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Metal complexes with non-innocent ligands

K P Butin (deceased), E K Beloglazkina, N V Zyk

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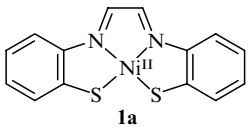
Abstract. The review summarises data on transition metal complexes with the so-called non-innocent ligands. The specific feature of these complexes is that the oxidation state of the central metal atom and the electronic structure of the ligands are impossible to determine *a priori* and unambiguously. The results of experimental studies (spectroscopic, electrochemical, X-ray diffraction) of complexes with various non-innocent ligands are analysed. Particular attention is given to their structures and redox properties. The bibliography includes 208 references.

I. Introduction

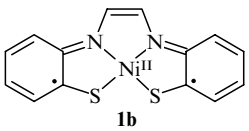
Transition metal complexes with the so-called non-innocent ligands have been known in coordination chemistry since the 1960s, when square-planar dithiolene (enedithiol) compounds were synthesised.[1] However, the term 'non-innocent' gained wide acceptance only in the 1990s, when such complexes attracted considerable attention.

The term 'non-innocent' is generally used in jurisprudence to distinguish the verdicts 'non-innocent' and 'innocent'. This term was introduced in chemistry by Jørgensen in 1966. According to the definition by Jørgensen, a ligand is innocent if it allows the unambiguous determination of the oxidation state of the central metal atom. This definition refers only to the ligand, but, in actuality, the innocent or non-innocent behaviour is related to the complex as a whole.[2]

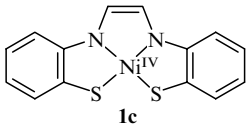
An example of complexes with a non-innocent ligand is the neutral nickel complex with glyoxalbis(2-mercaptoanil) $Ni(gma)_2$ (**1**) characterised by the presence of an extensive system of conjugated π bonds. This complex can be considered as a 16-electron Ni^{II} complex with diiminodithiolate (**1a**) or di(imino-thiosemiquinonate) (**1b**), as a 14-electron Ni^{IV} complex (**1c**) or, alternatively, as an 18-electron Ni^0 complex (**1d**).



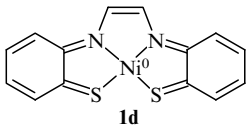
1a



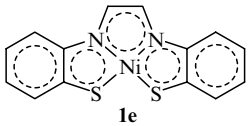
1b



1c



1d



1e

Consequently, neither the oxidation state of the central metal atom nor the charges on the donor atoms of the ligand can be *a priori* precisely defined, and these structures are often described by formulae with delocalised bonds (**1e**), which means that complex **1** is non-innocent.[3]

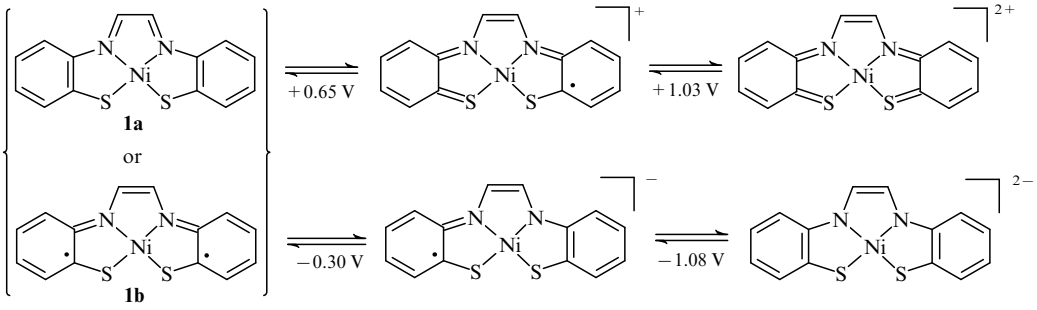
A ligand (or ligands) in non-innocent complexes cannot be unambiguously described by the formula acceptable to the free ligand [in the above example, this is the formula of the doubly-charged glyoxalbis(2-thiolatoanil) anion]. The introduction of metal changes the ligand (for example, the free ligand is irreversibly reduced or oxidised, whereas these transformations in the complex are reversible). Earlier,[3] we proposed the term 'non-indifferent ligand', which, in our opinion, correctly reflects the heart of the problem. The characteristic feature of complexes with non-indifferent (non-innocent) ligands is the involvement of both the ligand and metal in many chemical and physical processes, which were earlier assigned (on the basis of the theoretical formalism) to only either the metal or ligand.

To bring the metal in the above-mentioned structures to one oxidation state (Ni^{2+}), it is necessary to add two electrons to structure **1c** and abstract two electrons from structure **1d**. Consequently, ligand **1c** should exist as the doubly-charged anion, whereas ligand **1d** should occur as the doubly-charged cation of complex **1** provided that divalent nickel is retained in the structure. Therefore, if the ligand rather than the metal is reduced (oxidised), the ligand can have different structures in different states of the complex. These ligands are called 'redox-non-innocent'.

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Scheme 1



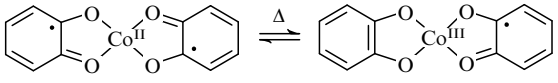
For example, two one-electron oxidation processes and two one-electron reduction processes in diiminodithiolate complexes occur, apparently, with the involvement of the ligand, whereas the divalent state of the metal remains unchanged (Scheme 1).[3]

In dithiolene complexes (and many other analogous complexes), the oxidation states of the metal and the ligand also could not be unambiguously determined, which results in confusion in the interpretation of electrochemical data (elucidation of whether the metal or ligand is subjected to oxidation and reduction) and UV-Vis spectroscopic data. The true nature of metals and ligands has been debated for decades.

After the synthesis and characterisation of first dithiolenes and metal dithiolenes, numerous other complexes exhibiting non-innocent behaviour were found. Pyrocatechol derivatives (catecholates) and other *ortho*-disubstituted benzene derivatives (*o*-phenylenediamines, *o*-aminophenols, *o*-aminothiophenols, *etc*.) belonging to the same structural type have received the most attention.

A reasonable question arises concerning the meaning of the term 'non-innocent'. Presently, this term is sometimes (incorrectly) used in the sense that a ligand in a complex is redox-active. Hence it follows that the term 'non-innocent ligand' is applicable, for example, to dithiolenes.

It should be noted that it is rather easy to determine which fragment of the molecule is involved in oxidation or reduction for complexes in which the frontier orbitals of the metal and the ligand differ substantially in energy. For example, the metal atom in $[Ru(bipy)_3]^{2+}$ (bipy is 2,2′-bipyridyl) is oxidised at the potential of +1.26 V, whereas a series of reduction steps involve the ligand, because the metal d(π) orbital (HOMO) and the ligand π* orbital (LUMO) differ substantially in energy.[4] In contrast, $[Cr(bipy)_3]^{3+}$ is involved in a series of reduction reactions,[5] which are much more difficult to interpret, because the metal- and ligand-centred orbitals involved in redox processes are comparable in energy. In actuality, the metal atom of $[Cr(bipy)_3]^{3+}$ is reduced in the first step to form $[Cr^{II}(bipy)_3]^{2+}$, and the successive two-electron reduction occurs at the π* orbital of the ligand to give a species described as $[Cr^{II}(bipy)_2(bipy^{\bullet -})]^{+}$ {or as $[Cr^{III}(bipy).(bipy^{\bullet -})_2]^{+}$}. Therefore, the ligand is redox-active both in $[Ru(bipy)_3]^{2+}$ and $[Cr^{II}(bipy)_3]^{2+}$, but the term 'non-innocent' is applicable only to the latter complex. Moreover, the difficulties of description of dithiolene complexes arise from strong mixing of the frontier orbitals of the ligand and metal rather than from the fact that the ligand is redox-active. Hence, it is difficult to draw conclusions about the oxidation states of the metal and the ligand in complexes. In some cases, the metal- and ligand-centred frontier orbitals can be so close in energy that so-called 'redox-isomeric' complexes appear. For example, Pierpont and Lange described[6] the cobalt dioxolene complex, which exists in either form **2a** or form **2b** depending on the temperature of the sample.



Consequently, the term 'non-innocent' refers to a combination of the metal and the ligand, *i.e*., to the complex as a whole rather than to the redox-active ligand by itself. Lever and co-authors[7] noted that the electron distribution in coordination compounds depends on the degree of mixing of the metal and ligand orbitals, which, in turn, is a function of energy, symmetry and overlap of the valence orbitals of the metal and ligand. This brings up questions about the true oxidation state of the central metal atom in these complexes and the electronic structures which correctly describe the complexes. These questions have been debated in the literature for more than four decades.[6,8]

When considering transition metal complexes with non-innocent ligands, the concept of the oxidation state of a metal in complexes should also be refined. It was suggested[9] that the formal oxidation state of a metal in mononuclear coordination compounds should be distinguished from the physical oxidation state. The former is generally determined as a charge remaining on the metal after removal of all ligands in the electronic configurations with complete shells, *i.e*., with lone pairs, whereas the physical oxidation state is determined by the true electronic state of the metal atom. For example, iron in Fe^{III} complexes can exist in the high-, medium- or low-spin state. The electronic configuration of a metal in complexes can be determined by spectroscopy. Hence, Jørgensen[10] suggested the term 'spectroscopic oxidation state' to describe this situation.

In many cases, the formal and physical oxidation states are identical {for example, the physical and formal oxidation states of low-spin Co (d^6) in the $[Co(NH_3)_6]^{3+}$ complex ion is +3}. However, this is not always the case. The physical oxidation state differs from the formal oxidation state, for example, if an open-shell organic radical is coordinated to a transition metal ion. For instance, the formal oxidation state of iron in the O-coordinated iron complex with the phenoxyl radical is +4. However, Mössbauer and Raman spectroscopy demonstrated that the iron ion in this complex with the radical ligand is in the physical oxidation state of +3 and has the d^5 configuration $(Ph-O^{\bullet})\cdots Fe^{III}$.[9] Evidently, the complex containing the $Ph-O-Fe^{IV}$ fragment differs in its electronic structure from the complex with the $(Ph-O^{\bullet})\cdots Fe^{III}$ fragment.†

The term 'physical oxidation state' is not commonly accepted. Moreover, the terms 'physical and formal oxidation states' are often used as synonyms. However, it is necessary to distinguish these terms in certain areas of coordination chemistry. In particular, it is worthwhile using the terms 'innocent' and 'non-innocent' as referring to the ligand only in combination with the term 'physical oxidation state', thus underlining that the ligands do not necessarily have closed shells.

Clear criteria for the assignment of ligands in non-innocent complexes to a particular oxidation state are presently available. Oxidation and reduction can be easily followed from structural changes in the ligand, in particular, from the changes in the bond lengths. For example, the length of the C−N single bond in *o*-phenylenediamine ligands[12] is ~1.46 Å. In *o*-diiminoquinones, both C=N bond lengths are ~1.31 Å, whereas these bond lengths in the *o*-diiminobenzosemiquinonate radical have an

† Mononuclear copper complexes with phenoxy radicals were found in the active sites of galactose oxidases.[11]

intermediate value of ~1.36 Å (these ligands are considered in more detail in Section II.2).

An analogous regularity was found for pyrocatechol and *o*-aminophenol complexes [13,14] and for *o*-aminothiophenol complexes.[12] Besides, the structures of the above-mentioned compounds are always characterised by the following feature: in aromatic ligands, which contain an even number of electrons and can exist as neutral molecules, singly-charged anions or doubly-charged anions depending on the degree of protonation, all six C–C bonds in the benzene ring are identical in length, whereas there are three alternating 'short–long–short' bonds and three adjacent long bonds in the six-membered rings of semiquinonate and quinone.

To determine the electron density distribution in complexes with non-innocent ligands, various spectroscopic methods (UV-Vis, IR, Mössbauer, X-ray electron spectroscopy and ESR), electrochemical and spectroelectrochemical methods are widely used along with the structural criteria. The spectroscopic methods allow one to reveal the presence of radical species and spin-density localisation.

As mentioned above, oxidation or reduction of ligands rather than metals is very typical of complexes with non-innocent ligands (for details, see below). In redox reactions, such ligands can serve as an 'electronic buffer',[15] which reversibly accepts and donates electrons, whereas the oxidation state of the central metal atom remains unchanged.

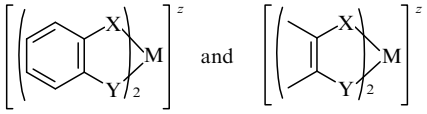
Below we consider complexes with various non-innocent ligands. Some widely known complexes with radical ligands, for example, complexes with a verdazyl radical, are beyond the scope of the present review. In such complexes, the ligand is unambiguously described as a radical (though delocalised) and the electronic structure and oxidation state of the metal are beyond doubt.

Several reviews have been devoted to various classes of non-innocent metal complexes: with oxygen-containing ligands based on pyrocatechols,[1,16,17] with dithiolene ligands,[18] with ligands based on aromatic diamines,[19,20] *p*-quinones,[21] corroles,[22] *etc*.[23–25] The present review summarises the results of investigations of complexes with non-innocent ligands carried out in the last decade, when the term 'non-innocent' has received wide recognition. Only the most important earlier studies are cited.

II. Complexes with 1,2-disubstituted benzenes and ethylenes as ligands

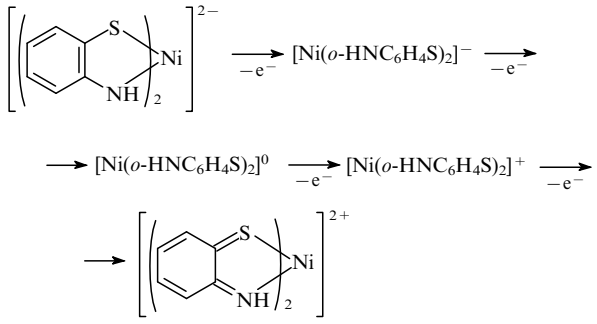
Dithiolenes, pyrocatechols, *o*-phenylenediamines, *o*-aminophenols and other analogous compounds belong to a well-known class of non-innocent ligands. The doubly deprotonated form of such ligands can be considered as a prototype of non-innocent ligands.

As early as the 1960s, Holm and co-authors (see, for example, Refs 26 and 27) noted that complexes belonging to the structural type



X, Y = O, NH, S; M = Ni, Pd, Pt.

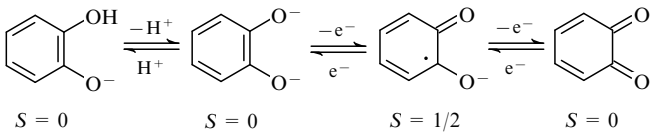
are readily subjected to chemical and electrochemical reversible one-electron oxidation and reduction. In early studies, the precise structures of most intermediates formed upon oxidation and reduction were not established. However, isoelectronic series of five compounds were proposed for their description, the *o*-quinoid structure being assigned to the ligand in the highest oxidised state based on ESR spectroscopic data.



1. Complexes with pyrocatechol-based ligands

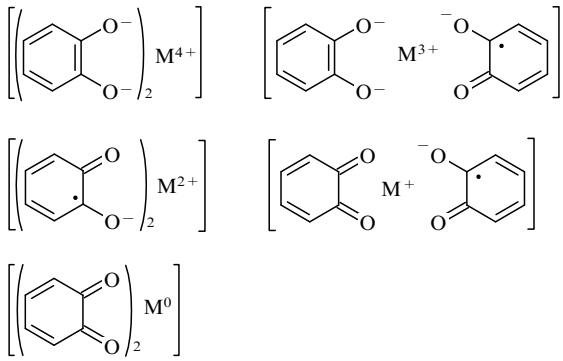
Complexes containing the deprotonated pyrocatechol fragment σ-bonded to a transition metal can exist as various electronic tautomers [28–30] due to the ease of electron transfer between the metal and the ligand.

It was found [12] that *o*-catecholates in complexes can exist as aromatic closed-shell singly- or doubly-charged anions, even-electron neutral *o*-quinones or open-shell *o*-benzosemiquinonate radicals ($S = 1/2$).

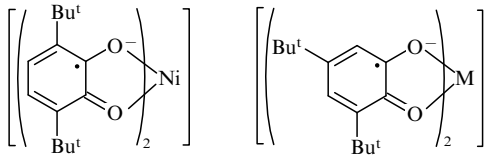


$S = 0$ $S = 0$ $S = 1/2$ $S = 0$

Correspondingly, a variable-valence transition metal atom can give a series of complexes with different forms of these ligands, which are described by the same empirical formula, but differ in the ligand structure and oxidation state of the central metal atom.

