponding ligands in aqueous solutions of HBF_4 or HF and/or KF.[135] In relation to *cis*-$[V^{IV}O(dbbpy)_2F]ClO_4$ (**141**), it was shown that the V–F bond is mainly ionic. The reaction of this complex with Me_3SiCl giving Me_3SiF leads to 100% conversion of the substrate within several minutes. The second product of the reaction is the chloride complex *cis*-$[V^{IV}O(dbbpy)_2Cl]$. The reactivity of complex **141** towards fluorination reactions of various substrates was

Scheme 33



141 = $[V^{IV}O(dppby)_2F]^+ClO_4^-$

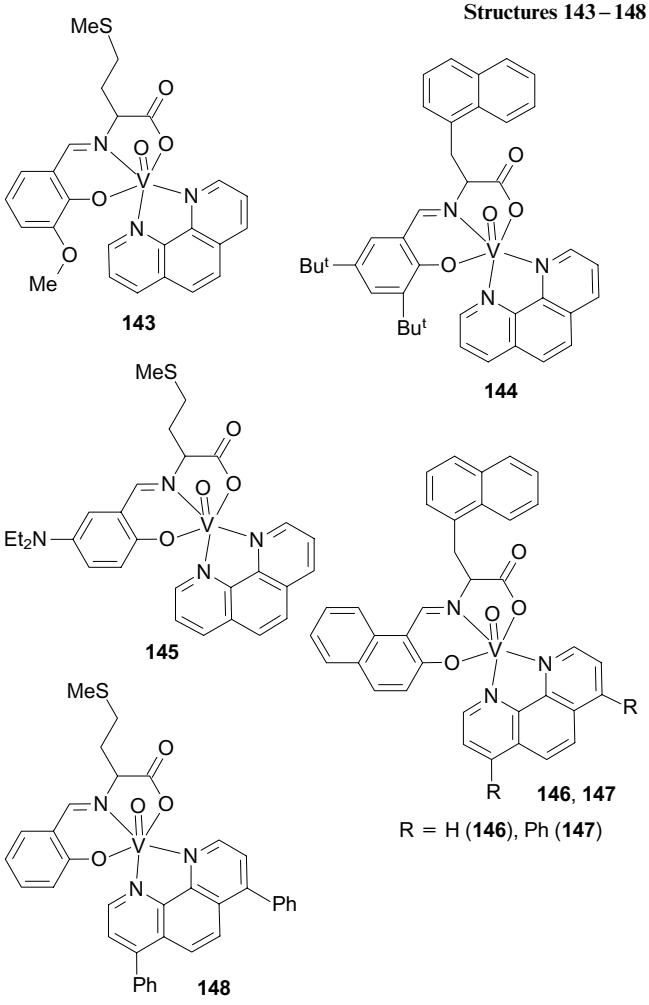
studied (Scheme 33); these reactions gave products in quantitative yields (based on vanadium).[135]

4.1.4. Oxovanadium complexes VOL

Oxovanadium complexes containing one diimine ligand are more abundant than VOL_2. These compounds are described by the general formula $[VO(L_{NN})L]$ (L_{NN} = bpy, phen and their derivatives; L are carboxylates, triazoles, hydroxide, alkoxides, halides, Schiff bases, *etc*.) and have an octahedral structure.

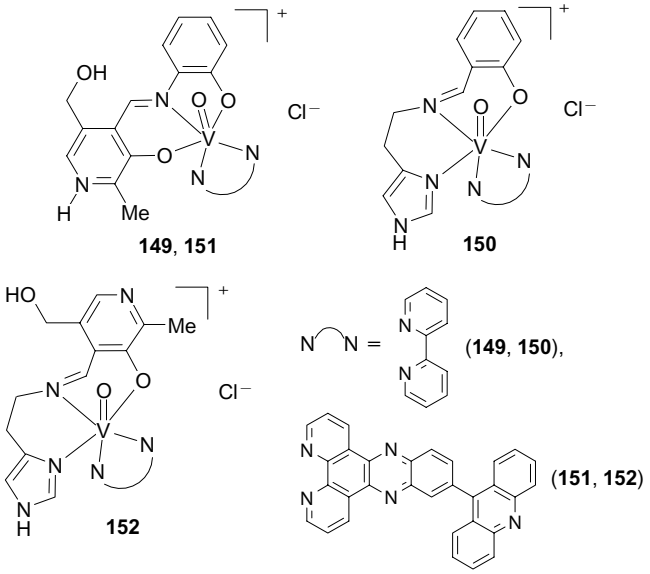
A large series of mixed-ligand complexes [VO(phen)X] containing various Schiff bases, along with bpy or phen derivatives, have been obtained. Complexes **143**–**146** show moderate antitumour activity against human lung cancer and hepatoma cells.[136] Similar complexes **147** and 1**48** containing 4,7-diphenyl-1,10-phenanthroline (Ph_2phen) as one of the ligands also exhibit antitumour activity. These complexes are considered as potential components for the development of new anticancer agents.[137]

Structures 143–148



Oxovanadium complexes with Schiff bases based on vitamin B_6 — compounds **149**–**152** — have been reported.[138] These complexes can be used as photoactivated anticancer agents. Their photoirradiation generates singlet oxygen, which induces programmed cell death (apoptosis), while in the dark the complexes are inactive. Complexes **149**–**152** selectively target cancer cells, while their uptake by normal cells is low. In addition, these complexes are

Structures 149–152

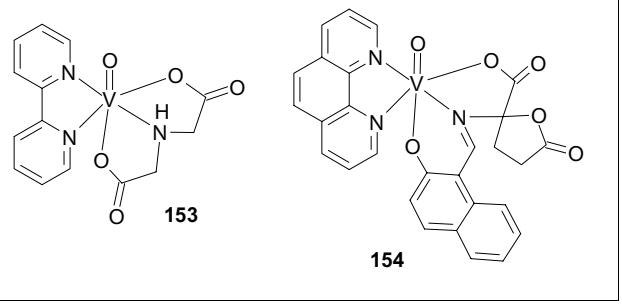


located in the endoplasmic reticulum, whereas other porphyrin-based agents for photodynamic therapy are mainly accumulated in the cancer cell mitochondria. Thus, this study opens up new opportunities for the photochemotherapy targeting the endoplasmic reticulum of cancer cells instead of the nuclear or mitochondrial DNA of a normal cell.

The iminodiacetate (IDA)- and bipyridine-containing complex $[VO(bpy)(IDA)]\cdot 2H_2O$ (**153**) exhibits antioxidant activity against superoxide radicals ($O_2^{-\bullet}$) and stable organic radicals — 1,1-diphenyl-2-picrylhydrazyl (DPPH) and 2,2-azinobis(3-ethylbenzothiazoline-6-sulfonic acid).[139]

Complex **154**, containing a vanadium-coordinated imine ligand based on 2-hydroxy-1-naphthaldehyde apart from phenanthroline, can form intercalates with DNA molecules of cancer cells.[140]

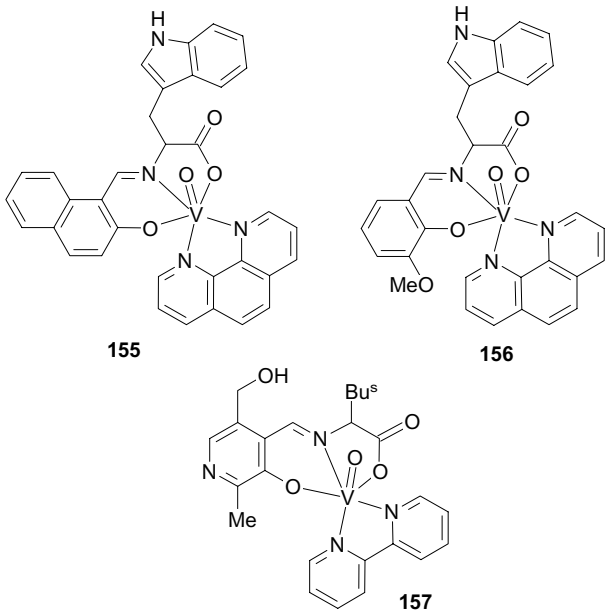
Structures 153, 154



Similar complexes have been obtained with other ligands, *e.g.*, tryptamine and Schiff bases derived from 2-hydroxy-1-naphthaldehyde (compound **155** as a MeOH solvate) and *ortho*-vanillin (compound **156** as a MeOH and H_2O solvate). Both complexes have high affinity for the tumour DNA and also promote DNA cleavage. They could find application as anticancer agents able to bind to the DNA of cancer cells.[141]

In addition, several complexes $[VO(L_{NN})(L)]$ (L_{NN} = bpy, phen) have been synthesized with Schiff bases obtained by condensation of amino acids (such as glycine, alanine, valine, leucine, isoleucine, methionine, phenylala-

Structures 155–157



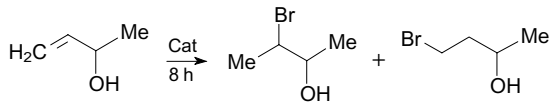
155 **156** **157**

nine, threonine, aspartic acid and histidine) with salicylaldehyde or its analogues.[68, 142] For example, in compound **157**, oxovanadium is coordinated to the adduct of 3-hydroxy-5-hydroxymethyl-2-methylpyridine-4-carbaldehyde and isoleucine.

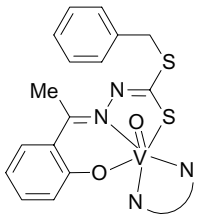
In the complex $[VO(bpy)(sal\text{-}L\text{-}Ser)]\cdot H_2O$ (**158**) (sal-L-Ser stands for the Schiff base derived from salicylaldehyde and L-serine), weak ferromagnetic ordering takes place at 12 K with the Weiss constant (θ) of 0.3 K. The effective magnetic moment equal to 1.67 μ_B virtually does not change as temperature decreases.[142] A similar complex [VO(phen)(sal-L-val)] (**159**) mimics the action of the VHPO enzyme by efficiently catalyzing the *in vitro* bromination of alkene alcohols, for example 3-butenyl alcohol, in the presence of KBr and H_2O_2 to give the corresponding bromine-containing products at room temperature (Scheme 34).[68]

All complexes described above contain ONO-donor Schiff bases; complexes with SNO-donor ligands are less

Scheme 34



Structures 160, 161



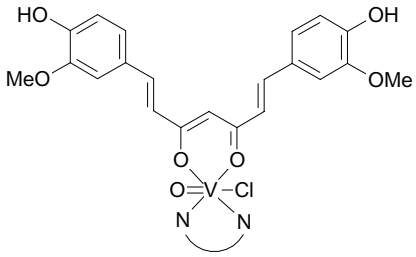
160, **161**

N⌒N = bpy (**160**, 73%), phen (**161**, 70%)

abundant. For example, mixed-ligand complexes $[V^{IV}O(L_{NN})L]$ have been prepared, where H_2L is S-benzyl-β-*N*-(2-hydroxyphenylethylidene)dithiocarbazate (the adduct of 2-hydroxyacetophenone and dithiocarbazate) and L_{NN} = bpy (**160**) or phen (**161**). For compounds **160** and **161**, quasi-reversible one-electron oxidations were detected at 0.421 and 0.418 V (against a calomel electrode), respectively.[143]

The curcumin (cur) dye and its vanadium complexes $[VO(L_{NN})(cur)Cl]$ [L_{NN} = phen (**162**), dppz (**163**)] show photocytotoxic behaviour; their cytotoxicity sharply decreases in the dark. The photocytotoxicity of the dppz complex is comparable with that for Photofrin used for the photodynamic therapy (PDT). These complexes are also active in DNA cleavage in the near-IR range (~785 nm) and are stable over a wide range of redox potentials. Curcumin binding to the VO^{2+} group increases its hydrolytic stability and enhances the biological activity.[144]

Structures 162, 163

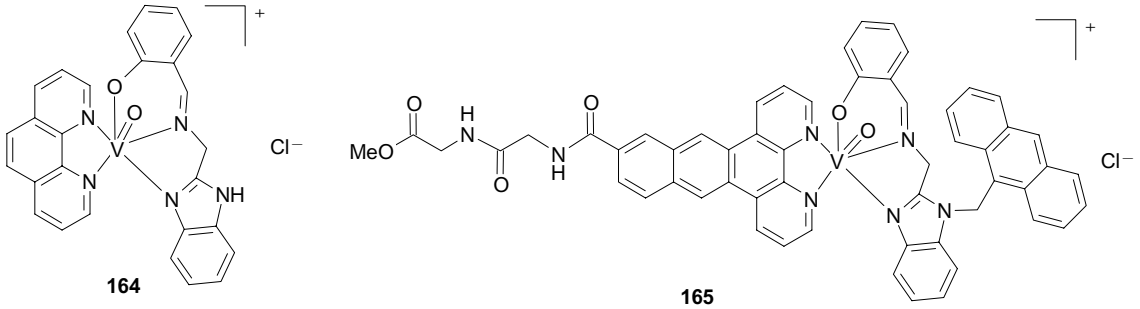


162, **163**

N⌒N = phen (**162**, 87%), dppz (**163**, 74%)

Complexes **164** and **165** contain a salicylaldehyde adduct with 2-aminomethylbenzimidazole or with its 1-(anthracen-9-ylmethyl) derivative as the NO-ligand and phenanthroline or its analogue annulated to naphthalene substituted by the Gly-Gly-OMe dipeptide as the NN-ligand. These complexes

Structures 164, 165



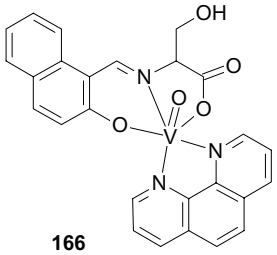
164 **165**

were prepared in ~70% yield by the reaction of $VOSO_4$ and $BaCl_2$ with the ligands in methanol.[145]

Complex **165** was found to bind to DNA and to show photocytotoxic activity in the near-IR range, specifically targeting the cancer cell mitochondria. The uptake of the complex by mitochondria induces apoptosis, which is related to the formation of HO$^{\bullet}$ radicals on exposure to light. The activity of the complex is comparable with the activity of Photofrin, a clinically approved PDT agent. It is expected that these results would open up new prospects for the development of mitochondria-targeting photochemotherapeutic agents based on metal complexes with potential *in vivo* applications.