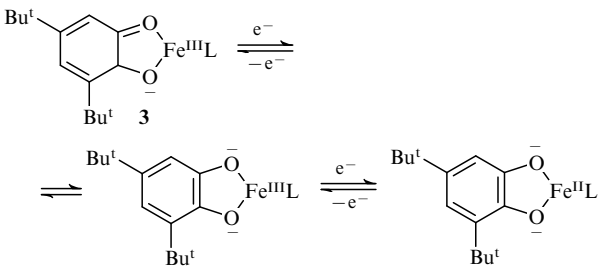


Pyrocatechol is the simplest representative of this class of ligands. Nickel,[28,29] palladium and platinum [30] complexes with ligands containing unsubstituted and 3,5- and 3,6-di-*tert*-butyl-substituted aromatic rings have square-planar structures and are diamagnetic. X-Ray diffraction study demonstrated that the structures of the above-mentioned three *tert*-butyl-substituted complexes correspond to the following formulae.



M = Pd, Pt

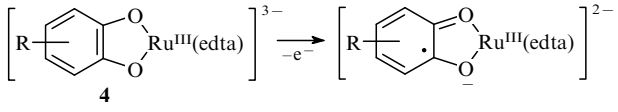
The non-innocent nature of the catecholate ligand allows the isolation of iron dioxolene complexes containing the ligand and metal atom in different oxidation states.[31]



L is a tetraazamacrocyclic ligand.

Iron complex **3** can serve as a structural model of the iron-containing enzyme nitrile hydratase.[32]

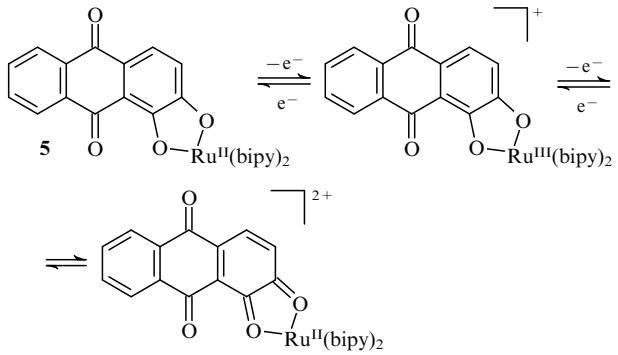
Free pyrocatechol is irreversibly oxidised by electrochemical methods at 0.3–0.6 V to give *o*-benzoquinone. The formation of the complex is accompanied by a substantial change in the redox characteristics. For example, oxidation of ruthenium complex **4** becomes reversible, occurs by a one-electron mechanism (at −0.6 to −0.5 V)[33] with the involvement of only the ligand and affords the semiquinone complex, *i.e.*, the addition of metal to the oxygen atoms of the ligand leads to a radical change in the nature of the ligand.



R = H, 4-CO_2H, 3,5-$(SO_3^-)_2$.

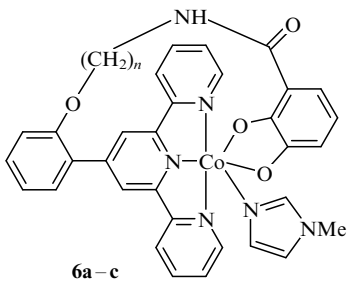
The Ru^{III} complexes with L-DOPA, $[Ru(edta)(L\text{-}DOPA)]Na_3 \cdot 3H_2O$ and $[Ru(edta)(L\text{-}DOPA)]Na_4 \cdot 3H_2O$ behave analogously. Upon the complex formation, oxidation and reduction processes become reversible.[34]

Electrochemical oxidation of ruthenium(II) complex **5** with doubly deprotonated alizarine (1,2-dihydroxy-9,10-anthraquinone) containing the 2,2′-bipyridyl fragment involves successive one-electron oxidation of the metal atom and the ligand, both oxidation products (as salts) being isolated preparatively.[35]



The structures of these complexes were confirmed by ZINDO calculations.

In a series of pentadentate ligands containing the terpyridyl fragment linked to the pyrocatechol fragment, which were synthesised in the study,[36] and their complexes with cobalt **6a**–**c**, the pyrocatechol fragment of the ligand also exists as the aromatic doubly-charged anion. Two of these complexes (**6a**,**b**) were characterised by X-ray diffraction. The authors hypothesised that two one-electron reduction steps in electrochemical redox reactions occur successively with the involvement of the terpyridyl fragment and the cobalt ion, whereas the pyrocatechol fragment of the ligand is oxidised.



n = 4 (**a**), 5 (**b**), 6 (**c**).

For copper catecholate complexes, Abakumov *et al.*[37] demonstrated that reversible intramolecular electron transfer between the metal and the ligand can occur and it is induced by the replacement of the neutral ligand.

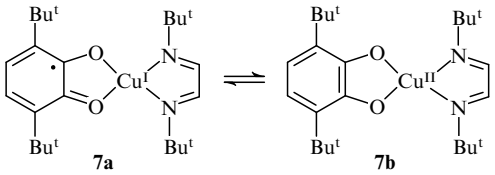
$$(Cat)Cu^{II}(bipy) + 2\,PPh_3 \rightleftharpoons (SQ)Cu^{I}(PPh_3)_2 + bipy$$

Cat is catecholate and SQ is semiquinone.

This reversible intramolecular metal–ligand electron transfer can occur also without changes in the composition of the coordination sphere about metal. For example, the reversible electron transfer in copper complexes with *N*,*N*′-disubstituted 1,4-diazabutadiene (DAD) is accompanied by a change in the geometry from square-planar (in the Cu^{II} catecholate complex) to tetrahedral (in the Cu^{I} semiquinone complex).[38]

$$(Cat)Cu^{II}(\eta^2\text{-}DAD) \rightleftharpoons (SQ)Cu^{I}(\eta^2\text{-}DAD)$$

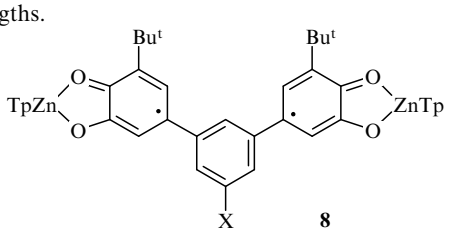
Abakumov and Eremenko with co-workers[39] studied a copper complex containing simultaneously the di-*tert*-butyl-substituted catecholate and 1,4-diazabutadiene fragments. In solution, this neutral complex exists as an equilibrium mixture of two isomers, *viz.*, copper(I) semiquinonate **7a** and copper(II) catecholate **7b**.



The addition of a neutral ligand (CO or ArNC) to a solution induces electron transfer from the catecholate fragment to Cu^{II} giving rise to a complex containing an additional neutral ligand. In the case of carbon monoxide, this transformation is reversible, and the position of equilibrium strongly depends on the temperature. At 300 K, an equilibrium mixture of derivatives of molecules **7a** and **7** is present in solution, whereas almost exclusively the $(SQ)Cu^{I}(\eta^1\text{-}DAD)CO$ complex exists at 200 K.

The electronic structures of the Cr^{III} semiquinone complex $[Cr(tren)(3,6\text{-}DTBSQ)]^{2+}$ [tren is tris(2-aminoethyl)amine, and 3,6-DTBSQ is 3,6-di-*tert*-butylthiosemiquinone] and its catecholate analogue $[Cr(tren)(3,6\text{-}DTBCat)]^{+}$ containing the doubly-charged anionic 3,6-di-*tert*-butylthiocatecholate ligand 3,6-DTBCat[40] were studied by the DFT method. The calculations demonstrated that the Cr ion ($S = 3/2$) is antiferromagnetically coupled to the semiquinone radical ($S = 1/2$), so that the spin state $S = 1$ is the major one. Both complexes were also characterised by X-ray diffraction, and there is a good agreement between the structural data and the results of calculations. A calculation method proposed[41] for chromium complexes, in which chromium is bound only to electron-donating oxygen atoms, allows one to determine the oxidation state of the metal atom based on the sum of the Cr–O bond lengths.

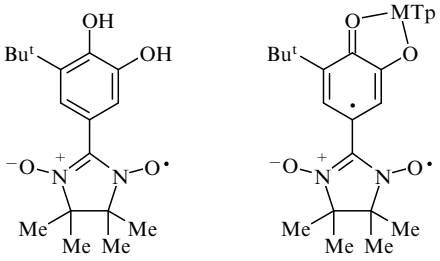
The ligands can include two *o*-semiquinone fragments (for example, in zinc complexes **8**).[42] All three known complexes were studied by X-ray diffraction, and the semiquinone structure of the ligand was confirmed by the characteristic C–C and C–O bond lengths.



8

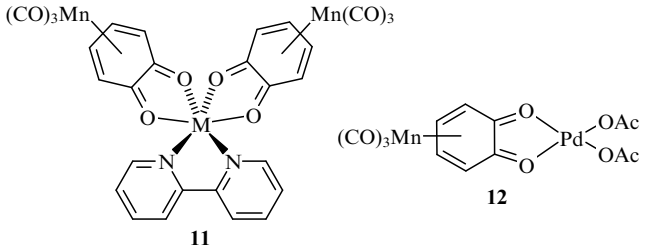
X = NMe_2, Bu^t, NO_2;
Tp is hydrotris(3-methyl-5-isopropylphenylpyrazolyl)borate.

Ligand **9** containing both the potential semiquinone and nitronyl-nitroxide radical centres was synthesised.[43] In the ground state, Ni, Mn, Co, Cu and Zn complexes **10** with this ligand exist as singlet biradicals.



9 **10**

In complexes **11** and **12**, the oxygen-containing ligand (according to the results of the study[44]) exists as *o*-quinone, and the $Mn(CO)_3$ fragment serves as a 'reservoir' accepting electrons during oxidation of the ligand, thus being responsible for the electron density distribution between the metal and ligand.

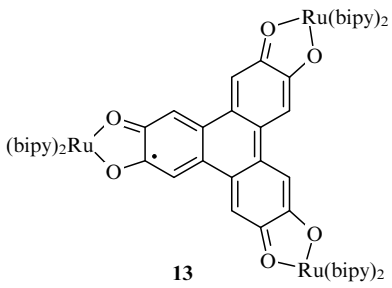


11 **12**

M = Mn, Co, Cd

However, the structural study[45] demonstrated that the C–O bonds in complexes **11** and **12** (~1.29 Å) are longer than those in *o*-quinones (1.26–1.27 Å), *i.e.*, it cannot be stated that the structure of the ligand in these complexes precisely corresponds to *o*-quinone.

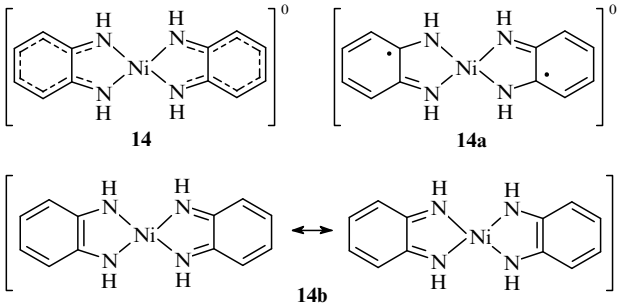
A comprehensive analysis of the literature data on polynuclear Ru^{II} complexes with bridging dioxolene ligands and binuclear tris(pyrazolylborato)Mo(V) or Mo(VI) complexes with bridging bis-phenolate or bis-pyridyl ligands was presented in the review,[1] where the results of spectroscopic and spectroelectrochemical investigations of such complexes were discussed in detail, and the conclusion was drawn that there is a strong electron interaction between the metal ion and the bridging ligand. Complex **13** containing three coordinating catecholate-type fragments in different oxidation states (one semiquinone fragment and two carbonyloxide fragments) in one ligand molecule is an interesting example cited in the review.[1]



13

2. Complexes with *o*-phenylenediamine-type ligands and their deprotonated and oxidised forms

Nickel *o*-phenylenediamine complex **14** is among the first synthesised and structurally characterised complexes with non-innocent ligands. Once the oxidation state of the central metal atom higher than +2 has been rejected, two different descriptions of the electronic structure of this complex were proposed. Gray and co-authors[46] suggested that this compound is the Ni^{II} d^8 complex with a singlet biradical (**14a**), whereas Holm and co-authors[8,47] described this compound by two resonance hybrids **14b**. Evidently, molecules **14a** and **14b** should differ in energy, and the question is which formula gives a more adequate description.

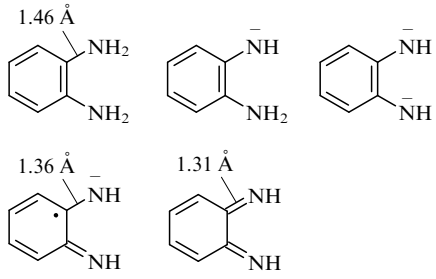


14 **14a**

14b

More recently, Abakumov *et al.*[28] and Pierpont with co-authors[29,30] have assigned the electronic structures of compound **14** and its palladium and platinum analogues to type **14a**, *i.e.*, to complexes with two intramolecular antiferromagnetically coupled iminosemiquinonate ligands, taking into account the available structural data.

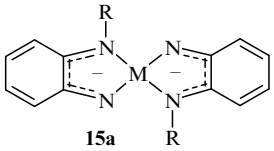
Generally speaking, *o*-phenylenediamines form complexes of different structural types with transition metals (Fe, Ni, Pd, Pt, Co) depending on the oxidation state and protonation of the ligand. Complexes in which the ligands belong to the forms listed below were synthesised and characterised by X-ray diffraction and electrochemical methods.[47–52]



The structural changes observed in these complexes were analysed in the review.[19]

Eremenko and co-workers[53–60] described complexes of platinum-group metals (Pd and Pt) and Ni with ligands of the *o*-phenylenediamine series. The reactions of *o*-phenylenediamine[53,54] and its *N*-methyl[55] and *N*-phenyl derivatives[53] with alkaline solutions of K_2MX_4 (M = Pt, Pd; X = Cl, NO_3) initially

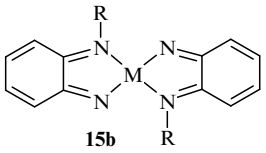
produce the tetraamine doubly-charged cationic complexes $M(o\text{-}NH_2C_6H_4NHR)X_2$, which are transformed in the presence of atmospheric oxygen into mononuclear Pt^{II} or Pd^{II} bis(semiquinonediiminate) complexes **15a**.



15a

M = Pt, Pd; R = H, Me, Ph.

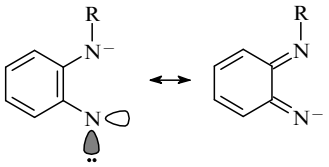
In earlier studies,[53, 54] these compounds were considered as the $M(o\text{-}NC_6H_4NR)$ (R = H, Me, Ph) complexes (**15b**) with anionic quinoneimide ligands.



15b

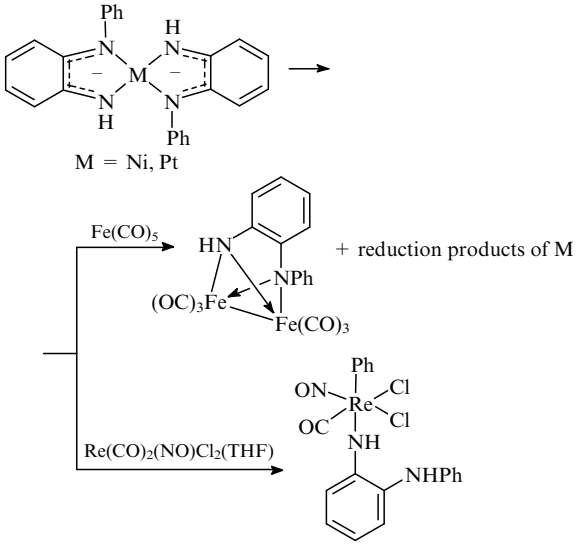
M = Pt, Pd; R = H, Me, Ph.

The bidentate ligand, *viz*., a *o*-phenylenediamine derivative, is described in terms of the nitrene – imide resonance.[53]

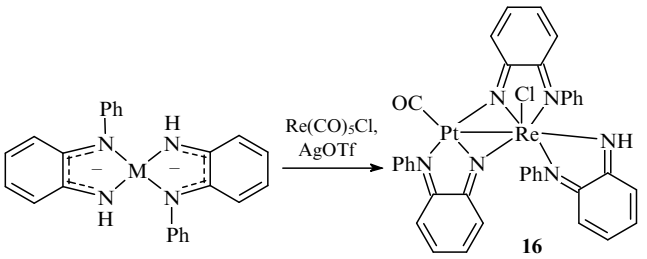


However, X-ray diffraction data [53, 55] are in better agreement with the semiquinone structure of the ligand [the C(ring)—N bond lengths are 1.335 and 1.352 Å, see above].

The reactions of the *o*-semiquinonediimine complexes $M(o\text{-}HNC_6H_4NPh)$ (M = Ni or Pt) with carbonyl-containing iron and rhenium compounds are accompanied by reduction of the ligand to give Fe or Re phenylenediamide complexes.[57]



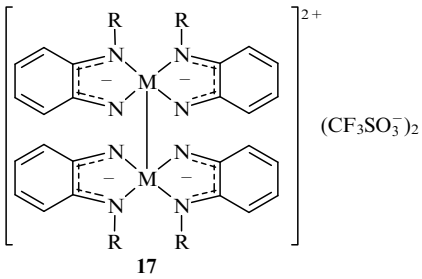
In the presence of silver triflate, the reaction yields heterobimetallic complex **16** containing an *o*-quinoneiminoimide-type ligand.[57, 58]



16

This deprotonated phenylenediimine ligand, but as a bridge, is present in the palladium complex generated in the reaction of the trinuclear complex $Pd_3(\mu\text{-}O_2CBu^t)_6$ with *N*-Ph-*o*-phenylenediamine.[58]

Oxidation of Pt [53, 59, 60] and Pd [60] bis(semiquinonediimine) complexes with AgOTf affords binuclear Pt^{III} and Pd^{III} complexes **17**.



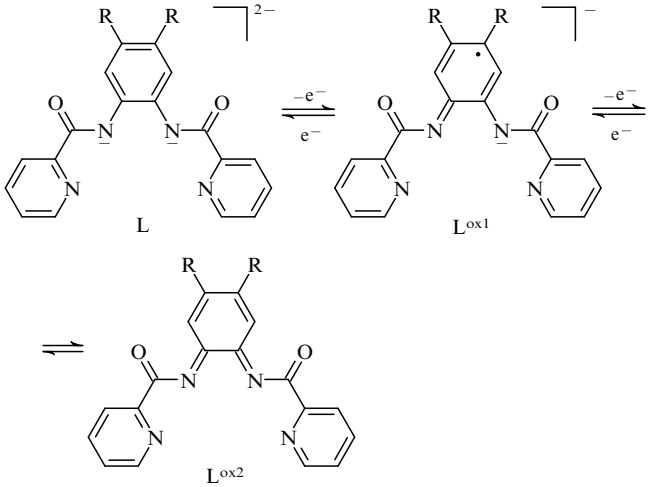
17

M = Pt, Pd; R = H, Ph.

The structures of the binuclear complexes were established by spectroscopic and electrochemical methods and X-ray diffraction.

The reactions of Ru^{III} salts with *o*-phenylenediamine in the presence of an oxidant (O_2 or Hal_2) produced a series of Ru^{II} complexes with the *o*-benzoquinonediimine-type ligand, and the complexes were characterised by X-ray diffraction, electrochemical and spectroscopic methods.[61] In such complexes, the ligands are reduced in two one-electron steps to form ruthenium *o*-phenylenediamide complexes.

Ligands of the 1,2-bis(pyridine-2-carboxamido)benzene (bpb) series similar in electronic structure to *o*-phenylenediamine ligands also belong to the category of non-innocent ligands and can be involved in coordination compounds as doubly-charged anions (L), one-electron oxidised radicals (L^{ox1}) or two-electron oxidised diamagnetic iminoquinone species (L^{ox2}).[62, 63]



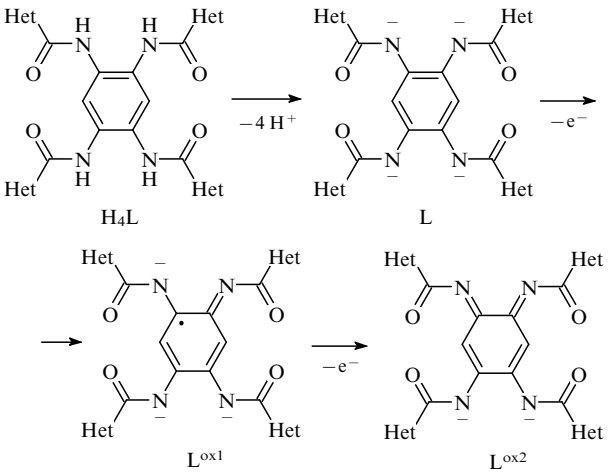
L L^{ox1} L^{ox2}

R = H (bpb), Cl (bpc).

The anion L is coordinated to Fe^{III} as a non-innocent ligand, because in a complex it can be oxidised to the paramagnetic π-radical cation and then to the diamagnetic neutral benzoquinone species.

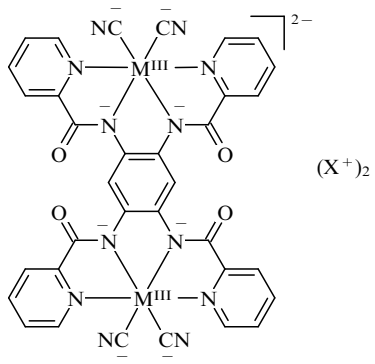
Mononuclear iron and cobalt complexes with the bpb and bpc ligands were synthesised and characterised.[62] It was demonstrated that these ligands in coordination compounds can exist in radical one-electron and diamagnetic two-electron oxidised forms, L^{ox1} and L^{ox2}. These complexes were studied by X-ray diffraction, ESR and UV-Vis spectroscopy and electrochemical methods. Photolysis of the high-spin $(Bu_4N)[Fe^{III}(bpb)(N_3)_2]$ complex and its $(bpc)^{2-}$ analogue in acetone at room temperature afforded the diamagnetic binuclear complex $(Bu_4N)[Fe_2^{IV}(\mu\text{-}N)(bpb)_2(N_3)_2]$ analogous to the complex with $(bpc)^{2-}$. However, photolysis in frozen acetonitrile produced a low-spin complex, whose structure was described as $[Fe^{III}(bpb^{ox2})(N)(N_3)_2]$. The mononuclear complexes $(Bu_4N)[Fe^{III}(bpb)(CN)_2]$, $(Et_4N)[Co^{III}(bpb)(CN)_2]$ and $Na[Co^{III}(bpc)(CN)_2]\cdot 3\,MeOH$ are chemically and electrochemically oxidised to the corresponding complexes L^{ox1}. The oxidised form of the complex with the radical-anionic ligand can be isolated after preparative electrolysis. An analogous reaction was carried out by a chemical method.

The binuclear Co^{III} and Fe^{III} complexes with the non-innocent 1,2,4,5-tetrakis(2-pyridinecarboxamido)benzene ligands were documented.[62–64]



Het is 2-pyridyl or 5-*tert*-butyl-2-pyridyl.

The general formula of the CN-containing complexes with an L-type ligand is as follows:



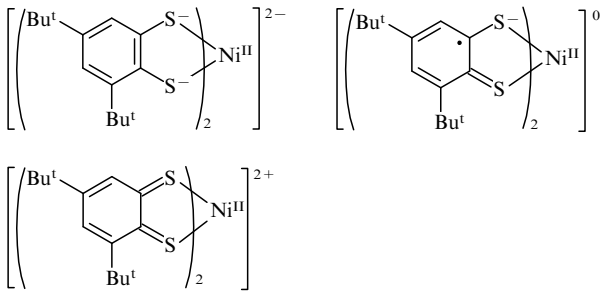
X = Na, NBu_4.

For iron complexes, the existence of the following five forms containing the central ligand and metal in different oxidation states was established: (1) doubly-charged anionic $[Fe_2^{III}L(CN)_4]^{2-}$; (2) one-electron reduced mixed-valence $[Fe^{III}Fe^{II}L(CN)_4]^{3-}$ with the diamagnetic L^{4-} bridge; (3) completely reduced $[Fe_2^{II}L(CN)_4]^{4-}$; (4) one-electron oxidised $[Fe_2^{III}L^{ox1}(CN)_4]^{-}$; (5) completely oxidised $[Fe_2^{rmIII}L^{ox2}(CN)_4]$. All forms were characterised by spectroscopic and electrochemical methods. The first and third forms were also studied by X-ray diffraction.[64] For cobalt complexes, three forms with different oxidation states of the ligand, $[Co_2^{III}L(CN)_4]^{2-}$ ($S = 0$), $[Co_2^{III}L^{ox1}(CN)_4]^{-}$ ($S = 1/2$) and $[Co_2^{III}L^{ox2}(CN)_4]$ ($S = 0$), were investigated by X-ray diffraction.[64] It was concluded that the central 1,2,4,5-tetraaminobenzene fragment in the above-mentioned complexes can be oxidised in two reversible one-electron steps to paramagnetic $(L^{ox1})^{3-}$ and diamagnetic $(L^{ox2})^{2-}$ species.

3. Complexes of *o*-benzenedithiols and their deprotonated and oxidised forms

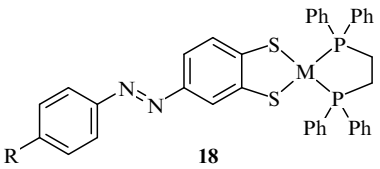
As early as the 1960s, it was found[26,27] that *o*-benzenedithiol complexes are readily involved in one-electron transfer reactions, the *o*-quinoid-type structure being assigned to the ligand in the highest oxidation state. However, although the existence of complexes with ligands in three oxidation levels has been rather easily established for *o*-catecholates, the situation for the corresponding *ortho*-dithio derivatives has remained unclear for a long time. For example, the existence of S,S-coordinated *o*-dithiobenzosemiquinonate radical anions (rather than aromatic doubly-charged dithiolate anions) has been proposed for many complexes,[65,66] but this fact has not been supported by experimental evidence. Later on, the presence of such radicals was confirmed for the paramagnetic square-planar $[Pd(bipy)(L^{Bu})]^{+}$ complex (where L^{Bu} is 3,5-di-*tert*-butylbenzene-1,2-dithiol)[67] by UV-Vis and ESR spectroscopy.

The nickel complex in which the metal is coordinated by two ligands with the molecular formula $C_{14}H_{20}S_2$,[68] exists in three different forms, anionic, neutral and cationic, and the ligand exists as the dithiolate anion, the dithiosemiquinone radical and dithioquinone, respectively.



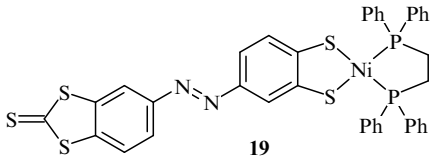
Recently, DFT calculations have convincingly demonstrated[69] that the spectroscopic oxidation state of the nickel atom in the diamagnetic square-planar NiL_2 complex (L is unsubstituted *o*-benzenedithiol) is +2 (d^8), and both ligands are present as *o*-dithiobenzosemiquinonates(1−). The Fe^{III} and Fe^{IV} complexes containing the *o*-benzenedithiolate ligands as doubly-charged anions were also studied by X-ray diffraction.[70] These results and the data published in the literature[71] have made it possible to propose structural criteria for assigning such ligands in complexes to a particular oxidation state.

The synthesis of a series of azo-coupled metal dithiolenes **18**–**20** containing Ni^{II}, Pd^{II} and Pt^{II} and bis(diphenylphosphino)-ethane (dppe) as an additional ligand and the synthesis of anionic nickel complex **21** were documented.[72]

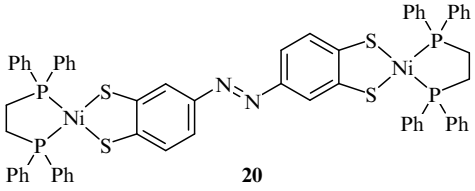


18

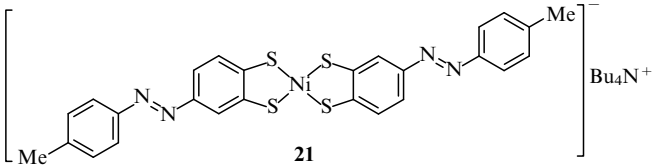
M = Ni, Pd, Pt; R = H, Me, Cl, OMe.



19



20



21

All these complexes were studied by X-ray diffraction.[65, 73, 74] These complexes were electrochemically reduced. In the study,[72] it was hypothesised that the metal atom in the nickel complexes undergoes reversible one-electron reduction, whereas reduction of the platinum and palladium complexes is a reversible two-electron process, though it also involves the metal atom.

The electronic structures of the bis(*o*-benzenedithiolato)Au(III) anion and its neutral one-electron oxidised form were determined.[65] Earlier, the latter was described (based on poor-quality X-ray diffraction data) as an Au^{IV} complex containing the central gold atom in the d^7 configuration.[72] Poor-quality X-ray diffraction data were also obtained for compounds containing the $[AuL_2]^-$ anion (L is deprotonated *o*-benzenedithiol),[75–79] but these data did not provide unambiguous evidence for the true structure of the ligand in the complexes. More recently,[74] the neutral $[AuL_2]$ complex was demonstrated to be diamagnetic, and DFT calculations for the isolated molecule of this complex confirmed that the HOMO and LUMO are virtually purely bonding and antibonding combinations of the HOMO of the ligands, respectively.[80] This is possible only in the presence of the diamagnetic Au^{III} ion in the d^8 electronic configuration, but this fact was not confirmed experimentally.

The square-planar diamagnetic Au^{III} complexes with 3,6-di-*tert*-butylbenzene-1,2-dithiolate are oxidised with iodine in acetone to form neutral paramagnetic complexes of the corresponding *o*-dithiobenzosemiquinonate radical (the facts that the ligand is oxidised and the reaction does not afford an Au^{IV} complex were unambiguously established by Mössbauer, UV-Vis and ESR spectroscopy).[65] Analogous complexes containing the unsubstituted ligand (H_2L is *o*-benzenedithiol), $(NBu_3H)[AuL_2]$ and AuL_2, were synthesised and characterised by X-ray diffraction. Taking into account the electronic structures of the paramagnetic neutral $Au(L^{Bu})_2$ and AuL_2 complexes, it was demonstrated[65] that these complexes contain the Au^{III} ion (d^8, $S = 0$) coordinated by two sulfur atoms of the *o*-dithiolate anion and the *o*-dithiobenzosemiquinonate(1−) π-radical, resulting in the ground state with $S = 1/2$. This fact was confirmed by the results of UV-Vis, IR and ESR spectroscopy.

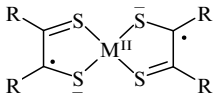
4. Dithiolene complexes

Quantum-chemical calculations demonstrated that the HOMO of dithiolene complexes is localised virtually completely on the ligand; consequently, the ligand should be oxidised in these reactions.[81] Transition metal dithiolene complexes, like the above-described *o*-benzenedithiol complexes, are characterised by the existence of a series of forms related to each other by reversible one-electron oxidation and reduction steps (M = Ni, Pd or Pt).[82–84]

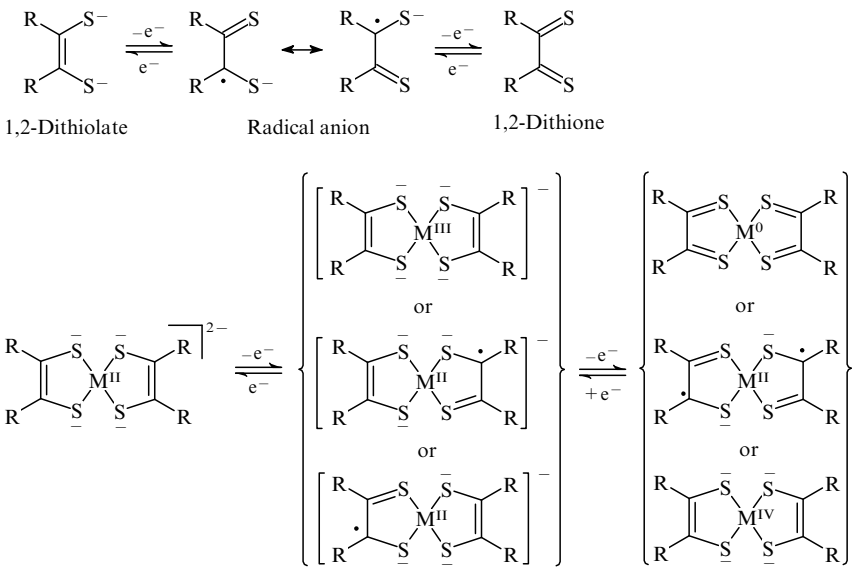
$$[M(S_2C_2R_2)_2] \underset{-e^-}{\overset{e^-}{\rightleftharpoons}} [M(S_2C_2R_2)_2]^- \underset{-e^-}{\overset{e^-}{\rightleftharpoons}} [M(S_2C_2R_2)_2]^{2-}$$

The end members of the series are diamagnetic, whereas the singly-charged anion is a radical. The existence of singly- and doubly-charged cations was also assumed, the latter cation containing M^{II} coordinated by two 1,2-dithione-type ligands. However, these cations have not been detected. The oxidation states of the metals and ligands are presented in Scheme 2.[85]

The non-innocent nature of the dithiolene ligands has been studied in considerable detail.[86–90] The structural changes in nickel complexes resulting from the transformation from one oxidation state to another were discussed in the study.[85] Both the reduced (anionic dithiolate) and oxidised (neutral dithiolene) forms of this ligand give stable complexes with transition metals. The latter form is more adequately described as a complex containing two radical-anionic ligands rather than by two resonance structures.