The possibility of binding to DNA was also studied for [VO(phen)(Naph-L-Ser)]·1.5 MeOH (**166**) (Naph-L-Ser stands for the Schiff base derived from L-serine and 2-hydroxy-1-naphthaldehyde). The results demonstrated that this complex can bind to tumour DNA *via* intercalation and weak electrostatic interactions.[146]

Structures 166

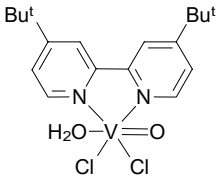


166

The complexes $[VO(L_{NN})_2(SO_4)]$ [L_{NN} = phen (**126**), dmphen (**127**)] are described in the previous Section.[129] In the same study, monosubstituted analogues of these complexes, that is, $[VO(L_{NN})(H_2O)_2(SO_4)]$ [L_{NN} = phen (**167**), dmphen (**168**)], were prepared by a similar procedure. Both the former and the latter complexes exhibited cytotoxic activities against human acute lymphoblastic leukemia cells.

The reaction of VCl_3 with dbbpy in acetonitrile in air gives $[VO(dbbpy)(H_2O)Cl_2]$ (**169**) in 95% yield. This complex is paramagnetic and shows a characteristic EPR signal, in a frozen dichloromethane solution, consisting of eight lines with S = 1/2, g-factors along the axes $g_{xx} = g_{yy} = 1.978$ and $g_{zz} = 1.945$, and hyperfine splitting (HFS) constants $A_{xx} = A_{yy} = 6.5$ mT and $A_{zz} = 17.86$ mT.[147]

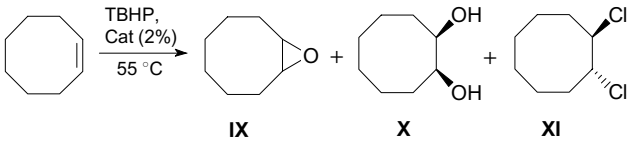
Structure 169



169

Complex **169** exhibits a moderate activity as a catalyst for the oxidation of cyclooctene with *tert*-butyl hydroperoxide under mild conditions in chloroform. The major reaction product is cyclooctene epoxide (**IX**), while *cis*-cyclooctane-1,2-diol (**X**) is formed in trace amounts. In addition, considerable amounts of *trans*-1,2-dichlorocyclooctane (**XI**) are formed (Scheme 35). Presumably, the source of chlorine is chloroform, which reacts with hydroperoxide to give the $Cl_3C^{\bullet}$ radical.[47]

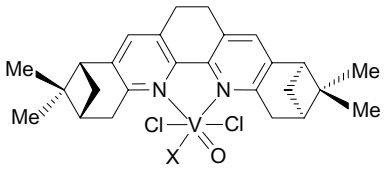
Scheme 35



IX **X** **XI**

The synthesis of complexes with a chiral dihydrophenanthroline derivative, (2*R*,4*R*,9*R*,11*R*)-3,3,10,10-tetramethyl-1,2,3,4,6,7,9,10,11,12-decahydro-2,4,-9,11-dimethanodibenzo[*b*,*j*][1,10]phenanthroline (esv) — $[V^{IV}O(esv)(H_2O)Cl_2]$ (**170**) and $[V^{V}O(esv)(OMe)Cl_2]$ (**171**) — has been reported. The latter complex is formed upon oxidation of the former in methanol. Compounds **170** and **171** are rare examples of chiral oxovanadium complexes; they can be considered as potential catalysts for oxidation reactions in the enantioselective organic synthesis.[148]

Structures 170, 171

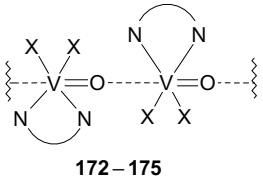


170, **171** X = H_2O (**170**), MeO (**171**, 10%)

The reactions of VX_3 and $V(THF)_3Cl_3$ (X = Cl, Br) with bpy or phen in 1 : 1 ratio in acetonitrile under solvothermal conditions afford the polymeric complexes $[VO(L_{NN})X_2]_n$ [L_{NN} = bpy; X = Cl (**172**), Br (**173**); L_{NN} = phen; X = Cl (**174**), Br (**175**)]. Their polymeric structure is formed *via* V=O···V=O contacts. They are insoluble in weakly coordinating solvents. Meanwhile, in strongly coordinating solvents, such as dimethylformamide, the polymeric structure {V=O···V=O} is destroyed to give mononuclear complexes $[VO(L_{NN})(DMF)X_2]$.[64]

Complexes **172** – **175** have high catalytic activities towards the oxidation of alkanes with hydrogen peroxide to the corresponding alcohols and ketones under mild conditions (Scheme 36). Complex **172** is the most active in this series, providing the 34.7% and 4.3% yields of the alcohol and the ketone, respectively, upon oxidation of cyclohexane. On the basis of experimental and theoretical data, it was shown that the reaction follows the radical Fenton mechanism (see Scheme 36), involving the decomposition of hydrogen peroxide to give HO$^{\bullet}$ species (rate-limiting step), which then induce the homolytic cleavage of the R – H bond of the alkane producing H$^{\bullet}$ and R$^{\bullet}$ radicals. The latter react with molecular oxygen to afford alkyl peroxide ROO$^{\bullet}$ radicals, which react with H$^{\bullet}$ to be con-

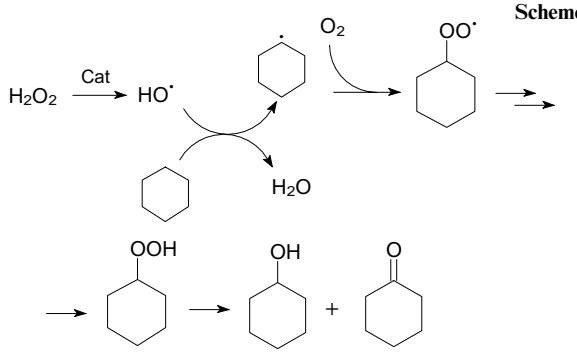
Structures 172 – 175



172 – 175

N⌒N = bpy: X = Cl (**172**, 90%), Br (**173**, 65%);
N⌒N = phen: X = Cl (**174**, 66%), Br (**175**, 43%);

Scheme 36

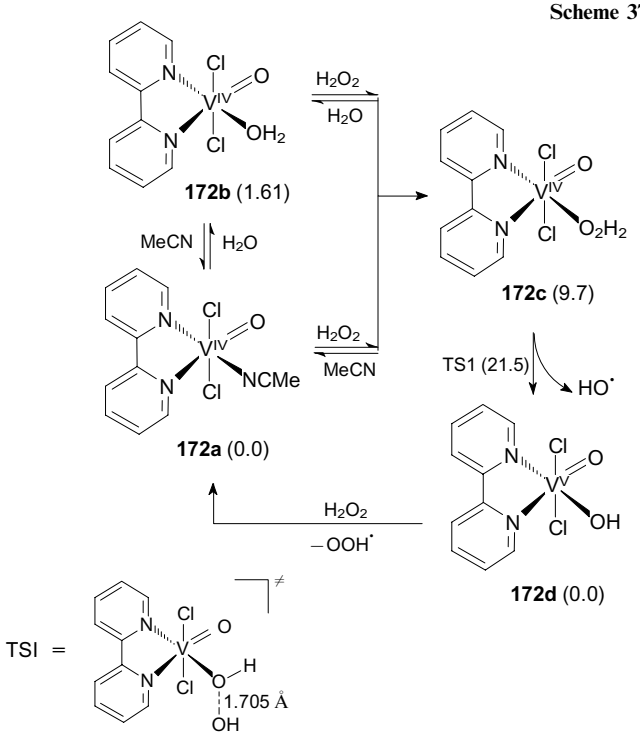


verted to alkyl hydroperoxide ROOH, as has been detected experimentally.[64]

It is assumed that under the reaction conditions, complex **172** is converted to molecular complexes **172a** and **172b** containing coordinated acetonitrile and water molecules, respectively (Scheme 37). In the presence of hydrogen peroxide, these molecules can be replaced by H_2O_2 to give $[VO(bpy)(H_2O_2)Cl_2]$ (**172c**). The H_2O_2 coordination to V^{IV} activates the molecule and facilitates the homolysis of the O–O bond to give intermediate **172d** and HO·. The activation barrier for the generation of HO· from compound **172c** *via* the transition state TS1 is 11.8 kcal mol^{-1}. The overall activation barrier for the formation of the HO· radical with respect to the most stable complex **172a** is 21.5 kcal mol^{-1} in terms of the Gibbs energy ($\Delta G^{\neq}$) and 19.6 kcal mol^{-1} in terms of the enthalpy ($\Delta H^{\neq}$). The latter value is in good agreement with the experimentally obtained activation energy for the oxidation of cyclohexane with hydrogen peroxide catalyzed by complex **172** (20 ± 2 kcal mol^{-1}).

Fluoride derivatives are also known among the complexes with the general formula VOL. The reaction of VOF_2 with phen in 30% HF resulted in the synthesis of $[V^{IV}O(phen)(H_2O)F_2]$ (**176**) in 86% yield.[149] This complex

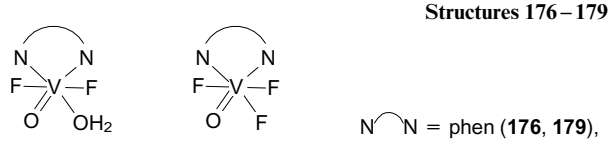
Scheme 37



and its bipyridine analogue $[V^{IV}O(bpy)(H_2O)F_2]$ (**177**) can be obtained from VF_4 under hydrothermal conditions.[150] In the same study, the complex $[VO(H_2O)_2F_2]\cdot H_2O$ was fully characterized for the first time; this is a convenient starting compound for the synthesis of other oxofluoride complexes.[150]

The isostructural complexes *fac*-$[V^{V}O(L_{NN})F_3]$ [L_{NN} = bpy (**178**), phen (**179**)] were prepared by the reaction of VOF_3 with L_{NN} in dry acetonitrile in ~80% yield. The crystal structure was determined only for the complex with phenanthroline. An attempted crystallization of $[VO(bpy)F_3]$ was accompanied by hydrolysis giving $[VO_2(bpy)F]$ (**180**).[151] Direct synthesis of $[VO_2(L_{NN})F]$ [L_{NN} = (py)$_2$ (**181**), phen (**182**)] from VOF_3 has been reported.[152]

Structures 176–179

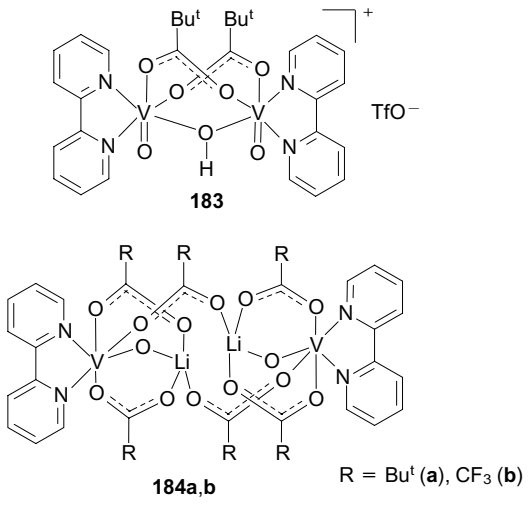


4.1.5. Binuclear complexes

Along with mononuclear complexes, binuclear oxovanadium complexes are also abundant in vanadium chemistry. They can be conceived as two oxovanadium groups linked by bridging ligands. In these compounds, magnetic exchange interactions often take place, which is of interest to researchers working in the field of molecular magnetism. Binuclear compounds can be obtained from mononuclear precursors by ligand exchange reactions in solution under ambient or solvothermal conditions. In addition, binuclear complexes are formed upon self-assembly reactions of simpler vanadium compounds (chlorides, oxides) in the presence of diimine and bridging ligands.