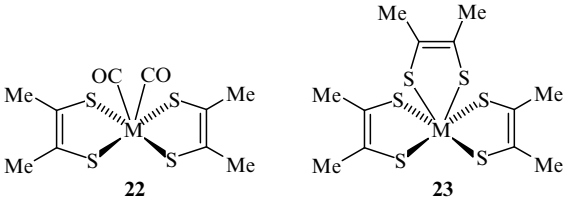


Scheme 2



Different members of the redox series under consideration (primarily for M = Ni) were either isolated or generated in solution by chemical or electrochemical reactions. For example, the $[Ni\{S_2C_2(CN)_2\}]^{2-}$ and $[Ni\{S_2C_2(CN)_2\}]^{-}$ complexes were characterised in early studies.[91,92] More recently, $[Ni(S_2C_2Et_2)]^z$ ($z = 0, 1-$), $[Ni\{S_2C_2(CF_3)_2\}]^z$ ($z = 0, 1-, 2-$) and $[Ni(S_2C_2Ph_2)]^z$ ($z = 0, 1-, 2-$) were isolated in individual form (see Ref. 85 and references cited therein).

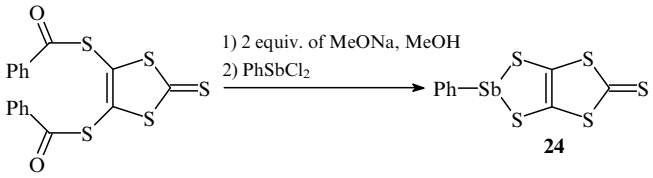
Calculated data on the electronic structures of the complexes were confirmed by the results of ESR spectroscopy for molybdenum-containing compounds **22** and **23** and the results of electrochemical investigations on molybdenum and tungsten complexes.[93,94]



22 **23**

M = Mo, W.

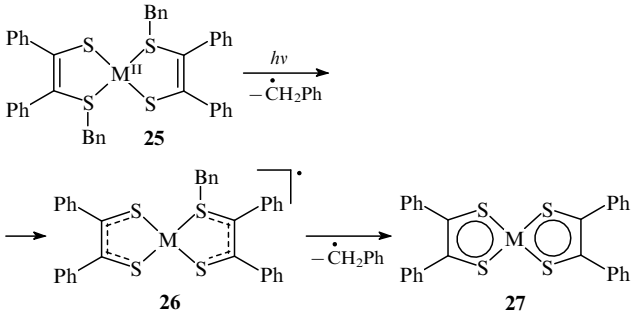
Neutral organoantimony dithiolene complex **24**[81] was synthesised by adding $PhSbCl_2$ to Na_2(dmit) (dmit is 4,5-dithiolato-1,3-dithiole-2-thione).



24

The complex was characterised by spectroscopy (NMR and IR) and X-ray diffraction.

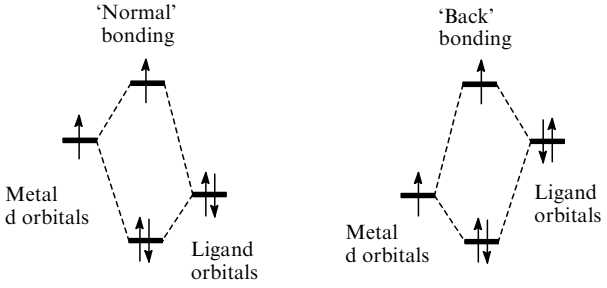
The dithione–dithiolate resonance cannot occur in nickel, palladium and platinum bis(*S*-benzyl-1,2-diphenylethylene-1,2-dithiolate) complexes **25**, and these compounds are 'classical' planar M^{II}-containing complexes.[95] However, irradiation of these complexes with visible light leads to successive elimination of both benzyl radicals from the ligand. Elimination of the first $CH_2Ph^{\bullet}$ radical gives rise to radical complex **26**, in which 77%–94% of spin density is delocalised on the ligand depending on the nature of the metal. The latter radical complex decomposes in the dark to give the corresponding dithiolene complex **27** within approximately 10^3 s.



25 **26** **27**

M = Ni, Pd, Pt.

The spectroscopic [ESR, ENDOR, X-ray absorption spectroscopy, electron spin echo (ESE)] and calculated (DFT) data on nickel dithiolene complexes and their anionic species were summarised in the study.[96] According to these data, all nickel bis(dithiolene) complexes are characterised by back bonding, *e.g.*, the energy of the valence orbitals of the ligands is higher than that of the d orbitals of the metal. A high energy of π orbitals of the ligand and good overlap of these orbitals with the Ni 3d orbitals are responsible for the efficient ligand → metal electron transfer.



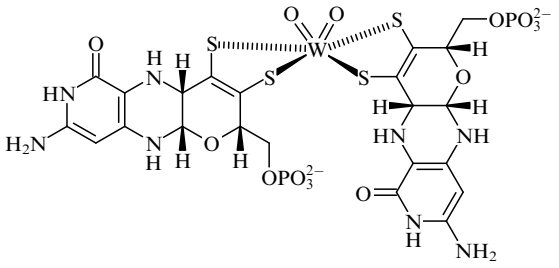
The lowest bonding molecular orbital of nickel complexes in all three oxidation states has more than 50% s-character; in the doubly-charged anionic complex, the LUMO is an antibonding combination of the Ni $3d_{xy}$ orbital (~25%) and the b_{1g}-symmetry S $3p_{x+y}$ orbital (~75%). The singly-occupied molecular orbital (SOMO) of the singly-charged anionic complex is an antibonding combination of the Ni $3d_{xz}$ orbital (~25%) and the b_{2g}-symmetry S $3p_z$ orbital (59%), whereas the LUMO is analogous to the corresponding orbital of the doubly-charged anionic complex. In the neutral complex, both the in-plane (b_{1g}) and out-of-plane (b_{2g}) orbitals are unoccupied and include ~20% of the Ni 3d orbital. On the whole, the singly-charged anionic complex is characterised by localisation of the unpaired electron predominantly on the sulfur atom.

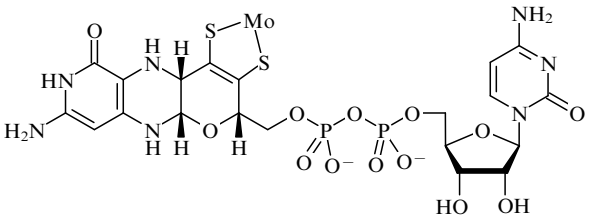
5. Magnetic properties of radical-ionic cyclopentadienyldithiolene complexes in the solid state

The ability of many non-innocent dithiolene square-planar $[M^{II}(S_2C_2R_2)_2]^{2-}$ complexes to be reversibly oxidised in two steps, *i.e.*, to exist in distinct oxidation states, allows the isolation of open-shell radical-anionic compounds (for example, $[Ni\{S_2C_2(CN)_2\}_2]^{-\bullet}$). In these compounds, efficient spin delocalisation over ligands is favourable for interactions in the solid state with a singlet–triplet, ferromagnetic or antiferromagnetic ground state. These complexes are of interest in materials science as potential solid materials with unique electronic properties, such as molecular metals, superconducting materials and magnetic crystals.[18]

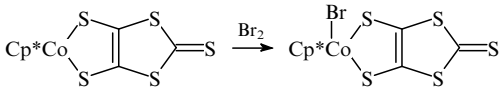
In 1986, Cassoux *et al.*[97] discovered superconductivity of mixed-valence salts containing $[Ni(dmit)_2]^{-\bullet}$, which gave rise to an outburst of activity in the field of synthesis of square-planar dithiolene complexes (with various new dithiolate ligands, different metals, two different dithiolene ligands or tetrathiafulvalene-based dithiolenes), nonplanar CpCo(mnt) (mnt is maleonitrile-2,3-dithiolate), Cp_2Ti(bdt) (bdt is benzene-1,2-dithiolate) complexes and the wedge-shaped sandwich complex Cp_2Nb(dmit).[18]

Dithiolene complexes have attracted widespread attention due to their analogy with the so-called molybdo- and tungstoenzymes (cofactors of oxomolybdoenzymes).[98] Different steps of the catalytic cycle during redox reactions of these enzymes involve conformational changes, in which non-innocent dithiolene complexes play a key role. Examples of such compounds are the structures of W- and Mo-containing (fragment) cofactors of aldehyde oxidoreductases from bacteria *Pirococcus furiosus* and *Desulfovibrio gigas* with one and two dithiolene fragments, respectively.





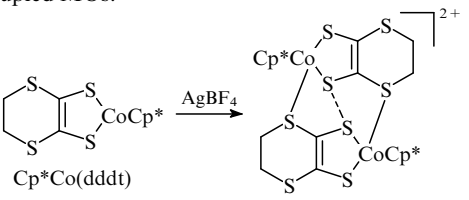
Based on the results of investigations of mixed complexes containing the dithiolene and Cp ligands, these complexes were classified into three groups.[18] The first group includes complexes generating radicals, in which the spin is completely or almost completely localised on the ligand. Examples are the trivalent cobalt complexes CpCo(dmit) and Cp*Co(dmit), where Cp* is the pentamethylcyclopentadienyl anion. Oxidation of these diamagnetic complexes with bromine results in the formation of the bromide ion that is involved in the metal coordination sphere.



Cp*Co(dmit)

Studies by ESR demonstrated that the spin is localised predominantly on the dmit ligand and the paramagnetic Cp*Co(dmit)Br complexes interact with the adjacent molecules *via* S···S contacts to form homogeneous chains, which are adequately described by the Heisenberg antiferromagnetic chain model with large negative coupling between the radicals along the chain (J/k −46.3 K or 32 cm^{-1}).

Upon oxidation of Cp*Co(dddt) (dddt is 5,6-dihydro-1,4-dithiine-2,3-dithiolate) with $AgBF_4$, the BF_4^- anion is not coordinated, and the $[Cp^*Co(dddt)]^{+\bullet}$ radical cation is unstable and is dimerised to the diamagnetic doubly-charged $[Cp^*Co(dddt)]_2^{2+}$ cation. The sulfur atoms of the six-membered ring are involved in the coordination sphere of the adjacent cation to form a two-electron bond, *i.e.*, complete spin localisation on the dddt ligand leads to its coupling in the antibonding combination of two singly-occupied MOs.[99]

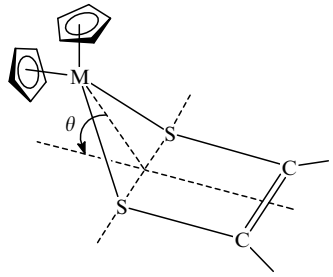


Cp*Co(dddt)

In both examples, intermolecular coupling occurs due to overlap of orbitals of different dithiolene fragments, and, if a covalent bond between the radicals is absent or this bonding can be precluded, the molecules possess properties of considerable interest in applied studies.

The second group includes complexes which form compounds containing an open-shell metal atom. Examples are the d^1-complexes $Cp_2V(dt)$ and $Cp_2Nb(dt)$ (dt is dithiolene). The d^0-complexes $Cp_2Ti(dt)$ do not form stable radical ions. They are reduced at strongly negative potentials and are reversibly oxidised.[100] However, uranium can be transformed into the oxidation state U^V, and, although the neutral $Cp_2U(dddt)$ complex does not form stable radical species, oxidation of [U(cot)(dddt)] (cot is cyclooctatetraene) with $AgBF_4$ affords the $[U^V(cot)(dddt)]^-$ radical anion [salt with Na(18-crown-6)(THF)]. The bond lengths in the dddt ligand of the radical anion are only slightly different from those in the starting doubly-charged anionic complex or in $Cp_2Ti(dddt)$, *i.e.*, the metal is subjected to oxidation to U^V. In the solid state, the spins are uncoupled.

Complexes of the third group, in which the unpaired electron is shared by the metal and the ligand, are intermediate between complexes of the first and second groups (an unpaired electron is completely localised on either the ligand or the metal). Examples are molybdenum and tungsten d^1-complexes of the $[Cp_2M(dt)_2]^+$ type. The $Cp_2Mo(dt)$ (Mo^{IV}, d^2) complexes give reversible oxidation waves.[101,102] The $Cp_2Mo(dddt)$ complex is oxidised by 7,7,8,8-tetracyanoquinodimethane (TCNQ), while $Cp_2Mo(dmit)$ is oxidised by the strong acceptor, $TCNQF_4$, to form the corresponding radical-ionic salts $Cp_2Mo(dddt)^{+\bullet}TCNQ^{-\bullet}$ and $Cp_2Mo(dmit)^{+\bullet}TCNQF_4^{-\bullet}$. Electrocrystallisation[103] afforded the $Cp_2Mo(dmit)^+$ salts with different anions: monoatomic (Br^-), tetrahedral (BF_4^-, ClO_4^-), octahedral (PF_6^-, AsF_6^-, SbF_6^-) and more complex ($ReO(dmit)_2^-$) anions. The most interesting result obtained in these investigations is the variability in the geometry of the d^1-radical cation and, particularly, in the puckering angle (θ) of the five-membered metallacycle with respect to the --S---S-- 'hinge'.



The puckering angle varies from 0 to 30° depending on the nature of the ligand as exemplified by the $Cp_2Mo(dmit)^+$ cation in Table 1 (see Ref. 18 and references cited therein).

Table 1. The puckering angle (θ) of the MoS_2C_2 metallacycle and the C−S and C=C bond lengths in selected molybdenum and titanium complexes.

Compound	θ/deg	C−S/Å	C=C/Å
$Cp_2Mo(dmit)$	4.2	1.745	1.357
$[Cp_2Mo(dmit)^+]PF_6^-$ (or AsF_6^-, SbF_6^-)	0.0	1.691	1.41
$[Cp_2Mo(dmit)^+][ReO(dmit)_2^-]$	5.6	1.688	1.383
$[Cp_2Mo(dmit)^+]TCNQF_4^-$	10.2	1.684	1.43
$[Cp_2Mo(dmit)^+]BF_4^-$	23.21	1.718	1.360
$[Cp_2Mo(dmit)^+]Br^-$	30.45	1.712	1.385
$Cp_2Ti(dt)$	43 – 51		

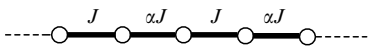
Similar puckering (even to a larger extent) was observed for the titanium d^0-dithiolene complexes (see Table 1). The reason is that puckering allows the free d^0 orbital of the Cp_2Ti fragment to be mixed with the HOMO of dithiolene, resulting in stabilisation of the d^0 system. This mixing is impossible at $\theta = 0°$ due to symmetry mismatch between the d^0 orbital and the HOMO in this conformation. According to this theory, puckering for the d^2 complexes CpMo(dt) is absent, which was confirmed experimentally.[18]

Great puckering was observed for 'heavier' complexes,[18] for example, upon the replacement of Mo with W, S with Se in the ligand or both elements simultaneously. This fact is consistent with the results of DFT calculations.[104] For example, electrocrystallisation of $Cp_2Mo(dsit)$ and $Cp_2W(dmit)$ (dsit is 1,3-dithiole-2-thione-4,5-diselenolate, a selenium analogue of dmit) in the presence of AsF_6^- affords isostructural salts with $\theta = 0°$, whereas heavier $Cp_2W(dsit)$ gives a radically different structure with $\theta = 30.1°$.[104]

A strongly puckered conformation cannot exist in structurally rigid *ansa*-metallocene dithiolene complexes, and, hence, oxidation of the unpuckered d^2 complexes $Me_2C(\eta^5\text{-}C_5H_4)_2Mo(dmit)$ and $Me_2C(\eta^5\text{-}C_5H_4)_2W(dmit)$ ($\theta_{Mo} = 0.68°$, $\theta_W = 0.29°$) in $TCNQF_4$ salts results in weak puckering ($\theta_{Mo} = 7.35°$, $\theta_W = 6.99°$).[105]

An increase in the puckering angle is indicative of enhancement of interactions between the frontier orbitals of the metallocene and dithiolate fragments, with the result that the unpaired electron is shared by the ligand and the metal (more precisely, by the Cp_2M fragment). Therefore, the non-innocent character is not an indication of only a redox-active ligand. If there is strong mixing of the ligand and metal orbitals, the non-innocent behaviour characterises the complex as a whole (oxidation states of the metal or the ligand are difficult to determine).

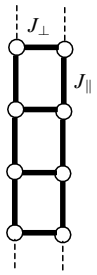
The formation of crystals of radical-cationic d^1 complexes in the presence of various anions involves a fine balance between the degree of intramolecular puckering, intermolecular spin–spin coupling and the counterion size aimed at decreasing the crystal free energy. Variations in the spin density on the dithiolene fragment and the crystal structure of the $Cp_2M(dt)^{+\bullet}$ salts would be expected to change the magnetic properties of the substance in the solid state, because the latter are controlled by the strength of dt···dt and dt···Cp intermolecular interactions. For the complexes under consideration, the following two main structural motifs were suggested: diads, which are associated with each other to a greater or lesser degree, or extended three-dimensional structures. Below are shown the possible models of interactions between the diads: uniform ($\alpha = 1$) and alternate ($0 < \alpha < 1$) chains and the so-called 'spin ladders'.[18]



$\alpha = 1$ is a uniform chain,

$0 < \alpha < 1$ is an alternate chain,

$\alpha = 0$ is an isolated dimer.



Spin ladder

Each circle indicates a spin carrier, and each line corresponds to interactions; J and αJ characterise interactions between the radicals along the chain. For example, the radical cations in the isostructural $[Cp_2Mo(dddt)][TCNQ]$ and $[Cp_2W(dddt)][TCNQ]$ complexes are actually arranged as diads with short S···S contacts. These diads are not isolated from each other, but form alternate chains ($0 < \alpha < 1$). The alternate chains are characterised by the following parameters: $J_{Mo}/k = -26$ K (18 cm^{-1}), $\alpha_{Mo} = 0.0-0.2$, $J_W/k = -16$ K (11 cm^{-1}), $\alpha_W = 0.5-0.6$. Interactions between the molybdenum diads are stronger than those between the tungsten diads, which is attributed to a greater localisation of the spin on the metal in the tungsten complex. The interaction is antiferromagnetic ($J < 0$) due to direct exchange interaction between SOMOs.

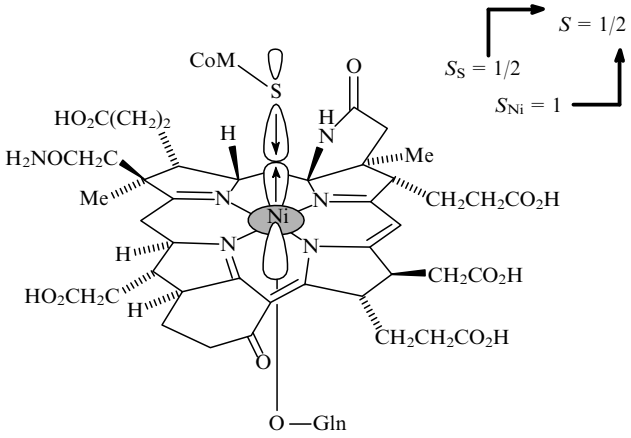
The model of a uniform chain ($\alpha = 1$) is better applicable to $[Cp_2Mo(dsit)][TCNQF_4]$, whereas $[Cp_2W(dsit)][TCNQF_4]$ is more adequately described by an alternate chain with $\alpha = 0.5$. Examples of molecular spin ladders are $[Cp_2Mo(dmid)]$. $[TCNQF_4]$ (dmid is 1,3-dithiol-2-one-4,5-dithiolate)[106] and $[Cp_2W(dsit)]AsF_4$.[104] In these salts, the diads formed by two organometallic cations are arranged one above another to form a ladder-like system ($|J_\perp| > |J_\parallel|$). In this case, stronger intermolecular interactions also occur in the molybdenum compounds, because the SOMO in molybdenum salts is localised to a larger degree on the dithiolene fragment compared to the tungsten complexes.

6. Non-innocent behaviour of thiolate ions

The results of experimental and calculated studies suggest that the HOMO of many metal thiolates is centred on the sulfur atom and has the character of its p orbital (see Ref. 107 and references cited therein). Hence, many reactions of transition metal thiolates, including redox reactions, would be expected to occur at the sulfur atom. Oxidation of thiolate complexes gives rise to thiolate radicals.

The oxidation states of the Ni cofactor F_{430} in methyl coenzyme M reductase were studied[108] by magnetic circular dichroism, X-ray absorption spectroscopy and DFT calculations, and it was hypothesised that the oxidised state of the enzyme containing the Ni–SR bond can formally be described as a Ni^{II} complex with the thiyl radical ($^{\bullet}$SCoM, CoM is the coenzyme M).

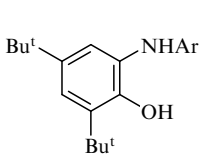
This state can alternatively be described as Ni^{III} thiolate, but this description is less probable. Earlier, an analogous non-innocent behaviour of sulfur-containing ligands (S-centred radical, thiolate) was assumed in biochemistry.[109]



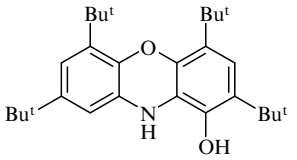
Methyl CoM reductase

7. Complexes of *o*-aminophenols

Like other compounds belonging to the *o*-XC_6H_4Y structural type (X, Y = O, S or NH), *o*-aminothiophenols are classical non-innocent ligands. Ligands in complexes with V, Cr, Fe and Co and the corresponding catecholate, *o*-phenylenediamine and *o*-benzenedithiolate complexes can be assigned to a particular oxidation state on the basis of the structural criteria proposed in the study.[110] Complexes of *o*-aminophenol and its substituted analogues H_2L^1 (see Refs 9 and 110) and L^2 (see Refs 111 and 112) with Fe^{III}, Ni^{II}, Co^{III}, Pd^{II} and Cu^{II} were documented. In these complexes, the ligand is present as the singly-charged anionic *o*-iminosemiquinonate radical.



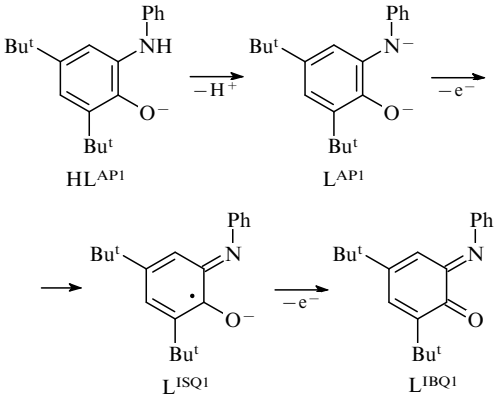
H_2L^1 (Ar = Ph),
$H_2^{Cl}L^1$ (Ar = 3,5-$Cl_2C_6H_3$)



L^2

The $Co^{III}(L^{ISQ1})_3$ (**28**), $[Cu(dmtacn)L^{ISQ1}]PF_6$ (**29**), $Cu(L^{ISQ1})_2$ (**30**), $Ni(L^{ISQ1})_2$, $Ni(^{Cl}L^{ISQ1})_2$ and $Pd(L^{ISQ1})_2$ compounds (L^{ISQ1} and $^{Cl}L^{ISQ1}$ are L^1 and $^{Cl}L^1$, respectively, in the semiquinone form, dmtacn is 1,4-dimethyl-1,4,7-triazacyclononane) were studied by X-ray diffraction.[9] The central metal atoms in copper complex **30** and divalent nickel and palladium complexes are in a square-planar environment. The ground state of complex **29** is $S = 1$, which is associated with the strong antiferromagnetic coupling between the Cu^{II} $d_{x^2-y^2}$ orbital and the π orbital of the radical ligand. Complex **28** contains three virtually orthogonal semiquinone ligands L^{ISQ1}, and its ground spin state is $S = 3/2$. Other complexes are singlet biradicals, the central divalent metal atoms in these complexes have the d^8 configuration, and the complexes are diamagnetic. A detailed study of electrochemical oxidation and reduction of all five complexes revealed a series of reversible one-electron steps, all processes occurring at the ligand.

For the HL^1 ligand (Ar = Ph) [110]



HL^{AP1} L^{AP1} L^{ISQ1} L^{IBQ1}

complexes with $Cr^{III}(L^{ISQ1})_3$ (**31**), $Co^{III}(L^{ISQ1})_3$ (**32**) and $Fe^{III}.(L^{ISQ1})_3$ (**33**) and a series of vanadium complexes, including $V^{V}L^{ISQ1}(L^{AP1})_2$ (**34**) and $V^{V}(L^{AP1})_2(HL^{AP1})$ (**35**), were described. All five compounds **31**–**35** were characterised by X-ray diffraction.

The electrochemical behaviour of the above-mentioned complexes was accounted for by redox processes involving both the metal and the ligand depending on the nature of the metal in the complex. For example, all redox processes in chromium complex **31** involve exclusively the ligand.

$$[Cr^{III}(L^{IBQ1})_3]^{3+} \overset{e^-}{\underset{-e^-}{\rightleftharpoons}} [Cr^{III}(L^{ISQ1})(L^{IBQ1})_2]^{2+} \overset{e^-}{\underset{-e^-}{\rightleftharpoons}}$$

$$\rightleftharpoons [Cr^{III}(L^{ISQ1})(L^{IBQ1})]^{+} \overset{e^-}{\underset{-e^-}{\rightleftharpoons}} \mathbf{31} \overset{e^-}{\underset{-e^-}{\rightleftharpoons}}$$

$$\rightleftharpoons [Cr^{III}(L^{ISQ1})_2(L^{AP1})]^{-} \overset{e^-}{\underset{-e^-}{\rightleftharpoons}} [Cr^{III}(L^{ISQ1})(L^{AP1})_2]^{2-}$$

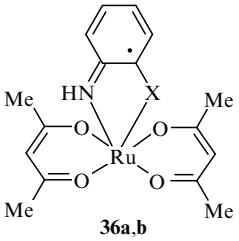
By contrast, the metal atom in vanadium complex **34** is reduced in the second and third steps, and, in addition, highly oxidised members of the redox series are electrochemically inaccessible.

$$[V^{V}(L^{ISQ1})_2(L^{AP1})]^{+} \overset{e^-}{\underset{-e^-}{\rightleftharpoons}} \mathbf{34} \overset{e^-}{\underset{-e^-}{\rightleftharpoons}} [V^{V}(L^{AP1})_3]^{-} \overset{e^-}{\underset{-e^-}{\rightleftharpoons}} \mathbf{35}$$

$$-e^- \Big\downarrow\uparrow e^-$$

$$[V^{IV}(L^{AP1})_3]^{2-} \overset{e^-}{\underset{-e^-}{\rightleftharpoons}} [V^{III}(L^{AP1})_3]^{3-}$$

The diamagnetic $LRu^{II}(acac)_2$ complexes (**36a**,**b**) [L is *o*-iminoquinone (**36a**) or *o*-iminothiosemiquinone (**36b**); compound **36a** was characterised by X-ray diffraction [113]] are irreversibly oxidised or reduced by electrochemical methods to form paramagnetic singly-charged cations and anions. Electrochemical, calculated and spectroscopic data demonstrated that the ligand is subjected to oxidation and reduction (below the acac ligands are omitted for simplicity; possible alternative formulae of the compounds are given in parentheses).



36a,**b**

X = O (**a**), S (**b**).

$$Ru^{III}(L^0)\ [\text{or } Ru^{IV}(L^{\bullet})]^{\bullet}$$

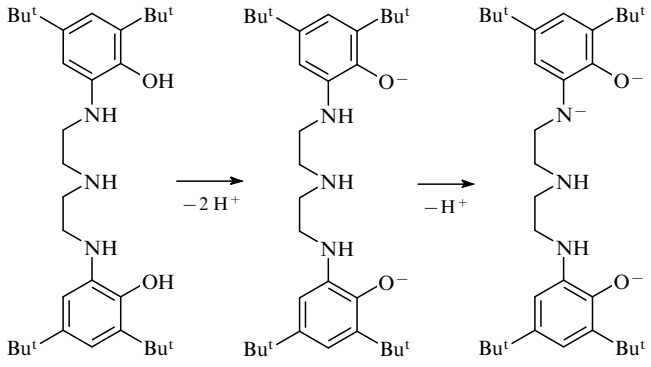
$$-e^- \Big\downarrow\uparrow e^-$$

$$[Ru^{II}(L^0)]\ Ru^{III}(L^{\bullet})\ [\text{or } Ru^{IV}(L^{2-})]$$

$$-e^- \Big\downarrow\uparrow e^-$$

$$[Ru^{II}(L^{\bullet})]\ Ru^{III}(L^{2-})$$

N,*N*′-Bis[2-(4,6-di-*tert*-butyl)hydroxyphenyl]diethylenetriamine **37** was studied in complexation reactions with first-row transition metals (vanadium, chromium, iron and cobalt).[110] The resulting complexes containing ligands in the above-mentioned three forms were studied in detail by electrochemical and spectroelectrochemical methods. The vanadium complex $V^{V}O[(HL^{AP})NH(L^{AP})]$ with the triply-charged anion **37b** as the ligand was studied by X-ray diffraction.

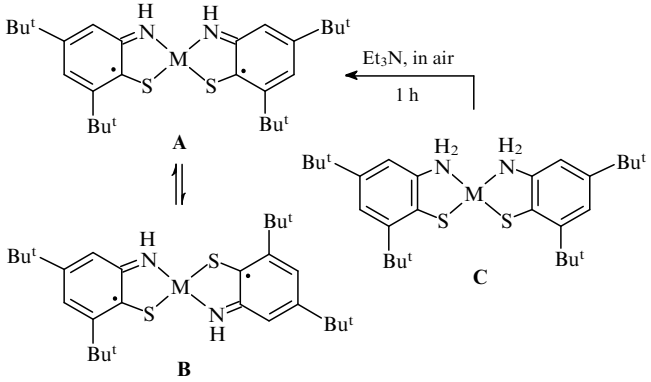


37 **37a** **37b**

$H_2[(HL^{AP})NH(HL^{AP})]$ $[(HL^{AP})NH(HL^{AP})]$ $[(HL^{AP})NH(L^{AP})]$

8. Complexes of *o*-aminothiophenols and their selenium- and tellurium-containing analogues

Neutral square-planar Ni^{II}, Pd^{II} and Pt^{II} bis(*o*-iminothiosemiquinonate) complexes were synthesised and characterised. Being singlet biradicals, these complexes are diamagnetic. The reaction of *o*-aminothiophenols with M^{2+} salts in ethanol or acetonitrile in air produced both complexes with ligands containing the unsubstituted benzene ring [46, 114–116] and black-blue complexes based on 6-amino-2,4-di-*tert*-butylthiophenol.[12, 117] The structures of all the complexes synthesised were confirmed by NMR, UV-Vis and ESR spectroscopy and, in most cases, by X-ray diffraction analysis. The NMR spectra suggest that the *cis* and *trans* forms **A** and **B** of the complexes with di-*tert*-butyl-substituted ligands are in rapid equilibrium in solution.



A **B** **C**

M = Ni^{II}, Pd^{II}, Pt^{II} (**A**, **B**); M = Ni^{II}, Pd^{II} (**C**).

Both the *cis* and *trans* forms of the complexes were isolated and studied by X-ray diffraction analysis. The *cis*–*trans* transformation is fast in the case of Ni and slow in the case of Pt, whereas the rate of this transformation in the case of Pd is intermediate. It should be noted that the beige-yellow 'classical' complex **C** is derived from *o*-aminothiophenols and M^{2+} salts under inert atmosphere.