The reaction of $[VO(H_2O)_5](OTf)_2$ with bpy and lithium trimethylacetate [Li(Piv), Hpiv is pivalic acid] in 1 : 1 : 2 ratio in acetonitrile affords the binuclear complex $[(VO)_2(\mu\text{-}OH)(\mu\text{-}Piv)_2(bpy)_2](OTf)$ (**183**). A change in the reactant ratio to 1 : 1 : 3 induces the formation of the bimetallic compound $[Li_2(VO)_2(\mu\text{-}Piv)_6(bpy)_2]$ (**184a**), which is isolated as two solvates with either MeCN or CH_2Cl_2. The replacement of Li(Piv) by lithium trifluoro-

Structures 183, 184



acetate Li(Tfac) (HTfac is trifluoroacetic acid) results in the formation of $[Li_2(VO)_2(\mu\text{-Tfac})_6(bpy)_2]$ (**184b**), whereas a similar reaction with lithium trichloroacetate Li(Tcac) in ethanol produces the mononuclear complex $[VO(bpy)_2(\mu\text{-Tcac})](OTf)$ (**184c**).[124]

The structure of the complex cation $[(VO)_2(OH)(Piv)_2(bpy)_2]^+$ in compound **183** is composed of two crystallographically nonequivalent vanadium(IV) atoms coordinated by two 2,2′-bipyridine molecules and linked to one another by two bridging carboxylates and one hydroxyl group. The complexes $[Li_2(VO)_2(\mu\text{-Piv})_6(bpy)_2]$ (**184a**) and $[Li_2(VO)_2(\mu\text{-Tfac})_6(bpy)_2]$ (**184b**) are structurally similar, they contain two crystallographically equivalent vanadium(IV) atoms, coordinated by two bpy molecules, and two equivalent lithium atoms. The vanadium and lithium atoms are connected by six bridging carboxylate anions. The complex $[Li_2(VO)_2(\mu\text{-Piv})_6(bpy)_2]$ (**184a**) was found to have additional interactions between the V and Li atoms *via* the oxygen atoms of the oxo ligand to form the Li–O=V moieties, resulting in some elongation of the V=O bond.[124]

The molar magnetic susceptibility of $[(VO)_2(\mu\text{-OH})(\mu\text{-Piv})_2(bpy)_2](OTf)$ (**183**) (Fig. 10) at room temperature is 0.47 cm^3 K mol^{-1}, which is markedly lower than the value (0.75 cm^3 K mol^{-1}) expected for two isolated V^{IV} ions with S = 1/2. This value decreases with decreasing temperature to reach 0.04 cm^3 K mol^{-1} at 2 K, which is attributable to intramolecular antiferromagnetic interactions. The magnetic behaviours of $[Li_2(VO)_2(\mu\text{-Piv})_6(bpy)_2]$ (**184a**) and $[Li_2(VO)_2(\mu\text{-Tfac})_6(bpy)_2]$ (**184b**) are similar (see Fig. 10), but they markedly differ from that of complex **183**. The $\chi_m T$ value in the temperature range of 8–300 K, equal to 0.73–0.75 cm^3 K mol^{-1} for $[Li_2(VO)_2(\mu\text{-Piv})_6(bpy)_2]$, and in the temperature range of 18–300 K, equal to 0.70–0.74 cm^3 K mol^{-1} for $[Li_2(VO)_2(\mu\text{-Tfac})_6(bpy)_2]$, virtually does not depend on the temperature and is close to the spin-only value of 0.75 cm^3 K mol^{-1} for two isolated V^{IV} ions. On further cooling, $\chi_m T$ decreases to 0.61 and 0.28 cm^3 K mol^{-1} for compounds **184a**,**b**, respectively, as a result of antiferromagnetic exchange.[124]

One more heterometallic binuclear complex $[Ru^{II}(NO)(NO_2)_3(OAc)(O)V^{V}O(dbbpy)]$ (**185**) was prepared by the reaction of $[VO(dbbpy)(H_2O)Cl_2]$ (**169**) with $Na_2[Ru(NO)(NO_2)_4(OH)]\cdot 2\,H_2O$ in acetonitrile (Scheme 38). The bridging acetate ion is presumably formed

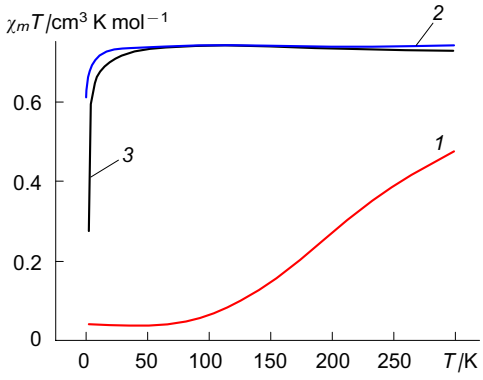
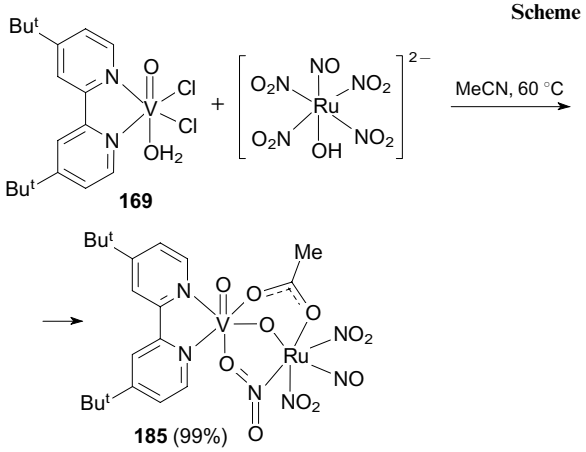


Figure 10. Temperature dependences of $\chi_m T$ for compounds **183** (*1*), **184a** (*2*) and **184b** (*3*).[124]

Scheme 38

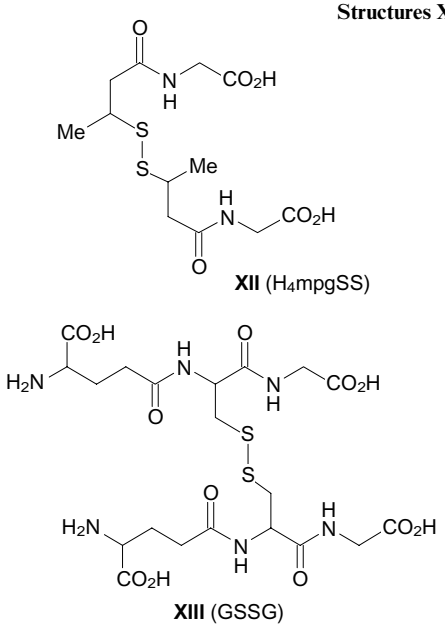


upon the hydrolysis of acetonitrile. In this reaction, vanadium(IV) is oxidized to vanadium(V).

When crystals of this complex are irradiated with light in the 365–405 nm range at 10 K, the ground state Ru–NO isomerizes into the metastable state Ru–ON (stable up to 140 K); this is accompanied by the formation of free NO, which does not take place for the initial ruthenium nitroso complex. Laser irradiation of complex **185** in acetonitrile at 445 nm induces release of NO and formation of the paramagnetic Ru^{III} complex with $g_1 = 2.627$, $g_2 = g_3 = 2.20$.

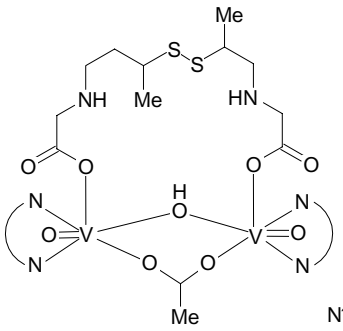
Binuclear vanadium complexes with oxidized *N*-(2-sulfanylpropionyl)glycine (H_4mpgSS, **XII**) containing the S–S bond, structurally resembling the oxidized form of glutathione (GSSG, **XIII**), have been synthesized.

Structures XII, XIII



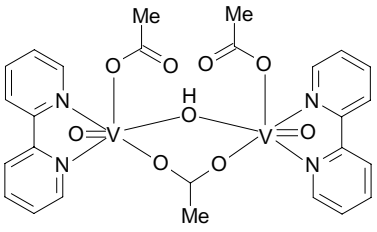
The successive addition of bpy or phen, H_4mpgSS and NaOAc to a solution of $VOSO_4$ in methanol in the presence of oxygen results in the formation of $[(V^{IV}O)_2(\mu\text{-OH})(\mu\text{-OAc})(\mu\text{-}H_2mpgSS)_2(L_{NN})_2]\cdot x\,MeOH\cdot y\,H_2O$ [L_{NN} = bpy (**186**), phen (**187**)] containing the oxidized dimer $[H_2mpgSS^{2-}]$. When glutathione is used instead of H_4mpgSS, the complex $[(V^{IV}O)_2(\mu\text{-OH})(\mu\text{-OAc})(OAc)_2(bpy)_2]$ (**188**) is obtained.[69]

Structures 186 – 188



N⌒N = bpy (**186**, 71%), phen (**187**, 66%)

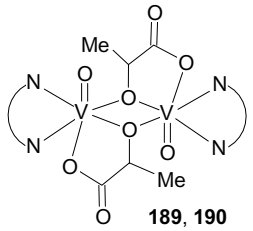
186, **187**



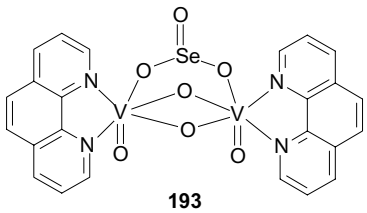
188 (40%)

Lactic acid (Hlact) in the *S*- and/or *R*-form can also serve as a bridging ligand capable of linking two oxovanadium moieties. A series of chiral and achiral complexes $[V_2O_2(bpy)_2(S\text{-lact})_2]$ (**189**), $[V_2O_2(phen)_2(S\text{-lact})_2]$ (**190**), $[V_2O_2(bpy)_2(R\text{-lact})(S\text{-lact})]$ (**191**) and $[V_2O_2(phen)_2(R\text{-lact})(S\text{-lact})]$ (**192**) were prepared by the reaction of V_2O_5, bpy or phen and excess lactic acid under solvothermal conditions. Complexes are structurally similar and contain a bidentate lactate anion, which is coordinated to vanadium *via* alkoxide and carboxylate groups; the other coordination sites of vanadium are occupied by diimine nitrogen and a terminal oxygen atom. Compounds **189** – **192** are paramagnetic, which is consistent with the presence of two V^{IV} centres with d^1 configuration, but the hyperfine coupling is not observed in their EPR spectra because of pronounced spin – spin coupling between the unpaired electrons within the molecule.[153]

Structures 189, 190, 193



189, **190**



193

N⌒N = bpy (**189**, 28%), phen (**190**, 59%)

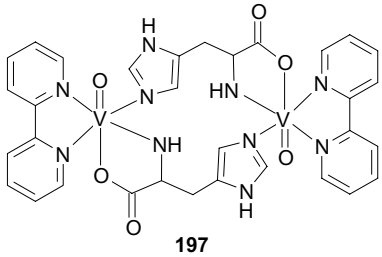
The binuclear complex $[(VO)_2(\mu_2\text{-}O)_2(\mu_2\text{-}SeO_3)(phen)_2]$ (**193**) with a bridging selenite ligand was prepared from V_2O_5, SeO_2, Et_4NOH and phen under hydrothermal conditions. When bpy was taken instead of phen, the polymeric chain complex $[VO(bpy)(\mu\text{-}SeO_3)]_n$ (**194**) was obtained.[70]

The reaction of $VOSO_4$ with dbbpy in methanol yields the binuclear complex $[(VO)_2(\mu_2\text{-}SO_4)_2(dbbpy)_2(CH_3OH)_2]\cdot 4\,MeOH$ (**195**) (Scheme 39). It is a centrosymmetric dimer consisting of two {VO(dbbpy)(MeOH)} moieties linked by two bridging sulfate anions. The subsequent reaction of this complex with sodium pivalate [Na(Piv)] results in the vanadium oxidation giving the complex $[(VO)_2(\mu_2\text{-}O)_2(\mu_2\text{-}SO_4)(dbbpy)_2]\cdot 2\,MeCN$ (**196**), which does not contain pivalate ligands, but has one bridging sulfate anion and two bridging O^{2-} ligands. The structure of compound **196** is similar to the structure of complex **193** described above.

Complex **195** dissociates in ethanol giving the mononuclear form $[VO(\mu_2\text{-}SO_4)(dbbpy)(MeOH)]$. Meanwhile, in dichloromethane, the binuclear structure is retained, and the EPR spectrum exhibits an HFS consisting of 15 lines due to spin exchange interactions between the two paramagnetic moieties [$I(^{51}V) = 7/2$]. The effective magnetic moment decreases from 2.62 to 0.57 μ_B with decreasing temperature. This behaviour is characteristic of binuclear compounds of this type and is related to antiferromagnetic exchange interaction within the molecule.[154]

Organic molecules with several donor heteroatoms can also serve as bridging ligands for the formation of binuclear structures. For example, the binuclear complex with a histidine bridge, $[V_2O_2(L\text{-}His)_2(bpy)_2]\cdot[(EG)\cdot(bpy)]$ (**197**) (His is histidine, EG is ethylene glycol) was obtained in 65% yield under hydrothermal conditions. In this compound, two VO^{2+} moieties are linked *via* the pyrazole nitrogen atom on one side of the histidine molecule and *via* the amino group nitrogen and carboxyl oxygen on the other side of the His molecule.[155]

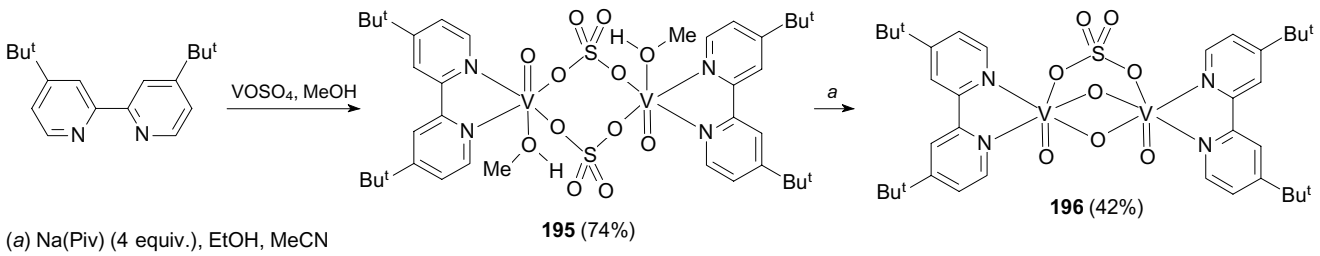
Structure 197



197

The temperature dependence of $\chi_m T$ (Fig. 11) for complex **197** has a minimum at ~180 K; further lowering of the temperature induces a sharp increase in $\chi_m T$. The dependence of $(\chi_m)^{-1}$ on temperature in the range of 4 – 180 K

Scheme 39



(*a*) Na(Piv) (4 equiv.), EtOH, MeCN

195 (74%)

196 (42%)

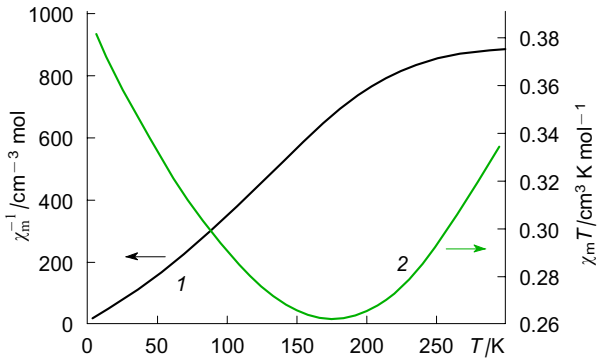
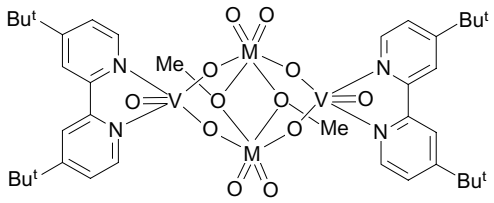


Figure 11. Temperature dependences of $(\chi_m)^{-1}$ (*1*) and $\chi_m T$ (*2*) for complex **197**.[155]

obeys the Curie–Weiss law with the Curie constant of 0.257 cm^3 K mol^{-1} and the Weiss constant of 6.8 K. Thus, ferromagnetic exchange interaction takes place between the V^{IV} ions. At 300 K, the calculated effective magnetic moment is 1.67 μ_B for each vanadium atom.[155]

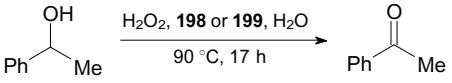
The bridging ligands can be represented by molybdate and tungstate ions. For example, the salt $[VO(dbbpy)_2](SO_4)$ reacts with Na_2WO_4 or Na_2MoO_4 in water to give the binuclear complexes $[V_2O_2(\mu\text{-}MeO)_2(\mu\text{-}WO_4)_2(dbbpy)_2]$ (**198**) or $[V_2O_2(\mu\text{-}MeO)_2(\mu\text{-}MoO_4)_2(dbbpy)_2]$ (**199**). The complexes are structurally similar, each containing two $\{VO(dbbpy)\}^{3+}$ moieties bridged by $\mu\text{-}MO_4^{2-}$ anions (M = W, Mo) and methoxy groups. Notably, the complexes exhibit catalytic activities towards the oxidation of 1-phenylethanol with hydrogen peroxide in water (Scheme 40), and the use of safe and cheap H_2O_2 and H_2O reagents complies with green chemistry principles. With the use of W catalyst **198**, the yield of the ketone is 63%, while in the case of Mo analogue **199**, the yield is 28%.[156]

Structures 198, 199



M = W (**198**, 40%), Mo (**199**, 37%)

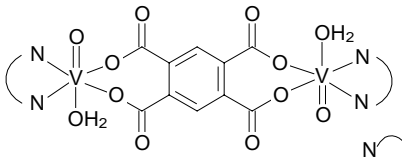
Scheme 40



The reaction of $V_2(SO_4)_3$, benzene-1,2,4,5-tetracarboxylic acid (H_4bta) and bpy or phen in methanol under solvothermal conditions was used to obtain the complexes $[(VO)_2(bpy)_2(bta)(H_2O)_2]$ (**200**) and $[(VO)_2(phen)_2(bta)(H_2O)_2]$ (**201**) with the bridging bta^{4-} anion.[157]

These complexes can be considered as model compounds for studying the mechanism of action of vanadium-dependent haloperoxidases that catalyze the oxidative bromination of organic substrates. Compounds **200** and **201** catalyze the oxidative bromination of phenol red (**XIV**) with hydrogen peroxide in the presence of KBr and phosphate buffered saline to give bromophenol blue (**XV**) (Scheme 41).[157]

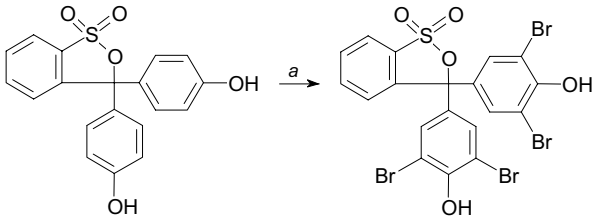
Structures 200, 201



200, **201**

N⌒N = bpy (**200**, 53%), phen (**201**, 63%)

Scheme 41

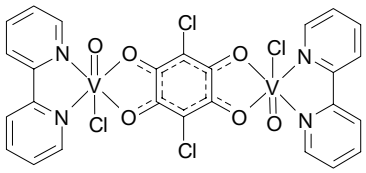


XIV **XV**

(*a*) H_2O_2, KBr, **200** or **201**

A redox-active ligand, which promotes magnetic exchange interactions due to the ability to accept or release electrons, can act as a bridging ligand in oxovanadium complexes. An example of such ligands is the chloranilic acid anion ca^{2-} (H_2ca is chloranilic acid), which can be converted to the semiquinone form. The reaction of $[V^{IV}O(bpy)(TCSQ)Cl]$ (HTCSQ is tetrachlorosemiquinone) with Bu^n_4NOH gives the binuclear complex $[Cl(bpy)V^{IV}O(ca)OV^{IV}(bpy)Cl]$ (**202**) in ~40% yield. In this reaction, the semiquinone radical anion ($TCSQ^{\bullet -}$) in a basic medium (Bu^n_4NOH) undergoes nucleophilic substitution of HO^- by Cl^- to give the ca^{2-} anion, which links two oxovanadium moieties into a binuclear structure.[158]

Structure 202



202

A binuclear complex of a similar structure [VO(dbbpy)Cl(ca)Cl(dbbpy)VO] (**203**) was synthesized by the direct method based on the reaction of $[VO(dbbpy)(H_2O)Cl_2]$ (**169**) with chloranilic acid in acetonitrile in the presence of Et_3N (79% yield). This method doubles the product yield. In both complexes, strong antiferromagnetic exchange exists between the two V^{IV} paramagnetic centres. The molar magnetic susceptibility monotonically decreases with decreasing temperature. At 300 K, the $\chi_m T$ values are 0.71 and 0.72 cm^3 K mol^{-1} for complexes **202** and **203**, while at temperatures below 5 K,

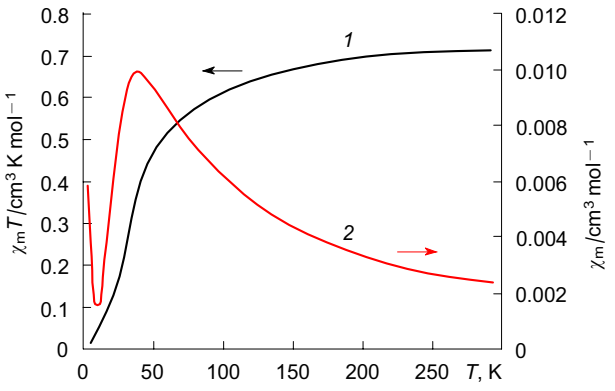


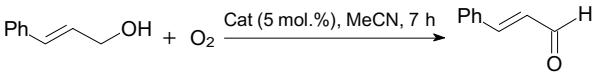
Figure 12. Temperature dependences of $\chi_m T$ (*1*) and χ_m(*2*) for [Cl(bpy)V^{IV}O(ca)OV^{IV}(bpy)Cl] (**202**).[158]

the $\chi_m T$ values are 0.01 and 0.02 cm^3 K mol^{-1}, respectively (Fig. 12).[158]

The cyclic voltammogram of a solid sample of [VO(dbbpy)Cl(ca)Cl(dbbpy)VO] (**203**) measured using a paste electrode shows a quasi-reversible reduction process with the half-wave potential $E_{1/2} = -0.83$ V (*versus* Ag/AgCl), which presumably corresponds to the V^{IV}/V^{III} pair.

There are reported vanadyl complexes with bridging phosphinate ligands with the general formula $[(VO)_2(L_{NN})_3(X)_2](NO_3)$ [L_{NN} = bpy; X = dppa (**204**), bmp (**205**); L_{NN} = phen; X = dppa (**206**), bmp (**207**)] [Hdppa is diphenylphosphinic acid, Hbmp is bis(4-methoxyphenyl)phosphinic acid]. The EPR spectra of these compounds show a signal consisting of 15 lines, which is typical of binuclear V^{IV} complexes. Only weak exchange interactions were detected. Complexes **204**–**207** catalyze the oxidation of cinnamic alcohol with molecular oxygen (Scheme 42). The highest activity was found for $[(VO)_2(bpy)_2(bmp)_3](NO_3)$ (**205**); the yield of the resulting aldehydes was 61% within 7 h.[159]

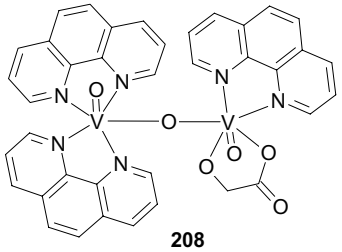
Scheme 42



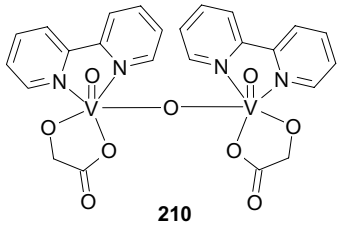
The {O=V–O–V=O} unit is a fairly widespread structural motif of binuclear oxovanadium complexes. A series of mixed-valence binuclear vanadium(IV/V) complexes with glycolate and lactate anions (Hglyc is glycolic acid) have been reported.[160] The complexes $[V_2O_3(phen)_3Y]Cl$ [Y = glyc (**208**), *S*-lact (**209**)], $(NH_4)_2[V_2O_3(bpy)_2Y_2]Cl$ [Y = glyc (**210**), *R,S*-lact (**211**)] and $(NH_4)_2[V_2O_3(bpy)_2(S\text{-lact})_2]$ (**212**) contain the mixed-valence moiety {O=V^{IV}–O–V^{V}=O}. In the complexes $[V_2O_3(phen)_3(glyc)]Cl$ (**208**) and $[V_2O_3(phen)_3(S\text{-lact})]Cl$ (**209**), the {VO(phen)$_2$} moiety is linked to the {VO(phen)(glyc)} and {VO(phen)(S-lact)} moieties, respectively, *via* the μ_2-O^{2-} bridge. In complexes **210**–**212**, the{VO(bpy)(glyc)} and {VO(bpy)(S-lact)} moieties are linked to the symmetrical binuclear complex also by the μ_2-O^{2-} bridge.