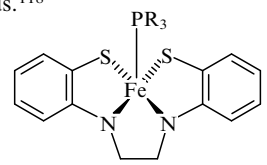
Spectroelectrochemical and electrochemical studies of the complexes **A** and **B** revealed a usual electron-transfer series, in which a singly-charged cation, a neutral species and singly- or doubly-charged anions were identified.[13] The ESR spectra of singly-charged cations of the nickel and platinum complexes confirmed that only the ligand is oxidised to form $[M^{II}(L^{ISQ})(L^{IBQ})]^{+}$, where L^{IBQ} is *o*-iminothioquinone. In contrast, the structures of the complexes for the corresponding singly-charged anions are most adequately described by the $[M^{II}(L^{ISQ})$.

.$(L^{AP})]^-$ and $[M^I(L^{ISQ})_2]^-$ resonance structures, the contribution of the latter being considerable (L^{AP} is the doubly-charged *o*-imidothiophenolate anion).

The *o*-iminothiosemiquinonate radical is characterised by two intense $\pi-\pi^*$-charge transfer bands in the visible region of the UV-Vis spectra at ~640 and 560 nm and by an intense ligand–ligand charge transfer band at the boundary between the visible and near-IR regions at 730–840 nm in the IR spectra.[12]

Analysis of the literature data on the geometric features of 120 complexes containing *o*-aminothiophenolate-type ligands [12] made it possible to propose criteria for the determination of the degree of protonation and oxidation of the ligands in these complexes. As in the *o*-phenylenediamine and *o*-catecholate complexes, the C–N and C–S bond lengths and the C=C bond lengths in the benzene ring are very characteristic. The bond lengths in the ligand are virtually independent of the nature of the coordinated metal. The radical form (L^{ISQ}) of non-innocent *o*-aminothiophenolates is the major one in coordination compounds.

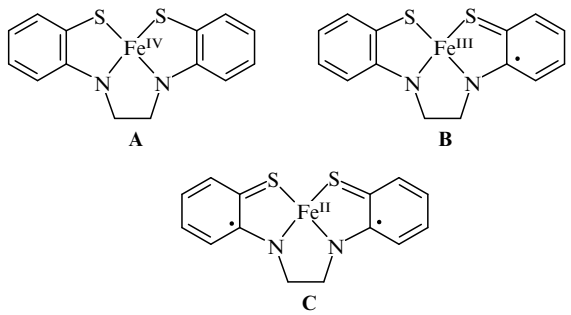
In 1997, a series of complexes **38** containing five-coordinate iron atoms and *o*-amidothiophenolate ligands were synthesised and characterised by X-ray diffraction and spectroscopic methods.[118]



38

R = Me, Et, Pr^n, Bu^n, Ph, cyclo-C_6H_{11}, OMe, OPh.

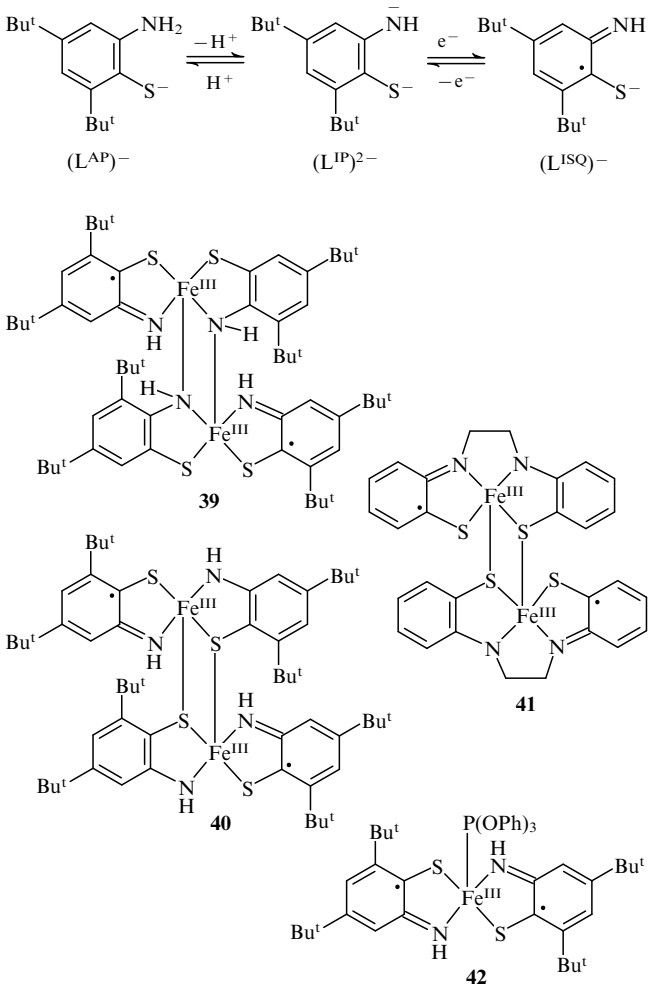
In the study,[118] the ligand was considered as the redox-innocent quadruply-charged 1,2-ethanediamido-*N*,*N*′-bis(2-benzenethiolate)$^{4-}$ anion, and the complex as a whole was described as an Fe^{IV} complex ($S = 1$) (**A**). This structure is consistent with the magnetic moment of 2.76 μ_B observed for this complex at room temperature and the data from cyclic voltammetry (reversible reduction of the complex at +0.04 and −0.86 V, which were assigned to the Fe^{IV}/Fe^{III} (**A**/**B**) and Fe^{III}/Fe^{II} (**B**/**C**) transitions, respectively) and Mössbauer spectroscopy, although a complete analysis of the latter spectrum was lacking.



A **B** **C**

However, the studies [12, 119] cast doubt on this description of the structures. In the study,[119] it was demonstrated that the bond lengths in this class of complexes determined by X-ray diffraction analysis are typical of complexes of the *o*-iminothiosemiquinonate radical, the physical oxidation state of iron in the complex is +2 (structure **C**), and the spin $S = 1$ observed for the ground state of the complex is attributed to strong intramolecular antiferromagnetic coupling between two organic radicals and the low-spin iron ion. Analysis of the spin-Hamiltonian [12] confirmed this assumption. Ghosh *et al.*[119] reproduced the experiment performed earlier by Sellmann *et al.*[118] and demonstrated that only the freshly prepared complex had the magnetic moment of 2.76 μ_B, whereas this value decreased to 0.6 μ_B after two crystallisations.

Analogous iron complexes containing the di-*tert*-butyl-substituted *o*-iminothiosemiquinonate fragments were described in the study.[119] The binuclear (μ-NH,NH)$[Fe^{III}L^{IP}L^{ISQ}]_2$ (**39**) and (μ-S,S)$[Fe^{III}L^{IP}L^{ISQ}]_2$ complexes (**40** and **41**) and the mononuclear $Fe^{III}(L^{ISQ2})_2[P(OPh)_3]$ complex (**42**) were synthesised and characterised by X-ray diffraction analysis.

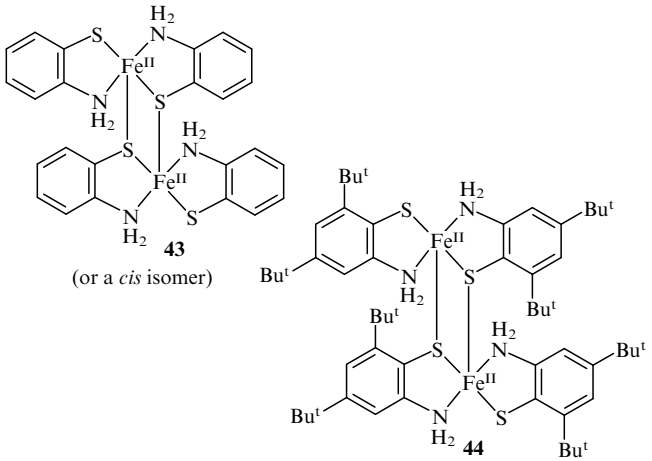


$(L^{AP})^-$ $(L^{IP})^{2-}$ $(L^{ISQ})^-$

39 **41** **40** **42**

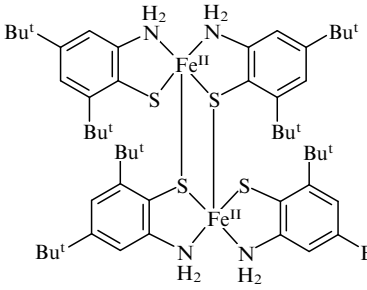
The oxidation state of the ligands was established by X-ray diffraction and ESR, UV-Vis and Mössbauer spectroscopy.

Dimeric complexes **43**–**46** were synthesised under inert atmosphere in a neutral medium, *i.e.*, under conditions precluding deprotonation.[120]

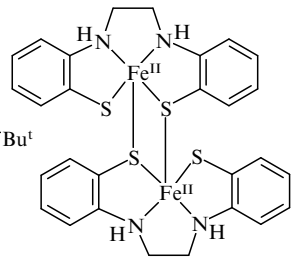


43
(or a *cis* isomer)

44

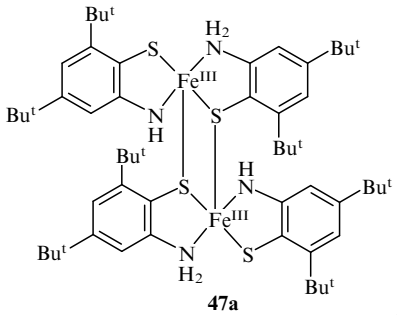


45

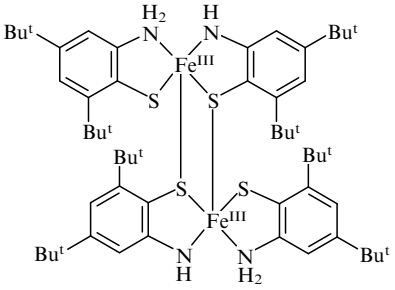


46

Complexes **43**–**45** are sensitive to atmospheric oxygen and moisture and are transformed into the $[Fe(L^{ABT})_2L^{ISQ}]$ complex (L^{ABT} is the *o*-aminobenzothiolate anion) in the presence of traces of oxygen. The latter complex is characterised by the ground spin state $S = 3/2$. Dimers **47a**,**b** are produced in the presence of Et_3N and traces of O_2.



47a

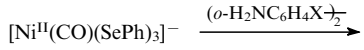


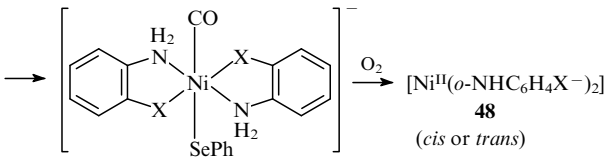
47b

The structures of compounds **44**, **46** and **47a** were determined by X-ray diffraction. Mössbauer spectra of compounds **43**–**45** unambiguously established the presence of the high-spin iron ion, whereas both medium-spin Fe ions ($S_{Fe} = 3/2$) in dimers **47a**,**b** are antiferromagnetically coupled, resulting in the ground state $S = 0$.

Di- and trivalent cobalt complexes with the same ligands as in complexes **31**–**35** and **39**–**47** were documented.[121] In all the complexes synthesised, the ligands are redox-non-innocent, but oxidation and reduction of either the metal or ligand depend on the state (anionic, radical-anionic or neutral) of the ligand and the oxidation state of the central metal atom in the starting complex.

In 2003, selenium- and tellurium-containing ligands (analogues of *o*-aminothiophenol) were synthesised and their complexes with nickel **48** were prepared by the oxidative addition of 2-aminophenyl dichalcogenides to the $[Ni(CO)(SePh)_3]^-$ anion.[122]

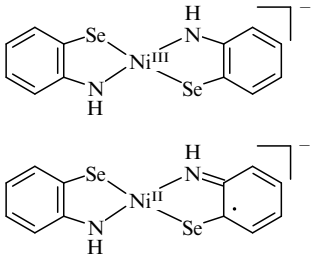




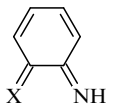
48
(*cis* or *trans*)

X = Se, Te

The *trans*-$[Ni(SeC_6H_4NH\text{-}o)_2]^-$ and *cis*-$[Ni(TeC_6H_4NH\text{-}o)_2]^-$ complexes [as salts with the $(PPh_3)_2N^+$ cation] were studied by X-ray diffraction. All complexes were also characterised by X-ray electron spectroscopy and DFT calculations. It was concluded that the singly-charged $[Ni(SeC_6H_4NH\text{-}o)_2]^-$ and $[Ni(TeC_6H_4NH\text{-}o)_2]^-$ anions are most adequately described as resonance hybrids of nickel(III) bis[*o*-amidochalcogenolate(2−)] and nickel(II) bis[*o*-iminochalcogenobenzosemiquinonate(1−)].



The delocalisation of the metal d-electrons in ruthenium bis(bipyridyl) complexes with redox-active quinoid ligands $Ru(bipy)_2LL$ was calculated.[123]



LL

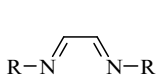
X = NH, O, S.

The results of calculations confirmed by UV-Vis spectra of the compounds synthesised demonstrate that the degree of coupling between the π-orbitals of ruthenium and the LL ligand increases in the series NH < O < S.

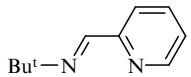
III. Complexes with diimine-containing ligands

1. Complexes of α-diimines and their phosphorus analogues, 2,2′-biphosphinines

Complexes of 1,2-diketone derivatives (**49**) and complexes with ligands in which the diimine fragment is involved in the heterocyclic system (**50**, bipy, *etc.*) are assigned to this structural type.



49



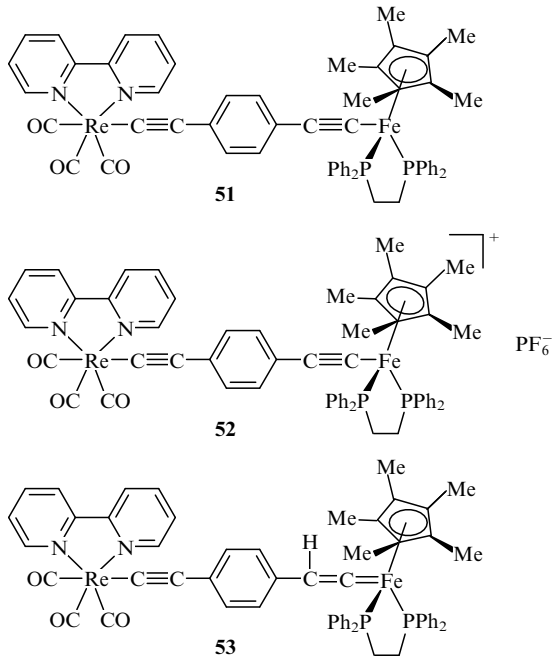
50 (Bu^t-Pyca)

R = Alk, Ar.

Complexes of 1,4-disubstituted 1,4-diazabutadienes **49** (R = Bu^t, cyclo-C_6H_{11}, 4-MeC_6H_4 and 2,6-$Me_2C_6H_3$) with $PtMe_2$, $PtMe_4$ and $PtMes_2$ were studied by spectroscopic methods and DFT calculations.[124] These data suggest considerable metal → ligand charge transfer. The results of spectroelectrochemical studies are consistent with reversible oxidation of the ligand to form the $[Pt^{II}L]^+$ or $[Pt^{IV}L]^+$ complexes. The reduction of analogous rhenium,[125] ruthenium, osmium, iridium and rhodium[126] complexes is also most adequately described as the reduction of the ligand to form the radical anion.

In complexes **6a**–**c** containing the terpyridyl fragment in the ligand (see Section II.1), the diimine fragment also undergoes one-electron reduction in the first step.[24]

Heteronuclear alkynyl-bridged complex **51** and its analogue **52** with oxidised iron (from Fe^{II} to Fe^{III}) were synthesised and characterised by X-ray diffraction.[127]



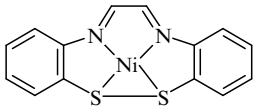
Vinylidene complex **53** was also documented.[127] This complex is reversibly oxidised at −0.19 V and quasireversibly reduced at −1.49 V. Electrochemical data and results of DFT calculations suggest that the LUMO of the complex is localised predominantly on the π* orbital of the bipyridyl ligand, whereas the HOMO has the character of the iron(II) d orbital.

Phosphorus analogues of α-diimines, in particular, 2,2′-biphosphines, can also be considered as non-innocent ligands. For example, 4,4′,5,5′-tetramethyl-2,2′-biphosphine (tmbp) is reduced with potassium mirror to the planar radical anion (studied by X-ray diffraction analysis as a lithium salt), in which the unpaired electron (DFT calculations) is delocalised over the PCCP fragment with a large contribution of the phosphorus p_π orbitals.[128] Electrochemical reduction of the $Ni^0(tmbp)_2$ complex afforded a 19-electron complex studied by X-ray diffraction. These data are consistent with the results of DFT calculations, which demonstrated that the unpaired electron in the $Ni^0(bp)_2^{-\bullet}$ complex (bp is 2,2′-biphosphine) is delocalised primarily on the ligand.[128] The calculations showed also that the metal–ligand back bonding in $Ni^0(bp)_2$ makes a considerable contribution to the metal–ligand bonding.

2. Complexes with ligands of the glyoxalbis(2-mercaptoanil) series

Oxidation and reduction of compounds with ligands of the glyoxalbis(2-mercaptoanil) series, which combine the α-diimine and *o*-aminothiophenol fragments, were studied for the first time by Holm and co-workers[26,129] in 1960s. They demonstrated that the $Ni(gma)_2$ compound (**1**), analogously to the N_2S_2 complexes with ligands of the *o*-disubstituted benzene series, is the central member of the electron-transfer series, the final oxidation product being a quinone complex. Holm and co-workers also described the chemical reduction of $Ni(gma)_2$ with sodium amalgam to the anionic $Ni(gma)_2^-$ species. The radical character of the latter was demonstrated by ESR spectroscopy. When discussing the electron distribution in the starting complex and the degree of mixing of the metal and ligand orbitals, the authors considered the delocalised ground state and did not draw an unambiguous conclusion about localisation of the unpaired electron (on either the metal or the ligand) in the reduced radical-anionic form of the complex.

Complex **1** and other Ni^{II} diiminodithiolate and diiminodisulfide N_2S_2 complexes of this type, *i.e.*, with complete π-conjugation between all four donor centres, were synthesised.[3] These complexes were studied by ^1H NMR, ESR and UV spectroscopy, mass spectrometry and electrochemical methods. In solutions of complex **1** in DMF, the ESR signal first appears and then attenuates with time, which is accompanied by an analogous change in the intensity of the absorption band at 931 nm. The electrochemical behaviour also varies with time. After storage of compound **1** in solution for 5 h, the cyclic voltammogram becomes similar to the curve measured for the corresponding diiminodisulfide complex **54**.

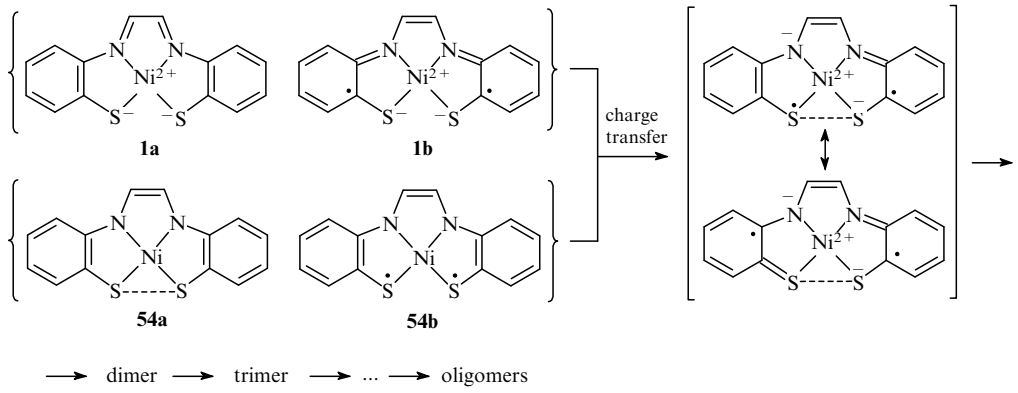


The results of this study suggest that non-innocent compounds of the glyoxalbis(2-mercaptoanil)nickel(II) type were synthesised as classical diiminodithiolate structures, but then the ligands were transformed successively (rapidly in solution and slowly in the solid state) into the *o*-iminothiosemiquinonate biradicals and oligomeric structures, the latter remaining unchanged over a long period of time (Scheme 3).

3. Complexes of pyridine-2,6-dialdimine and its derivatives

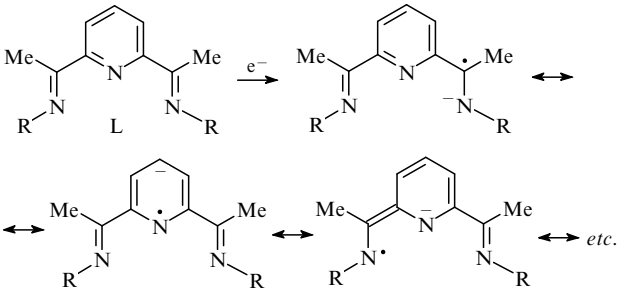
Most complexes with this ligand were described as the five-coordinate $[M^{II}X_2L^0]$ complexes or the six-coordinate $[M^{II}L^0_2]X_2$ complexes (M = Mn, Fe, Co, Ni, Cu, Zn or Cd; X = Cl or Br) containing one or two neutral tridentate ligands; and the ligands were always described as redox-innocent.[130–134] However, more recent studies by electrochemical methods and NMR, ESR and

Scheme 3



Mössbauer spectroscopy demonstrated that pyridine-2,6-dialdimines are non-innocent ligands, which can be coordinated to a transition metal ion as the neutral ligand L^0 or the radical anionic ligand $L^{-\bullet}$.[134] This was suggested earlier by Toma and co-workers,[130, 131] but has not been strictly proved.

Metal complexes with pyridine-2,6-dialdimine with the general formula $[M^{II}L_2](PF_6)_n$ (M = Mn, Fe, Co, Ni, Cu or Zn) are reversibly reduced to $[ML_2]^+$ and $[ML_2]^0$.[135] X-ray diffraction study of $[MnL_2]PF_6$ and $[CoL_2]PF_6$ demonstrated that the former complex is $[Mn^{III}(L^{-\bullet})_2]PF_6$ (reduction of the ligand), whereas the latter complex is $[Co^{I}L_2]PF_6$ (reduction of the metal).



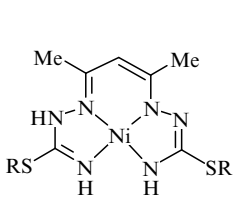
R = 4-$MeOC_6H_4$.

4. Complexes with pentane-2,4-dionebis(2-alkylisothiosemicarbazone)-type ligands

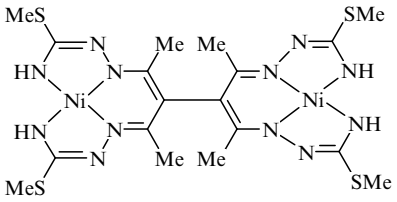
Template condensation of pentane-2,4-dione with *S*-alkylisothiosemicarbazide hydrochloride in the presence of divalent metal ions (Ni,[136, 137] Co,[138] Fe[139–141]) affords complexes containing pentane-2,4-dionebis(2-alkylisothiosemicarbazone) (H_3L) as the ligand (Scheme 4).

This ligand exhibits a complex coordination behaviour towards transition metals, because it, first, can exist in different protonated forms, $(H_3L)^0$, $(H_2L)^-$, $(HL)^{2-}$ and $(HL)^{3-}$, and, second, can undergo two-electron oxidation also to two different protonated forms, $(HL)^0$ and $(L)^-$.

Mono- and binuclear nickel complexes with the non-innocent pentane-2,4-dionebis(2-alkylisothiosemicarbazonate) ligands exist in two forms containing the ligand in different oxidation states,[142] *viz*., the red-brown $Ni^{II}(HL)$ complexes **55** sensitive to oxidation with atmospheric oxygen and the paramagnetic black-green oxidised Ni(L–L)Ni complexes **56** (in this formula, the nickel atom is in the formally trivalent oxidation state; however, in the real complex studied by X-ray diffraction, the ligand is apparently oxidised and the nickel atom is reduced to the oxidation state of +2).



55



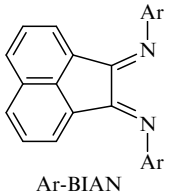
56

R = Me, n-dodecyl.

Both oxidation and reduction of the dinuclear complex occur with the involvement of the ligand and with retention of the oxidation state of the nickel atoms.

5. Complexes of bis(arylimino)acenaphthenes

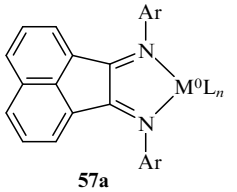
In recent years, bis(arylimino)acenaphthenes (Ar-BIAN) have attracted considerable attention. Their complexes with transition metals can serve as catalysts for some reactions of organic compounds.[143–151]



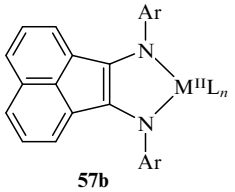
Ar-BIAN

Compared to other diimine ligands, BIAN derivatives are more rigid molecules (due to the presence of the naphthalene fragment), and this rigidity provides, first, the directionality of the lone electron pairs of the nitrogen atoms favourable for coordination and, second, almost complete inertness to hydrolysis and cleavage of the central C–C bond.[151] (Hydrolysis presents a serious problem in reactions with the use of most diimine ligands as catalysts.)

The neutral (Ar-BIAN)ML_n complex can *a priori* be represented as a compound of either zero-valent metal **57a** or divalent metal **57b**, *i.e*., this complex is non-innocent.

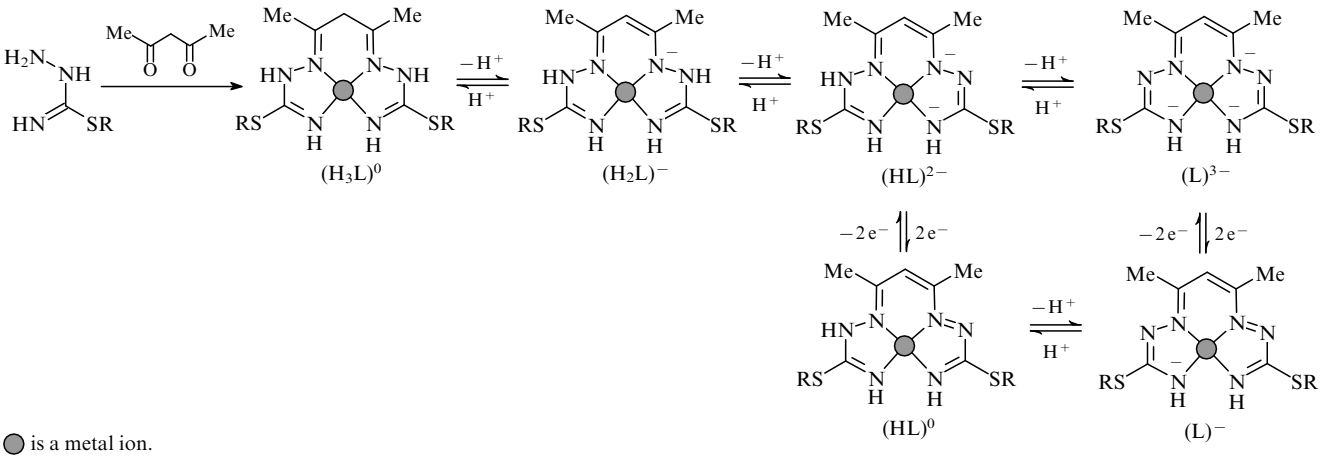


57a



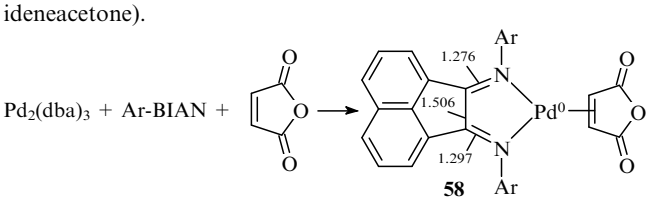
57b

Scheme 4

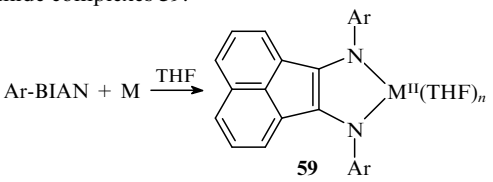


● is a metal ion.

The reactions of Ar-BIAN with zero-valent transition metals generally give rise to diimine structures. An example is palladium complex **58** [146] (the bond lengths are given in Å; dba is dibenzylideneacetone).



Alkali and alkaline-earth metals react with Ar-BIAN to give diamide complexes **59**.[144, 147]

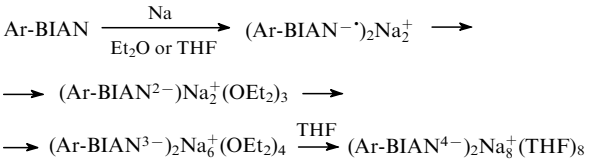


Ar = 2,6-$Pr^i_2C_6H_3$; M = Mg, Ca.

M	C–N /Å	C=C /Å
Mg	1.401, 1.408	1.389
Ca	1.391, 1.402	1.409

Complexes with Ar-BIAN are very easily reduced, the ligand being subjected to reduction [148–150] and reduction occurring at much less negative potentials than for other diimine ligands. For example, electrochemical studies demonstrated that Re^I(Ph-BIAN)$(CO)_3Cl$ is reduced at potentials (−0.65 V), which are 1 V less negative compared to Re^I(bipy)$(CO)_3Cl$ (−1.64 V).[150] This is evidence that the π-acceptor properties of Ar-BIAN are much stronger than those of other diimines.

Chemical reduction of free 2,6-$Pr^i_2C_6H_3$-BIAN with Na or Li in ethereal solvents involves the successive formation of the radical anion, the doubly-charged anion, the triply-charged radical anion and, finally, the quadruply-charged anion, which were isolated and studied by UV-Vis spectroscopy and X-ray diffraction.[151, 152] The singly-, triply-, and quadruply-charged anions have dimeric structures.

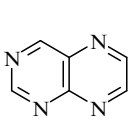


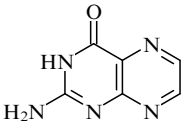
During reduction, the first two electrons are transferred to the diazadiene fragment, and the next two electrons are transferred to the π-system of the naphthalene moiety.[152]

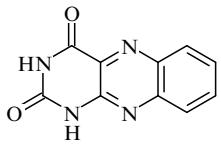
Undoubtedly, the possibility of four-electron reduction indicates that two almost degenerate LUMOs of Ar-BIAN are very low-lying.

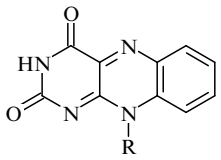
IV. Pterin complexes

Yet another group of non-innocent nitrogen-containing ligands includes pterins, pteridines and structurally related alloxazines and flavins. In complexes with these ligands, there is a strong interaction between the transition metal ion and the ligand.[153]


Pteridine

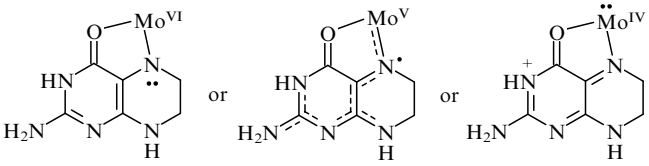

Pterin


Alloxazine


Flavins

Since the degree of electron delocalisation between the metal and the coordinated pterin varies in different complexes, the problem is to determine the formal oxidation states of the metal and the pterin in each particular complex. Evidently, the molecules of pterin, pteridine and their analogues are redox-active, and generally their coordination to transition metals results in a high degree of electron delocalisation between the metal and the ligand.[153] As in the case of other non-innocent ligands, it is most convenient to determine the redox characteristics of transition metals and ligands in metal pterin and metal pteridine complexes by X-ray diffraction and UV-Vis spectroscopy in the visible range. For molybdenum complexes with pterin ligands, the structural criteria for this assignment were reported in the studies.[154, 155]

In particular, UV-Vis and photoelectron spectroscopy demonstrated that the $Mo^V(H_3pterin^{\bullet})$ structure is preferable for the molybdenum complex with tetrahydropterin (a fragment of the complex is shown).[153]

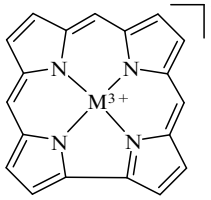


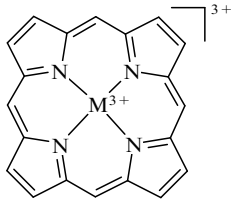
Preferable structure

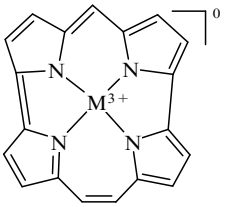
The redox-resonance of analogous structures was suggested in the study [156] for the structures of molybdenum complexes with reduced pterin and flavin. A considerable metal → ligand charge transfer and stabilisation of ruthenium, copper and rhenium complexes with the reduced ligand were established by cyclic voltammetry and UV-Vis spectroscopy in the visible region.[157] Iridium,[158] copper,[159–162] iron(II),[160] cobalt(II)[160] and zinc[161] complexes with pterin and pteridine were studied by spectroscopic and electrochemical methods and characterised by X-ray diffraction.