These complexes show similar redox behaviours. Both oxidation (in the 0.4–0.5 V range corresponding to the V^{IV}V^{V} → V^{V}V^{V} transition) and reduction (at potentials below −0.2 V corresponding to the V^{IV}V^{V} → V^{IV}V^{IV} transition) waves were detected in the cyclic voltammograms. These compounds catalyze the oxidation of thioanisole to afford methyl phenyl sulfoxide and methyl phenyl sulfone (Scheme 43); with moderate amounts of the catalyst and relatively short reaction time, 98% yield of methyl phenyl sulfoxide and ~50% conversion of the substrate can be attained.[160]

Structures 208, 210

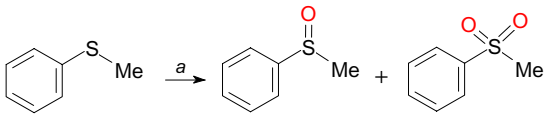


208



210

Scheme 43

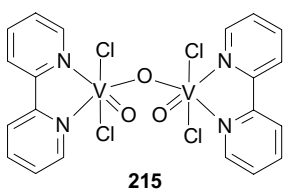


(*a*) H_2O_2, Cat, H_2O, EtOH

In the heterometallic compound $[Cu_2(bpy)_4(C_2O_4)]\cdot[(VO)_2O(bpy)_2(C_2O_4)_2]_2\cdot 10\,H_2O$ (**213**), the anionic part is a mixed-valence binuclear vanadium complex structurally similar to the above-described $[V_2O_3(bpy)_2(L)_2]^-$ anions (L = glyc, lact) (**210**–**212**).[161] At 100 K, the $\chi_m T$ value for complex **213** is 1.53 cm^3 K mol^{-1}. This value is consistent with the presence of one vanadium(IV) centre and two isolated copper(II) centres. The $\chi_m T$ value increases with decreasing temperature, which is due to ferromagnetic exchange between Cu^{II} ions.[161]

An attempted crystallization of the complex [V^{V}O(bpy)Cl$_3$] (**214**) obtained by the reaction of $VOCl_3$ with bpy in 1 : 1 ratio in dichloromethane affords crystals of the binuclear complex $[(VO)_2(\mu\text{-}O)(bpy)_2Cl_4]$ (**215**). This complex consists of two V^{V}O groups bridged by an oxygen atom.[162]

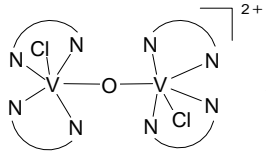
Structure 215



215

Binuclear vanadium(III) complexes are also known. The symmetrical complexes $[V_2^{III}(\mu\text{-}O)(bpy)_4Cl_2]Cl_2 \cdot$ (**216**)[133] and $[V_2^{III}(\mu\text{-}O)(phen)_4Cl_2]Cl_2 \cdot$ (**217**) have been reported.[71] The bpy-containing complex is formed by the reaction of VCl_3 with bpy in 1 : 3 ratio in water, while the phen complex is formed in ethanol. In both compounds, weak antiferromagnetic interactions take place at room temperature with $\mu_{eff} = 3.24$ and 3.18 μ_B, respectively. Complex **216** is oxidized by air oxygen to give $[V^{IV}O(bpy)_2Cl](ClO_4)$ (**218**) and $[V^{V}O_2(bpy)_2]Cl$ (**219**).

Structures 216, 217



216, **217**

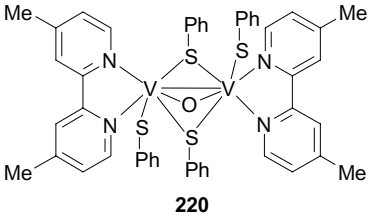
N⌒N = bpy (**216**), phen (**217**, 80%)

Complex **217** is able to bind to DNA molecules and initiate their cleavage.[72]

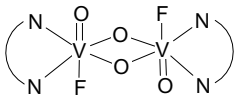
Hydrolysis of $(Et_4N)[V^{III}(dmbpy)(SPh)_4]$ furnishes the binuclear complex $[V_2O(dmbpy)_2(SPh)_4]$ (**220**), in which two vanadium atoms are bridged by the $\mu\text{-}O^{2-}$ and $\mu\text{-}SPh^-$ groups. The V–V distance is 2.579(3) Å, which is consistent with the $V^{III}-V^{III}$ single bond length. In this complex, strong antiferromagnetic interactions take place. The effective magnetic moment is 1.35 μ_B (for two V^{III} centres) at 300 K and gradually decreases to 0.095 μ_B at 5 K, which is much lower than expected for two d^2 ions (for one d^2 ion, $\mu_{eff} = 2.83$ μ_B).[163]

Fluorine-containing binuclear vanadium complexes are very rare. For example, the compounds $[(V^{V}O)_2(\mu\text{-}O)_2(bpy)_2F_2]$ (**221**) and $[(V^{V}O)_2(\mu\text{-}O)_2(phen)_2F_2]$ (**222**) have been reported.[59,152]

Structures 220–222



220



221, **222**

N⌒N = bpy (**221**), phen (**222**)

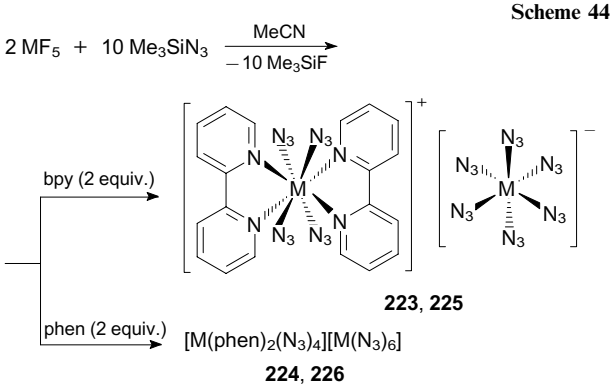
4.2. Niobium and tantalum

Niobium and tantalum complexes with bpy and phen type ligands are much less typical than vanadium complexes. Professor Christe's research team[60] obtained the unique niobium and tantalum azide complexes $[M(L_{NN})_2(N_3)_4][M(N_3)_6]$ [M = Nb; L_{NN} = bpy (**223**), phen (**224**); M = Ta; L_{NN} = bpy (**225**), phen (**226**)], which were formed from pentafluorides (MF_5) *via* the exchange reaction with Me_3SiN_3 in the presence of the appropriate ligand in acetonitrile (Scheme 44). The yields of tantalum complexes **225** and **226** were quantitative (99%).

In the $[M(L_{NN})_2(N_3)_4]^+$ cation, the metal atom has a distorted square-antiprism geometry, that in the $[M(N_3)_6]^-$ anion has a distorted octahedral environment.

The formation of these complexes is stepwise and, in the case of bpy, it was possible to isolate the structurally similar

Scheme 44



223, **225**

224, **226**

M = Nb (**223**, **224**), Ta (**225**, **226**)

Scheme 45

$$2\,MF_5 + 6\,Me_3SiN_3 \xrightarrow[-6\,Me_3SiF]{bpy\ (2\ equiv.)} [M(bpy)_2F_4][M(N_3)_6]$$

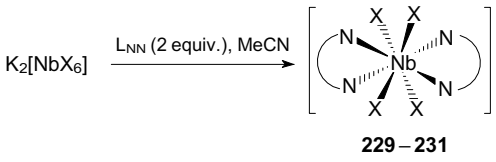
227, **228**

M = Nb (**227**), Ta (**228**, 99%)

intermediate compounds $[M(bpy)_2F_4][M(N_3)_6]$ [M = Nb (**227**), Ta (**228**)] (Scheme 45).[60]

The square-antiprismatic complexes $[Nb^{IV}(L_{NN})_2X_4]$ [L_{NN} = bpy, X = NCSe (**229**); L_{NN} = dmbpy; X = NCS (**230**), NCSe (**231**)] are formed upon the reactions of $K_2[NbX_6]$ with 2 equiv. of an NN ligand in acetonitrile (Scheme 46) or upon the reduction of $K[NbX_6]$ in the presence of bpy.[164,165] Also, the structurally similar complex $[Nb(bpy)_2Br_4]Br$ (**232**) was obtained by the reaction of $NbBr_5$ with bpy at 0 °C. It is of interest that an analogous reaction of $NbCl_5$ with bpy gives the complex $[Nb(bpy)Cl_5] \cdot MeCN$ (**233**) with C.N. 7.[166]

Scheme 46



229–231

N⌒N = bpy (**229**), dmbpy (**230**, **231**); X = NCSe (**229**, **231**), NCS (**230**)

The reactions of $K[TaX_6]$ with 1 equiv. of bpy produce the complexes $[Ta^{V}(bpy)X_5]$ [X = NCS (**234**), NCSe (**235**)], which are structurally similar to complex **233** (Scheme 47).[164]

Scheme 47

$$K[TaX_6] \xrightarrow{bpy,\ MeCN} [Ta^{V}(bpy)X_5]$$

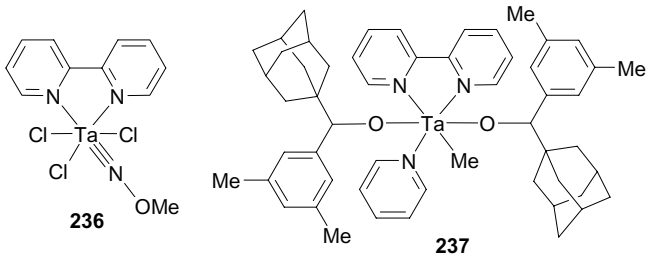
234, **235**

X = NCS (**234**), NCSe (**235**)

In the presence of bipyridine, $TaCl_5$ reacts with *O*-methylhydroxylamine or bis(trimethylsilyl)-*O*-methylhydroxylamine to give *mer*-[(Ta≡NOMe)(bpy)Cl_3] (**236**) in 70% yield.[167]

The reaction of $[Ta^{V}Me_3(OC(Ad)C_6H_3Me_2\text{-}3,5)_2]$ (Ad is 1-adamantyl) with excess pyridine in the presence of H_2 leads unexpectedly to dimerization of two pyridine rings in the bpy ligand, giving rise to $[TaMe(OCH(Ad)C_6H_3Me_2\text{-}3,5)_2(py)(bpy)]$ (**237**) in 45% yield.[168]

Structures 236, 237

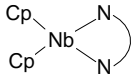


236 **237**

The niobium(IV) complexes $[Nb(L_{NN})(Cp)_2](PF_6)_2$ [L_{NN} = bpy (**238**), phen (**239**)] were synthesized in ~50% yields by the reactions of $[Nb(Cp)_2Cl_2]$, the appropriate ligand and $TlPF_6$ in 1 : 1 : 3 ratio in dibromoethane. The crystal structure of compound **238** was determined; the coordination environment of niobium is pseudo-tetrahedral and includes two η^5-Cp ligands coordinated in an angular fashion and one bpy molecule.[169]

The cyclic voltammogram of complex **238** in acetonitrile exhibits two reversible redox peaks at $E_{1/2} = -0.305$ and -1.350 V (against a calomel electrode). The first peak refers to the one-electron reduction of Nb^{IV} to Nb^{III}, while the second one is associated with the bpy reduction. In the case of compound **239**, a reversible process attributable to the reduction of Nb^{IV} takes place at -0.310 V, whereas the reduction of phen at -1.340 V is fully irreversible.[169]

Structures 238, 239



238, **239**

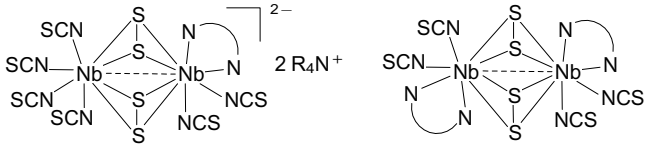
N⌒N = bpy (**238**), phen (**239**)

Niobium and tantalum tris-chelates $[M(L_{NN})_3]^n$ (M = Nb, Ta; L_{NN} = bpy, dbbpy; $n = 0, -1$) have been reported. The complex $[Nb(bpy)_3]$ (**240**) was prepared by the reaction of $NbCl_5$ with bpy in 1 : 3 ratio in cold THF in the presence of Li as a reducing agent. The anionic complex $Li[Nb(bpy)_3]$ (**241**) was obtained in 54% yield by the reaction of $NbCl_5$ with bpy in 1 : 3 ratio in THF, which also proceeds in the presence of Li.[170] The neutral complex $[Nb(dbbpy)_3]$ (**242**) is formed when $NbCl_5$ is allowed to react with dbbpy in 1 : 3 ratio in THF with sodium amalgam as a reducing agent (65% yield). The complex $Na[Ta(dbbpy)_3]$ (**243**) is obtained in a similar way. The addition of an equimolar amount of tropylium tetrafluoroborate in THF to compound **243** results in the formation of the neutral complex $[Ta(dbbpy)_3]$ (**244**) in 92% yield.[171] For tantalum, the complexes $[Ta(bpy)_3]$ (**245**) and $Na[Ta(bpy)_3]$ (**246**) are also known.[172]

Anionic complexes **241**, **243** and **246** are diamagnetic (S = 0), but they have different electronic structures. According to DFT calculations and X-ray diffraction data, compound **241** is best described by the formula $[Nb^{IV}(bpy^{\bullet})(bpy^{2-})_2]^-$, whereas in the case of complex **246**, all bpy ligands are equivalent and occur in the reduced dianion form: $[Ta^{V}(bpy^{2-})_3]^-$. Like in the case of vanadium, neutral complexes **242** and **244** are paramagnetic (S = 1/2). The EPR spectrum of niobium complex **242** tends to show the HFS, namely, a signal consisting of 10 lines with the parameters $g_{iso} = 1.985$ and $A_{iso} = 88.3$ G, which implies strong interaction of the electron with the ^{93}Nb nucleus (I = 9/2). The structure of **242** is best described as $[Nb^{IV}(bpy^{2-})_2(bpy^{0})]^0$. Conversely, the EPR spectrum of a similar tantalum complex **244** exhibits no HFS; instead, a broad single peak is present. Presumably, in compound **244**, tantalum is in the pentavalent state, while one bipyridine ligand is in the radical anion state, which is described as $[Ta^{V}(dbbpy^{\bullet})(dbbpy^{2-})_2]^0$.[171]

Binuclear niobium and tantalum complexes are scarcely known. Only one publication [173] considers binuclear sulfide clusters $\{Nb_2S_4\}$ with one or two coordinated diimine molecules. These are mixed-ligand niobium(IV) complexes: $(Et_4N)_2[Nb_2S_4(L_{NN})(NCS)_6]$ [L_{NN} = bpy (**247**), dcbpy (**248**), dnbpy (**249**), phen (**250**)], $(Bu^{n}_4N)_2[Nb_2S_4(Hpbz)(NCS)_6]$ (**251**) and $[Nb_2S_4(L_{NN})_2(NCS)_4]$ [L_{NN} = phen (**252**), Hpbz (**253**)]. They are formed in the reactions of $(R_4N)_4[Nb_2S_4(NCS)_8]$ (R = Et, Bu^n) with appropriate ligands in acetonitrile. Even in the presence of excess ligand, the isothiocyanate is not completely displaced; only one or two diimine molecules can be introduced into the complexes.

Structures 247–253



247–251 **252**, **253**

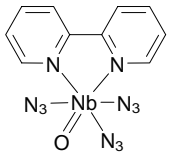
N⌒N = bpy (**247**, 99%), dcbpy (**248**, 80%), dnbpy (**249**, 55%), phen (**250**, 30%), hpbz (**251**, 30%); R = Et (**247–250**), Bu^n (**251**); N⌒N = phen (**252**, 40%), Hpbz (**253**, 24%);
dcbpy is 2,2′-bipyridine-3,4-dicarboxylic acid,
dnbpy is 4,4′-di(non-5-yl)-2,2′-bipyridine,
Hbpz is 2-(2-pyridyl)benzimidazole

All of these complexes are intensely coloured [the molar absorption coefficient (ε) $\approx 10^3$ L mol^{-1} cm^{-1}]. Their electronic absorption spectra (EAS) show broad bands in the visible range, which apparently refer to the charge transfer from the $\{Nb_2S_4\}$ cluster core to the diimine ligand. It was shown that compounds **247–249** are capable of reversible absorption saturation and show nonlinear light transmission, *i.e.*, they possess optical limiting properties and can be considered as potential broad-band optical limiters. In addition, P25 type TiO_2 nanoparticles modified by $(Et_4N)_2[Nb_2S_4(NCS)_6(bpy)]$ (**247**) demonstrate a moderate photocatalytic activity towards the hydrogen evolution reaction (HER) on irradiation at >410 nm. The photocatalyst activity is 12 mol of H_2 per gram of the catalyst per hour (or ~15 H_2 molecules per formula unit per hour). The results are modest in comparison with efficient systems based on molybdenum disulfide, but demonstrate the conceptual applicability of niobium sulfides as the catalysts for hydrogen evolution.[173]

4.3. Oxoniobium complexes

Generally, niobium is less prone to form oxo derivatives than vanadium. Professor Christe's research team[174] prepared the complex $[NbO(bpy)(N_3)_3]$ (**254**) in 94% yield by the reaction of $[NbO(N_3)_3]$ with bpy in acetonitrile.

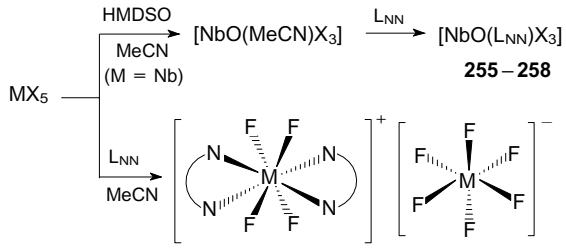
Structure 254



254

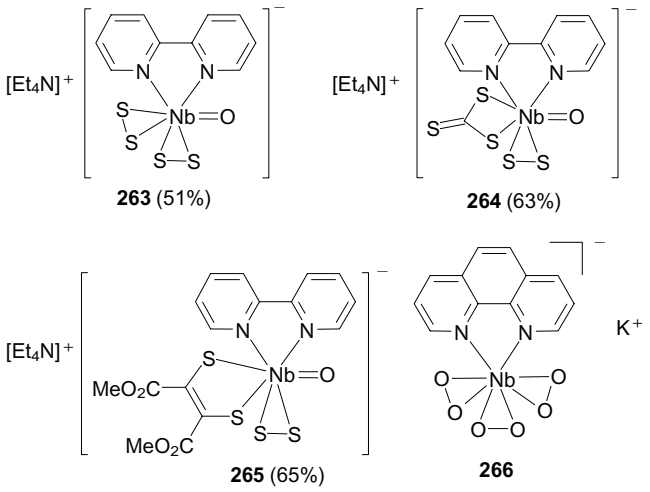
A series of oxoniobium(V) complexes $[NbO(L_{NN})X_3]$ [X = Cl; L_{NN} = bpy (**255**), phen (**256**); X = Br; L_{NN} = bpy (**257**), phen (**258**)] have been synthesized in high yields by the reaction of NbX_5, hexamethyldisiloxane (HMDSO) and the appropriate ligand in 1 : 1 : 1 ratio. These complexes are structurally similar to $[NbO(bpy)(N_3)_3]$.[174] If no HMDSO is added, the reaction gives the complexes $[Nb(L_{NN})_2F_4][NbF_6]$ [L_{NN} = bpy (**259**), phen (**260**)], which presumably have the same structure as azide complexes **223** – **226**. Analogous tantalum complexes $[Ta(L_{NN})_2F_4][TaF_6]$ [L_{NN} = bpy (**261**), phen (**262**)] have also been obtained (Scheme 48), but oxo derivatives $[TaO(L_{NN})X_3]$ are not formed under these conditions.[175]

Scheme 48



X = Cl: L_{NN} = bpy (**255**, 52%), phen (**256**, 61%); X = Br: L_{NN} = bpy (**257**), phen (**256**, ~50%); M = Nb: N⌒N = bpy (**259**, 86%), phen (**260**, 89%); X = Ta: N⌒N = bpy (**261**, 86%), phen (**262**, 83%)

Structures 263 – 266



263 (51%) **264** (63%)

265 (65%) **266**

The oxoniobium(V) sulfide complexes $[Et_4N][NbO(S_2)_2(bpy)]$ (**263**), $[Et_4N][NbO(CS_3)(S_2)(bpy)]$ (**264**) and $[Et_4N][NbO(S_2C_2(CO_2Me)_2)(S_2)(bpy)]$ (**265**) have been prepared. Complex **263** is formed upon the reaction of $NbO(SPh)_4$ with elemental sulfur in the presence of bpy in DMF. Complexes **264** and **265** are formed upon the reaction of compound **263** with carbon disulfide and dimethyl acetylenedicarboxylate, respectively. In all of these compounds, the niobium atom has a distorted pentagonal-bipyramidal geometry.[176]

The crystal structures of the peroxoniobium complex $K[Nb(O_2)_3(phen)]\cdot 3H_2O$ (**266**) and its hydrogen peroxide adduct $K[Nb(O_2)_3(phen)]\cdot 3H_2O\cdot H_2O_2$ (**267**) have been reported.[177] The niobium atom has a dodecahedral ligand environment.

5. Conclusion

The present review demonstrates the great diversity of group 5 metal complexes with diimine ligands of various nature, which possess practically valuable properties, including redox ability, magnetic behaviour and catalytic and biological activities. Vanadium tends to form complexes with 2,2′-bipyridine and 1,10-phenanthroline ligands and their derivatives. The known vanadium compounds include both mononuclear complexes with and without oxovanadium group and binuclear structures with different bridging groups. Most often, vanadium is in the tetra- or pentavalent state and, more rarely, in the trivalent state. Oxovanadium derivatives are most abundant, because of high oxophilicity of vanadium. The coordination environment of vanadium in these compounds is, most often, an octahedron and, more rarely, a square pyramid. In binuclear vanadium(III, IV) complexes, ferro- and antiferromagnetic exchange interactions are often present, which attracts the attention of researchers working in the field of molecular magnetism. On the other hand, high-valent vanadium diimine complexes are of interest as catalysts for various oxidation reactions of organic substrates (alkenes, alkanes, organic sulfides, alcohols, *etc.*). They are considered as model compounds for processes catalyzed by vanadium-containing enzymes. In addition, oxovanadium complexes containing diimine and Schiff base ligands can form intercalates with DNA molecules. In some cases, these complexes selectively bind to the tumour DNA. This fact, in combination with their phototoxicity, makes these compounds promising for the development of anticancer drugs capable of competing with clinically approved drugs.

Niobium and tantalum, unlike vanadium, tend to form mononuclear complexes with redox-active α-diimines, in particular, 1,4-diazabuta-1,3-dienes, in which the DAD ligands occur, most often, in the reduced form. The ability of the DAD ligand to exist in different oxidation states and the ease of its modification account for extensive application of metal complexes based on these ligands as catalysts in various redox transformations, including polymerization of alkenes, hydrodehalogenation of halohydrocarbons, chlorination of benzyl ethers, radical addition of CCl_4 to alkenes and so on.

Thus, the chemistry of vanadium, niobium and tantalum coordination compounds with diimine ligands is a rapidly developing area both for fundamental research and for solving applied problems, including the development of new materials, the search for new biologically active compounds and catalysts.

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References

1. Y.Tanabe, Y.Nishibayashi. *Coord. Chem. Rev.*, **379**, 135 (2019)
2. D.Rehder. *Coord. Chem. Rev.*, **182**, 297 (1999)
3. J.C.Pessoa, S.Etcheverry, D.Gambino. *Coord. Chem. Rev.*, **301 – 302**, 24 (2015)
4. M.Sutradhar, L.M.D.R.S.Martins, M.F.C.Guedes da Silva, A.J.L.Pombeiro. *Coord. Chem. Rev.*, **301 – 302**, 200 (2015)
5. C.J.Chang, J.A.Labinger, H.B.Gray. *Inorg. Chem.*, **36**, 5927 (1997)
6. K.I.Smith, L.L.Borer, M.M.Olmstead. *Inorg. Chem.*, **42**, 7410 (2003)
7. T.Hirao, M.Mori, Y.Ohshiro. *J. Org. Chem.*, **55**, 358 (1990)
8. J.Rocek, D.E.Aylward. *J. Am. Chem. Soc.*, **97**, 5452 (1975)
9. S.K.Hanson, R.T.Baker, J.C.Gordon, B.L Scott, L.A."Pete" Silks, D.L.Thorn. *J. Am. Chem. Soc.*, **132**, 17804 (2010)
10. S.K.Hanson, R.Wu, L.A. "Pete" Silks. *Angew. Chem., Int. Ed.*, **51**, 3410 (2012)
11. G.Zhang, B.L.Scott, R.Wu, L.A."Pete" Silks, S.K.Hanson. *Inorg. Chem.*, **51**, 7354 (2012)
12. N.B.Barhate, C.-T.Chen. *Org. Lett.*, **4**, 2529 (2002)
13. S.Takizawa, H.Grìger, H.Sasai. *Chem. – Eur. J.*, **21**, 8992 (2015)
14. G.B.Shul'pin. In *Comprehensive Inorganic Chemistry II*. (2nd Edn.). (Eds J.Reedijk, K.Poeppelmeier). (Amsterdam: Elsevier, 2013). P. 79
15. K.H.Thompson, J.H.McNeill, C.Orvig. *Chem. Rev.*, **99**, 2561 (1999)
16. K.H.Thompson, C.Orvig. *Coord. Chem. Rev.*, **219 – 221**, 1033 (2001)
17. D.C.Crans, A.M.Trujillo, P.S.Pharazyn, M.D.Cohen. *Coord. Chem. Rev.*, **255**, 2178 (2011)
18. A.Bishayee, A.Waghray, M.A.Patel, M.Chatterjee. *Cancer Lett.*, **294**, 1 (2010)
19. H.Sakurai, Y.Kojima, Y.Yoshikawa, K.Kawabe, H.Yasui. *Coord. Chem. Rev.*, **226**, 187 (2002)
20. R.R.Langeslay, D.M.Kaphan, C.L.Marshall, P.C.Stair, A.P.Sattelberger, M.Delferro. *Chem. Rev.*, **119**, 2128 (2019)
21. E.B.Vickers, T.D.Selby, M.S.Thorum, M.L.Taliaferro, J.S.Miller. *Inorg. Chem.*, **43**, 6414 (2004)
22. P.Mialane, J.Marrot, E.Rivière, J.Nebout, G.Hervé. *Inorg. Chem.*, **40**, 44 (2001)
23. J.M.Lauzon, P.Eisenberger, S.-C.Roşca, L.L.Schafer. *ACS Catal.*, **7**, 5921 (2017)
24. L.P.Spencer, C.Beddie, M.B.Hall, M.D.Fryzuk. *J. Am. Chem. Soc.*, **128**, 12531 (2006)
25. A.Baunemann, D.Rische, A.Milanov, Y.Kim, M.Winter, C.Gemel, R.A.Fischer. *Dalton Trans.*, 3051 (2005)
26. I.Nowak, M.Ziolek. *Chem. Rev.*, **99**, 3603 (1999)
27. D.Bayot, M.Devillers. *Coord. Chem. Rev.*, **250**, 2610 (2006)
28. R.J.Burford, A.Yeo, M.D.Fryzuk. *Coord. Chem. Rev.*, **334**, 84 (2017)
29. B.M.Cossairt, N.A.Piro, C.C.Cummins. *Chem. Rev.*, **110**, 4164 (2010)
30. M.Aresta, A.Dibenedetto, A.Angelini. *Chem. Rev.*, **114**, 1709 (2014)
31. K.C.Gupta, A.K.Sutar. *Coord. Chem. Rev.*, **252**, 1420 (2008)
32. X.Liu, J.R.Hamon. *Coord. Chem. Rev.*, **389**, 94 (2019)
33. J.Zhang, L.Xu, W.Y.Wong. *Coord. Chem. Rev.*, **355**, 180 (2018)
34. M.Kojima, H.Taguchi, M.Tsuchimoto, K.Nakajima. *Coord. Chem. Rev.*, **237**, 183 (2003)
35. K.C.Gupta, A.Kumar Sutar, C.C.Lin. *Coord. Chem. Rev.*, **253**, 1926 (2009)
36. C.P.Pradeep, S.K.Das. *Coord. Chem. Rev.*, **257**, 1699 (2013)
37. X.Liu, G.J.Ma, G.Sun, Y.P.Duan, S.H.Liu. *Appl. Surf. Sci.*, **258**, 1033 (2011)
38. H.R.Chen, Y.C.Chen, T.C.Chang, K.C.Chang, T.M.Tsai, T.J.Chu, C.C.Shih, N.C.Chuang, K.Y.Wang. *Nanoscale Res. Lett.*, **11**, (2016)
39. K.Y.Liu, J.W.Lee, F.B.Wu. *Surf. Coat. Technol.*, **259**, 123 (2014)
40. M.Sindler, R.Tesar, J.Kolácek, P.Szabó, P.Samuely, V.Hasková, C.Kadlec, F.Kadlec, P.Kuzel. *Supercond. Sci. Technol.*, **27**, (2014)
41. K.Ilin, D.Henrich, Y.Luck, Y.Liang, M.Siegel, D.Y.Vodolazov. *Phys. Rev. B: Condens. Matter*, **89**, 184511 (2014)
42. K.Smirnov, A.Divochiy, Y.Vakhtomin, P.Morozov, P.Zolotov, A.Antipov, V.Seleznev. *Supercond. Sci. Technol.*, **31**, Art. ID 035011 (2018)
43. H.-L.Du, T.R.Gengenbach, R.Hodgetts, D.R.MacFarlane, A.N.Simonov. *ACS Sustain. Chem. Eng.*, **7**, 6839 (2019)
44. N.Kaeffer, M.Chavarot-Kerlidou, V.Artero. *Acc. Chem. Res.*, **48**, 1286 (2015)
45. W.Kaim. *Inorg. Chem.*, **50**, 9752 (2011)
46. G.A.Abakumov, A.V.Piskunov, V.K.Cherkasov, I.L.Fedushkin, V.P.Ananikov, D.B.Eremin, E.G.Gordeev, I.P.Beletskaya, A.D.Averin, M.N.Bochkarev, A.A.Trifonov, U.M.Dzhemilev, V.A.D yakonov, M.P.Egorov, A.N.Vereshchagin, M.A.Syroeshkin, V.V.Jouikov, A.M.Muzafarov, A.A.Anisimov, A.V.Arzumanyan, Y.N.Kononevich, M.N.Temnikov, O.G.Sinyashin, Y.H.Budnikova, A.R.Burilov, A.A.Karasik, V.F.Mironov, P.A.Storozhenko, G.I.Shcherbakova, B.A.Trofimov, S.V.Amosova, N.K.Gusarova, V.A.Potapov, V.B.Shur, V.V.Burlakov, V.S.Bogdanov, M.V.Andreev. *Russ. Chem. Rev.*, **87**, 393 (2018)
47. M.G.Chegerev, A.V.Piskunov. *Russ. J. Coord. Chem.*, **44**, 258 (2018)
48. A.Raghavan, A.Venugopal. *J. Coord. Chem.*, **67**, 2530 (2014)
49. O.R.Luca, R.H.Crabtree. *Chem. Soc. Rev.*, **42**, 1440 (2013)
50. V.K.K.Praneeth, M.R.Ringenberg, T.R.Ward. *Angew. Chem., Int. Ed.*, **51**, 10228 (2012)
51. V.Lyaskovskyy, B.de Bruin. *ACS Catal.*, **2**, 270 (2012)
52. W.Kaim, B.Schwederski. *Coord. Chem. Rev.*, **254**, 1580 (2010)
53. M.Villa, D.Miesel, A.Hildebrandt, F.Ragaini, D.Schaarschmidt, A.Jacobi von Wangelin. *ChemCatChem*, **9**, 3203 (2017)
54. W.Kaim. *Dalton Trans.*, **48**, 8521 (2019)
55. J.I.van der Vlugt. *Chem. – Eur. J.*, **25**, 2651 (2019)
56. D.L.J.Broere, R.Plessius, J.I.Van Der Vlugt. *Chem. Soc. Rev.*, **44**, 6886 (2015)
57. H.Tsurugi, T.Saito, H.Tanahashi, J.Arnold, K.Mashima. *J. Am. Chem. Soc.*, **133**, 18673 (2011)
58. L.R.Chamberlain, I.P.Rothwell, J.C.Huffman. *J. Chem. Soc., Chem. Commun.*, 1203 (1986)
59. J.Sala-Pala, J.E.Guerchais. *J. Mol. Struct.*, **20**, 169 (1974)
60. R.Haiges, P.Deokar, K.O.Christe. *Angew. Chem., Int. Ed.*, **53**, 5421 (2014)
61. G.B.Shul'pin, Y.N.Kozlov, L.S.Shul'pina. *Catalysts*, **9**, 1046 (2019)
62. I.Gryca, K.Czerwiåska, B.Machura, A.Chrobok, L.S.Shul'pina, M.L.Kuznetsov, D.S.Nesterov, Y.N.Kozlov, A.J.L.Pombeiro, I.A.Varyan, G.B.Shul'pin. *Inorg. Chem.*, **57**, 1824 (2018)
63. I.S.Fomenko, A.L.Gushchin, L.S.Shul'pina, N.S.Ikonnikov, P.A.Abramov, N.F.Romashev, A.S.Poryvaev, A.M.Sheveleva, A.S.Bogomyakov, N.Y.Shmelev, M.V.Fedin, G.B.Shul'pin, M.N.Sokolov. *New J. Chem.*, **42**, 16200 (2018)

64. I.S.Fomenko, A.L.Gushchin, P.A.Abramov, M.N.Sokolov, L.S.Shul'pina, N.S.Ikonnikov, M.L.Kuznetsov, A.J.L.Pombeiro, Y.N.Kozlov, G.B.Shul'pin. *Catalysts*, **9**, 217 (2019)
65. F.A.Cotton, W.J.Roth. *J. Am. Chem. Soc.*, **105**, 3734 (1983)
66. M.Wang, T.Weyhermüller, J.England, K.Wieghardt. *Inorg. Chem.*, **52**, 12763 (2013)
67. M.Wang, T.Weyhermüller, K.Wieghardt. *Eur. J. Inorg. Chem.*, 3246 (2015)
68. U.Saha, T.K.Si, P.K.Nandi, K.K.Mukherjea. *Inorg. Chem. Commun.*, **38**, 43 (2013)
69. E.J.Tolis, M.J.Manos, A.Terzis, C.P.Raptopoulou, T.A Kabanos. *Dalton Trans.*, 775 (2003)
70. Z.Dai, Z.Shi, G.Li, D.Zhang, W.Fu, H.Jin, W.Xu, S.Feng. *Inorg. Chem.*, **42**, 7396 (2003)
71. T.Otieno, M.R.Bond, L.M.Mokry, R.B.Walter, C.J.Carrano. *Chem. Commun.*, 37 (1996)
72. H.Kumagai, S.Kitagawa, M.Maekawa, S.Kawata, H.Kiso, M.Munakata. *J. Chem. Soc., Dalton Trans.*, 2390 (2002)
73. A.Nakamura, K.Mashima. *J. Organomet. Chem.*, **621**, 224 (2001)
74. J.P.Neu, P.Di Martino-Fumo, B.Oelkers, Y.Sun, A.Neuba, M.Gerhards, W.R.Thiel. *Dalton Trans.*, **47**, 9643 (2018)
75. F.Hartl, P.Rosa, L.Ricard, P.Le Floch, S.Zális. *Coord. Chem. Rev.*, **251**, 557 (2007)
76. I.L.Fedushkin, A.A.Skatova, V.A.Chudakova, G.K Fukin. *Angew. Chem., Int. Ed.*, **42**, 3294 (2003)
77. I.L.Fedushkin, A.N.Lukoyanov, E.V.Baranov. *Inorg. Chem.*, **57**, 4301 (2018)
78. Z.Guan, C.S.Popeney. *Top. Organomet. Chem.*, **26**, 179 (2009)
79. S.Mecking, L.K.Johnson, L.Wang, M.Brookhart. *J. Am. Chem. Soc.*, **120**, 888 (1998)
80. S.Kar, B.Sarkar, S.Ghumaan, D.Roy, F.A.Urbanos, J.Fiedler, R.B.Sunoj, R.Jimenez-Aparicio, W.Kaim, G.K.Lahiri. *Inorg. Chem.*, **44**, 8715 (2005)
81. V.A.Dodonov, A.G.Morozov, R.V.Rumyantsev, G.K.Fukin, A.A.Skatova, P.W.Roesky, I.L.Fedushkin. *Inorg. Chem.*, **58**, 16559 (2019)
82. I.L.Fedushkin, O.V.Maslova, A.G.Morozov, S.Dechert, S.Demeshko, F.Meyer. *Angew. Chem., Int. Ed.*, **51**, 10584 (2012)
83. Y.Bai, W.Chen, J.Li, C.Cui. *Coord. Chem. Rev.*, **383**, 132 (2019)
84. K.M.Clark, J.Bendix, A.F.Heyduk, J.W.Ziller. *Inorg. Chem.*, **51**, 7457 (2012)
85. J.Bendix, K.M.Clark. *Angew. Chem., Int. Ed.*, **55**, 2748 (2016)
86. T.Tezgerevska, K.G.Alley, C.Boskovic. *Coord. Chem. Rev.*, **268**, 23 (2014)
87. I.L.Fedushkin, A.A.Skatova, V.A.Chudakova, G.K.Fukin. *Angew. Chem., Int. Ed.*, **42**, 3294 (2003)
88. I.L.Fedushkin, O.V.Maslova, E.V.Baranov, A.S.Shavyrin. *Inorg. Chem.*, **48**, 2355 (2009)
89. I.L.Fedushkin, D.S.Yambulatov, A.A.Skatova, E.V.Baranov, S.Demeshko, A.S.Bogomyakov, V.I.Ovcharenko, E.M.Zueva. *Inorg. Chem.*, **56**, 9825 (2017)
90. S.Milione, G.Cavallo, C.Tedesco, A.Grassi. *J. Chem. Soc., Dalton Trans.*, 1839 (2002)
91. S.-y.Xu, X.-m.Chen, L.-c.Huang, F.Li, W.Gao. *Polyhedron*, **164**, 146 (2019)
92. C.D.Nunes, P.D.Vaz, V.Félix, L.F.Veiros, T.Moniz, M.Rangel, S.Realista, A.C.Mourato, M.J.Calhorda. *Dalton Trans.*, **44**, 5125 (2015)
93. H.Nishiyama, H.Ikeda, T.Saito, B.Kriegel, H.Tsurugi, J.Arnold, K.Mashima. *J. Am. Chem. Soc.*, **139**, 6494 (2017)
94. B.F.Parker, H.Hosoya, J.Arnold, H.Tsurugi, K.Mashima. *Inorg. Chem.*, **58**, 12825 (2019)
95. H.Nishiyama, H.Hosoya, B.F.Parker, J.Arnold, H.Tsurugi, K.Mashima. *Chem. Commun.*, **55**, 7247 (2019)
96. B.Richter, J.Scholz, J.Sieler, K.-H.Thiele. *Angew. Chem., Int. Ed. Engl.*, **34**, 2649 (1996)
97. J.Scholz, H.Görls. *Polyhedron*, **21**, 305 (2002)
98. T.Spaniel, H.Görls, J.Scholz. *Angew. Chem., Int. Ed.*, **37**, 1862 (1998)
99. F.A.Cotton, S.A.Duraj, W.J.Roth. *J. Am. Chem. Soc.*, **106**, 6987 (1984)
100. L.R.Chamberlain, L.D.Durfee, P.E.Fanwick, L.M.Kobriger, S.L.Latesky, A.K.McMullen, B.D.Steffey, I.P.Rothwell, K.Foltin, J.C.Huffman. *J. Am. Chem. Soc.*, **109**, 6068 (1987)
101. P.J.Daff, M.Etienne, B.Donnadieu, S.Z.Knottenbelt, J.E.McGrady. *J. Am. Chem. Soc.*, **124**, 3818 (2002)
102. L.G.Hubert-Pfalzgraf, A.Zaki, L.Toupet. *Acta Crystallogr., Sect. C*, **49**, 1609 (1993)
103. K.Mashima, Y.Matsuo, K.Tani. *Organometallics*, **18**, 1471 (1999)
104. A.J.Churchill, J.C.Green, A.G.Moody, M.Müller. *Inorg. Chim. Acta*, **369**, 120 (2011)
105. H.Kawaguchi, Y.Yamamoto, K.Asaoka, K.Tatsumi. *Organometallics*, **17**, 4380 (1998)
106. K.Mashima, Y.Matsuo, K.Tani. *Chem. Lett.*, **26**, 767 (1997)
107. K.Mashima. *Macromol. Symp.*, **159**, 69 (2000)
108. Y.Matsuo, K.Mashima, K.Tani. *Angew. Chem., Int. Ed.*, **40**, 960 (2001)
109. H.Tsurugi, T.Ohno, T.Kanayama, R.A.Arteaga-Müller, K.Mashima. *Organometallics*, **28**, 1950 (2009)
110. H.Tsurugi, T.Ohno, T.Yamagata, K.Mashima. *Organometallics*, **25**, 3179 (2006)
111. J.Lu, D.Q.Chu, J.H.Yu, X.Zhang, M.H.Bi, J.Q.Xu, X.Y.Yu, Q.F.Yang. *Inorg. Chim. Acta*, **359**, 2495 (2006)
112. A.C.Bowman, S.Sproules, K.Wieghardt. *Inorg. Chem.*, **51**, 3707 (2012)
113. D.Hass. *Z. Chem.*, **7**, 432 (1967)
114. M.J.Manos, A.J.Tasiopoulos, C.Raptopoulou, A.Terzis, J.D.Woollins, A.M.Z.Slawin, A.D.Keramidas, T.A.Kabanos. *J. Chem. Soc., Dalton Trans.*, 1556 (2001)
115. I.S.Tidmarsh, L.J.Batchelor, E.Scales, R.H.Laye, L.Sorace, A.Caneschi, J.Schnack, E.J.L.McInnes. *J. Chem. Soc., Dalton Trans.*, 9402 (2009)
116. R.H.Laye, E.J.L.McInnes. *Eur. J. Inorg. Chem.*, 2811 (2004)
117. J.C.Dobson, H.Taube. *Inorg. Chem.*, **28**, 1310 (1989)
118. A.Butler. *Coord. Chem. Rev.*, **187**, 17 (1999)
119. A.Butler, J.N.Carter-Franklin. *Nat. Prod. Rep.*, **21**, 180 (2004)
120. D.Wischang, O.Brücher, J.Hartung. *Coord. Chem. Rev.*, **255**, 2204 (2011)
121. R.L.Robson, R.R.Eady, T.H.Richardson, R.W.Miller, M.Hawkins, J.R.Postgate. *Nature (London)*, **322**, 388 (1986)
122. B.J.Hales, E.E.Case, J.E.Morningstar, M.F.Dzeda, L.A.Mauterer. *Biochemistry*, **25**, 7251 (1986)
123. G.D.Triantafillou, E.I.Tolis, A.Terzis, Y.Deligiannakis, C.P.Raptopoulou, M.P.Sigalas, T.A.Kabanos. *Inorg. Chem.*, **43**, 79 (2004)
124. E.S.Bazhina, G.G.Aleksandrov, M.A.Kiskin, N.N.Efimov, E.A.Ugolkova, A.A.Korlyukov, O.M.Nikitin, T.V.Magdesieva, V.V.Minin, A.A.Sidorov, J.S.Miller, I.L.Eremenko. *Polyhedron*, **137**, 246 (2017)
125. E.J.Tolis, M.J.Manos, A.J.Tasiopoulos, C.P.Raptopoulou, A.Terzis, M.P.Sigalas, Y.Deligiannakis, T.A.Kabanos. *Angew. Chem., Int. Ed.*, **41**, 2797 (2002)
126. C.R.Waidmann, X.Zhou, E.A.Tsai, W.Kaminsky, D.A.Hrovat, W.T.Borden, J.M.Mayer. *J. Am. Chem. Soc.*, **131**, 4729 (2009)
127. P.K.Sasmal, S.Saha, R.Majumdar, R.R.Dighe, A.R.Chakravarty. *Chem. Commun.*, 1703 (2009)
128. P.K.Sasmal, S.Saha, R.Majumdar, S.De, R.R.Dighe, A.R.Chakravarty. *Dalton Trans.*, **39**, 2147 (2010)
129. Y.Dong, R.K.Narla, E.Sudbeck, F.M.Uckun. *J. Inorg. Biochem.*, **78**, 321 (2000)
130. C.R.Waidmann, A.G.DiPasquale, J.M.Mayer. *Inorg. Chem.*, **49**, 2383 (2010)
131. C.-C.Su, G.-S.Huang, S.-J.Liu, S.-L.Wang, F.-L.Liao. *J. Chin. Chem. Soc.*, **45**, 67 (1998)

132. Y.Qi, Y.Yang, M.Cao, C.Hu, E.Wang, N.Hu, H.Jia. *J. Mol. Struct.*, **648**, 191 (2003)
133. S.G.Brand, N.Edelstein, C.J.Hawkins, G.Shalimoff, M.R.Snow, E.R.T.Tiekink. *Inorg. Chem.*, **29**, 434 (1990)
134. D.W.Aldous, N.F.Stephens, P.Lightfoot. *J. Chem. Soc., Dalton Trans.*, 4207 (2007)
135. S.S.Passadis, C.Tsiafoulis, C.Drouza, A.C.Tsipis, H.N.Miras, A.D.Keramidas, T.A.Kabanos. *Inorg. Chem.*, **55**, 1364 (2016)
136. Y.Cao, C.Yi, H.Liu, H.Li, Q.Li, Z.Yuan, G.Wei. *Transit. Met. Chem.*, **41**, 531 (2016)
137. Y.Cao, H.Liu, Z.Yuan, G.Wei. *Aust. J. Chem.*, **70**, 608 (2017)
138. S.Banerjee, A.Dixit, A.A.Karande, A.R.Chakravarty. *Dalton Trans.*, **45**, 783 (2016)
139. J.Pranczk, D.Wyrzykowski, D.Jacewicz, A.Sikorski, A.Tesmar, L.Chmurzyåski. *Polyhedron*, **100**, 74 (2015)
140. L.Li, Z.Guo, Q.Zhang, T.Xu, D.Wang. *Inorg. Chem. Commun.*, **13**, 1166 (2010)
141. L.Bian, L.Li, Q.Zhang, J.Dong, T.Xu, J.Li, J.Kong. *Transit. Met. Chem.*, **37**, 783 (2012)
142. J.C Pessoa, I.Cavaco, I.Correia, M.T.Duarte, R.D.Gillard, R.T.Henriques, F.J.Higes, C.Madeira, I.Tomaz. *Inorg. Chim. Acta*, **293**, 1 (1999)
143. M.Sutradhar, T.R.Barman, G.Mukherjee, M.G.B.Drew, S.Ghosh. *Inorg. Chim. Acta*, **363**, 3376 (2010)
144. S.Banerjee, P.Prasad, A.Hussain, I.Khan, P.Kondaiah, A.R.Chakravarty. *Chem. Commun.*, **48**, 7702 (2012)
145. P.Prasad, I.Khan, P.Kondaiah, A.R.Chakravarty. *Chem. – Eur. J.*, **19**, 17445 (2013)
146. S.Zhai, Q.Guo, J.Dong, T.Xu, L.Li. *Transit. Met. Chem.*, **39**, 271 (2014)
147. I.S.Fomenko, S.Vincendeau, E.Manoury, R.Poli, P.A.Abramov, V.A.Nadolinny, M.N.Sokolov, A.L.Gushchin. *Polyhedron*, **177**, 114305 (2020)
148. Y.S.Fomenko, A.L.Gushchin, A.V.Tkachev, E.S.Vasilyev, P.A.Abramov, V.A.Nadolinny, M. M.Syrokvashin, M.N.Sokolov. *Polyhedron*, **135**, 96 (2017)
149. A.Demsar, P.Bukovec. *J. Fluorine Chem.*, **24**, 369 (1984)
150. Y.P.Chang, L.Furness, W.Levason, G.Reid, W.Zhang. *J. Fluorine Chem.*, **191**, 149 (2016)
151. M.F.Davis, W.Levason, J.Paterson, G.Reid, M.Webster. *Eur. J. Inorg. Chem.*, 802 (2008)
152. M.F.Davis, M.Jura, A.Leung, W.Levason, B.Littlefield, G.Reid, M.Webster. *Dalton Trans.*, 6265 (2008)
153. X.Li, J.W.Dai, H.X.Wang, A.A.Wu, Z.H.Zhou. *Inorg. Chim. Acta*, **453**, 501 (2016)
154. E.S.Bazhina, M.E.Nikiforova, G.G.Aleksandrov, N.N.Efimov, H.A.Ugolkova, O.M.Nikitin, T.V.Magdesieva, A.S.Bogomyakov, V.V.Minin, A.A.Sidorov, V.M.Novotortsev, I.L.Eremenko. *Inorg. Chim. Acta*, **392**, 192 (2012)
155. H.Yue, D.Zhang, Y.Chen, Z.Shi, S.Feng. *Inorg. Chem. Commun.*, **9**, 959 (2006)
156. S.Kodama, A.Nomoto, S.Yano, M.Ueshima, A.Ogawa. *Inorg. Chem.*, **50**, 9942 (2011)
157. R.Zhang, X.X.Zhang, F.Y.Bai, C.Chen, Q.L.Guan, Y.N.Hou, X.Wang, Y.H.Xing. *J. Coord. Chem.*, **67**, 1613 (2014)
158. P.B.Chatterjee, K.Bhattacharya, N.Kundu, K.-Y.Choi, R.Clérac, M.Chaudhury. *Inorg. Chem.*, **48**, 804 (2009)
159. K.Koga, M.Ueno, M.Koikawa, T.Tokii. *Inorg. Chem. Commun.*, **6**, 374 (2003)
160. W.-T.Jin, W.-Z.Weng, Z.-H.Zhou. *Eur. J. Inorg. Chem.*, 1228 (2019)
161. O.Costisor, M.Brezeanu, Y.Journaux, K.Mereiter, P.Weinberger, W.Linert. *Eur. J. Inorg. Chem.*, 2061 (2001)
162. C.D.Beard, R.J.Barrie, J.Evans, W.Levason, G.Reid, M.D.Spicer. *Eur. J. Inorg. Chem.*, 4391 (2006)
163. N.S.Dean, S.L.Bartley, W.E.Streib, E.B.Lobkovsky, G.Christou. *Inorg. Chem.*, **34**, 1608 (1995)
164. J.N.Smith, T.M.Brown. *Inorg. Chem.*, **11**, 2697 (1972)
165. E.J.Peterson, R.B.Von Dreele, T.M.Brown. *Inorg. Chem.*, **15**, 309 (1976)
166. G.W.A.Fowles, D.J.Tidmarsh, R.A.Walton. *J. Chem. Soc. A*, 1547 (1969)
167. K.Haug, W.Hiller, J.Strähle. *Z. Anorg. Allg. Chem.*, **533**, 49 (1986)
168. H.S.Soo, P.L.Diaconescu, C.C.Cummins. *Organometallics*, **23**, 498 (2004)
169. M.J.Calhorda, M.A.A.F.Maria, A.Bram, P.N.Olsen, A.R.Dias, A.M.Freitas, M.H.Garcia, M.F.M.Piedade. *J. Organomet. Chem.*, **426**, 195 (1992)
170. S.Herzog, E.Wulf. *Z. Chem.*, **6**, 434 (1966)
171. A.C.Bowman, J.England, S.Sproules, T.Weyhermüller, K.Wieghardt. *Inorg. Chem.*, **52**, 2242 (2013)
172. J.Quirk, G.Wilkinson. *Polyhedron*, **1**, 209 (1982)
173. A.V.Rogachev, A.L.Gushchin, P.A.Abramov, E.A.Kozlova, C.Vicent, D.Piryazev, A.Barlow, M.Samoc, M.G.Humphrey, R.Llusar, V.P.Fedin, M.N.Sokolov. *Eur. J. Inorg. Chem.*, 2865 (2015)
174. R.Haiges, M.Vasiliu, D.A.Dixon, K.O.Christe. *Dalton Trans.*, **45**, 10523 (2016)
175. W.Levason, G.Reid, J.Trayer, W.Zhang. *Dalton Trans.*, **43**, 3649 (2014)
176. B.J.Kim, J.W.Park, S.M.Koo. *Polyhedron*, **20**, 2279 (2001)
177. G.Mathern, R.Weiss. *Acta Crystallogr., Sect. B*, **27**, 1582 (1971)