V. Porphyrins, corroles and isocorroles

Porphyrins and corroles stabilise high-valence states of coordinated metal atoms. Studies by Raman spectroscopy and DFT calculations demonstrated that the valence orbitals of corroles are qualitatively similar to those of porphyrins.[163] Isocorroles, as a whole, are also similar to corroles, but their ground states differ in symmetry ($^2A''$ for corroles and $^2A'$ for isocorroles), resulting in different $d_\pi-p_\pi$ metal–ligand interactions.[163, 164] Porphyrins, corroles and isocorroles can exist in two oxidised radical-cationic forms, which are very similar in energy. For copper corrole and isocorrole complexes, the Cu^{II} π-radical cation has a slightly higher energy than the diamagnetic Cu^{III} d^8 complex. In contrast, for the nickel complexes, the low-spin Ni^{II}-containing π-radical cation has a lower energy than the state with Ni^{III}, which is consistent with experimental data.[163]


Metallocorrole


Metalloporphyrin

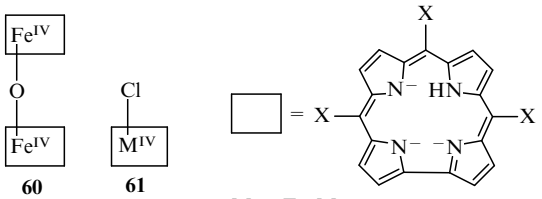


Metalloisocorrole

Iron-containing metalloporphyrin radical cations are postulated as intermediates in processes catalysed by natural peroxidases, catalases and their synthetic analogues.[165] Formally, the oxidation state of iron in these intermediates is +5. However, it is better to consider the intermediates as Fe^{IV}-oxo porphyrin π-radical cations.[166]

It was demonstrated [167] that one-electron reduction of Au^{III} complexes with substituted porphyrin ligands occurs in different ways depending on the nature of the substituent in the β positions of the pyrrole fragments of the macrocycle. If the porphyrin moiety contains the electron-donating 3,5-di-*tert*-butylbenzene substituents, the metal atom is reduced to give Au^{II} porphyrin. If the ligand contains the electron-withdrawing NO_2 groups, reduction affords the Au^{III} complex with the porphyrin π-radical cation.

The Fe^{IV} and Mn^{IV} triarylcorrole complexes (**60** and **61**) were characterised in the study.[168]

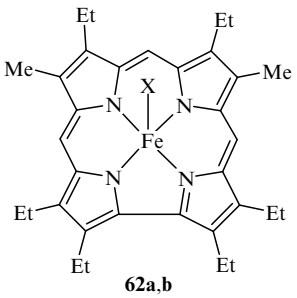


60 **61**

M = Fe, Mn;
X = 4-C_6H_4, 4-MeC_6H_4, 4-$CF_3C_6H_4$.

The first oxidation potentials of complexes **61** are higher than that of the corresponding oxo dimer **60**, which confirms the higher oxidation state of the corrole ligand in complexes **61** (the ligand is already oxidised to a radical-like state).[168] This conclusion agrees with the hypothesis proposed by Walker and co-workers [169] that the iron ion in chloro(octaalkylcorrolato)iron(IV) complexes has an intermediate spin ($S = 3/2$) and is antiferromagnetically coupled to the corrole π-radical. Calculations by the DFT method demonstrated that this coupling results from interaction between the metal d_{z^2} orbital and the b_1-symmetry π orbital of the corrole. By contrast, the corrole ligand in dimer **60** is not, apparently, a radical.

Two iron octaalkylcorrolate complexes **62a**,**b** with axial ligands were studied by ^1H NMR and Mössbauer spectroscopy. The temperature dependence of the magnetic susceptibility of these complexes was studied [170] to determine the true electronic configuration of the anionic iron corrolates, *e.g.*, to determine whether they are Fe^{IV} corrolates(3−) or Fe^{III}-corrolates(2−•) with antiferromagnetic coupling of the electrons of the iron ion to the electrons of the macrocyclic ligand. In both cases, the total spin is 1.

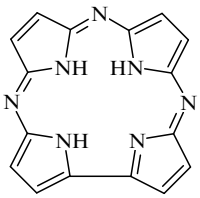


62a,**b**

X = Cl (**a**), Ph (**b**).

Magnetic susceptibility measurements and results of DFT calculations provided evidence for the non-innocent properties of the macrocyclic corrolate ligand in chlorine-containing complex **62a**. As for phenylcorrolate complex **62b**, no unambiguous conclusion has been drawn. However, it has been hypothesised that the corrolate in both complexes behaves as a non-innocent ligand, but this behaviour is much more pronounced in the chlorine-containing complex.

In contrast, calculations for the Fe^{IV} and Mn^{IV} complexes with corrolazine (**63**)



63

demonstrated [171] that this ligand is much more similar to classical ligands and stabilises a 'more pure' high-valence state of the transition metal ion.

The Cu^{II} and Fe^{III} complexes with β-octafluorocorrole ligands were synthesised and characterised in the study.[171] Study by NMR spectroscopy and DFT calculations showed that the radical character of the electron-deficient fluorine-containing corrole ligand in the LFeCl complex is much less pronounced than that in the complex with the corresponding nonfluorinated ligand. It was shown that the copper complex with octafluorocorrole can exist in a thermally accessible paramagnetic excited state, in which the ligand is present as a radical.

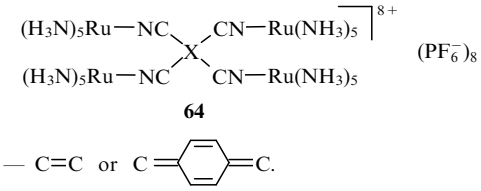
X-ray diffraction studies [172–177] of metalloporphyrins (M = Zn, Cu, Mg, Fe) revealed considerable bond length alternation in the 16-membered ring of the porphyrin ligands. The structural data, results of various spectroscopic studies [163, 169] and DFT calculations led the authors [170] to the conclusion that the real structures of these complexes are similar to those of lower-valence metal complexes with a π-radical-cationic ligand, *i.e.*, porphyrins and corroles are typical non-innocent ligands (it should be remembered that numerous valence-tautomeric electron distributions can be displayed for high-valence transition metal complexes with porphyrin and corrole ligands).

Simple rules, which allow one to predict whether the spin density is localised on the metal or the ligand in iron complexes with aromatic macrocycles (porphyrins, corroles and chlorins), were formulated [178] using the results of pulse spectroscopy (ESR, ESE, ENDOR).

VI. Tetracyanoethylene, tetracyanoquinodimethane and tetraiminoethylene complexes

The tetracyanoethylene (TCNE) and 7,7,8,8-tetracyanoquinodimethane (general notation is TCNX) molecules are (see the study [179]) 'the least innocent' organic ligands, because their π* orbitals are very low-lying. Generally, reactions of easily reducible tetracyanoethylene and 7,7,8,8-tetracyanoquinodimethane with transition metal salts produce mono-, di-, tri- or tetranuclear complexes of the $TCNX^{-\bullet}$ radical anions and doubly-charged $TCNX^{2-}$ anions, π complexes with coordination at the C=C bond or ion-pair $TCNX^{-\bullet}(ML_n^+)$ compounds without direct coordination.[180]

The tetranuclear ruthenium complexes with TCNX (**64**)



64

X — C=C or C = ⟨⟩ =C.

were characterised in the studies.[40, 181] These complexes were described as completely delocalised symmetrical π systems with the partially reduced ligand and the partially oxidised metal atoms.

These compounds were studied by ESR, NMR and IR spectroscopy and cyclic voltammetry. It is unusual that the first reduction potentials of the tetranuclear complexes are more negative than that of the free ligand (an analogous phenomenon is observed also for the iron complexes with TCNX).[40] This fact is attributable to considerable metal → ligand charge transfer in the resulting complex ($0 \leqslant \delta \leqslant 2$).

$$4\,[(L)Ru(NH_3)_5]^{2+} + TCNX \xrightarrow[-4\,L]{} [(TCNX^{\delta-})\{Ru^{II+\delta/4}(NH_3)_5\}_4]^{8+}$$

In the analogous complexes with 1,2,4,5-tetracyanobenzene and 2,3,5,6-tetracyanopyrazine, which were synthesised and described in this study,[40] the degree of metal → ligand charge transfer is much smaller.

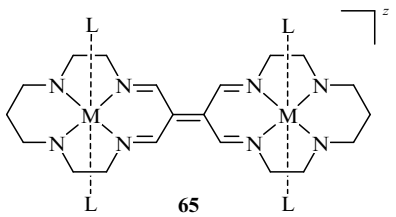
The ruthenium complexes with TCNX were characterised also in the studies.[182–185] Analogous conclusions about the metal → ligand charge transfer were drawn on the basis of the results of ESR and IR spectroscopy and electrochemical studies of discrete manganese,[40, 184–186] osmium,[187] rhenium[188] and iron[189] complexes. It was hypothesised[189] that the reaction of the Fe^{II} cyclopentadienyl complex with TCNX afforded the radical-anionic iron(III) complex.

$$[Cp(dppe)Fe^{II}]^+ + TCNX \longrightarrow [Cp(dppe)Fe^{III}(TCNX^{-\bullet})]$$

Then the ligand is presumably reduced to the doubly-charged anion.

In the present review, we restrict ourselves to the discussion of discrete tetracyanoethylene and tetracyanoquinodimethane complexes. However, a large number of analogous coordination polymers, in which the TCNX ligands serve as bridges, have also been described.[179]

The ground electronic state of related complexes **65** with four imino groups has been described earlier[190–194] as a mixed-valence form, in which one metal atom has the oxidation state of +2, whereas another metal atom is in the oxidation state of +3. However, UV-Vis spectroscopy and semiempirical quantum-chemical calculations provided evidence that such nickel complexes are more adequately described as an identical pair of Ni^{II} centres linked *via* a bridging radical-anionic ligand.[195]

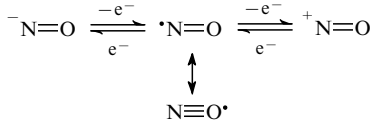


65

M = Ni, Fe, Ru; L is Hal^- or a solvent molecule.

VII. Complexes with nitrogen(II) oxide

The NO species is a typical non-innocent ligand,[196] because it can exist in three forms: diamagnetic π-acceptor cationic, paramagnetic neutral radical and diamagnetic anionic.



The $[(NC)_5M(NO)]^{3-}$ complexes (M = Fe, Ru, Os) with $NO^{\bullet}$ as ligands were synthesised and studied by ESR[197–201] and IR[202] spectroscopy, electrochemical methods[202] and DFT calculations.[201] The calculations demonstrated that the spin density is localised predominantly on the nitrosyl fragment of the molecule, and the electronic structures of these complexes are adequately described as a resonance hybrid of two structures, the contribution of the second structure being insignificant.

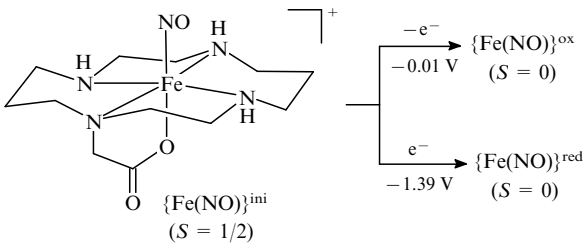
$$[(NC)_5M^{II}(NO^{\bullet})]^{3-} \longleftrightarrow [(NC)_5M^{I}(NO^{+})]^{3-}$$

The binuclear ruthenium complex $[(NC)Ru(py)_4(CN).Ru(py)_4(NO)](PF_6)_3$ was synthesised and studied by spectroscopic and electrochemical methods,[203] which revealed a considerable charge transfer from the ruthenium ion, so that the $\{Ru^{II}-NO^{\bullet}\}$ resonance structure makes a large contribution to the structure of the complex.

The five-coordinate $[Fe(OEP)(NO)]ClO_4$ complex and the six-coordinate $[Fe(OEP)(im)(NO)]ClO_4$ complex (im is imidazole, OEP is octaethylporphyrin) were synthesised and characterised by X-ray diffraction and spectrophotometry.[204] Mössbauer spectroscopy provided evidence that the oxidation state of iron in the five-coordinate complex is higher than +3. However, the IR spectroscopic data are inconsistent with such a large charge transfer to NO.

The results of X-ray diffraction study and the data from Mössbauer and ESR spectroscopy for the neutral paramagnetic binuclear iron complexes $[Fe_2(\mu_2\text{-}SR)_2(NO)_4]\cdot n\,H_2O$ (n = 1 or 2; R is 5-amino-1,2,4-triazol-3-yl, 1,2,4-triazol-2-yl, 1-methyltetrazol-5-yl, benzotriazol-2-yl[205] or benzimidazolyl[206]) indicate that the Fe^+ ion has the d^7 configuration and the NO groups are electroneutral.

The reaction of the low-spin $[Fe^{II}Cl(cyclam\text{-}ac)]$ complex (cyclam-acH is 1,4,8,11-tetraazacyclotetradecan-1-ylacetic acid) with NO in MeCN produced the octahedral $[Fe(NO)(cyclam\text{-}ac)]^+(PF_6)^-$ complex ($\{Fe(NO)\}^{ini}$; $S = 1/2$), which can be subjected to chemical one-electron oxidation to the $[Fe(NO)(cyclam\text{-}ac)]^{2+}(PF_6^-)_2$ ($\{Fe(NO)\}^{ox}$; $S = 0$) or $[Fe(NO)(cyclam\text{-}ac)]^{2+}.(Cl^-)(ClO_4^-)$ complex and also subjected to chemical or electrochemical one-electron reduction to the neutral $[Fe(NO).(cyclamac)]^0$ molecule ($\{Fe(NO)\}^{red}$; $S = 0$).[207]



The oxidation states of iron and the NO ligand can be *a priori* represented as follows (the numbers below the formulae indicate the spin states of the iron ion and NO).

{Fe(NO)}^{ox}	{Fe(NO)}^{ini}	{Fe(NO)}^{red}
$Fe^{II}NO^{+}$ 0 0	$Fe^{II}NO^{\bullet}$ 0 1/2	$Fe^{II}NO^{-}$ 0 0
$Fe^{III}NO^{\bullet}$ 1/2 1/2	$Fe^{III}NO^{-}$ 1/2 0	$Fe^{III}NO^{-\bullet}$ 1/2 1/2
$Fe^{IV}NO^{-}$ 1 1	$Fe^{III}NO^{-}$ 1/2 1	

The electronic structures of these three complexes were established by ESR, UV-Vis, Mössbauer and IR spectroscopy. The crystal and molecular structures were determined by X-ray diffraction. Calculations by the DFT method provided information on the bonding in these haeme-free iron complexes. It was concluded that the oxidised complex (ox) contains the N-coordinated NO^{+} cation, the starting complex (ini) contains the neutral $NO^{\bullet}$ radical, and the reduced complex (red) contains the NO^{-} anion. Therefore, only the NO ligand is involved in redox processes.

VIII. Conclusion

The aim of the present review is to attract attention to the results of investigations on the nature of bonding between metals and ligands in non-innocent metal complexes synthesised primarily in the last decade. There is a great diversity of structural types of non-innocent ligands, from small molecules (NO) to macrocycles. In most cases, these ligands contain conjugated π systems capable of either accepting or donating electrons. In many cases, ligands rather than the central metal atom are redox-active.

As mentioned above, non-innocence is a property not only of ligands but of complexes as a whole, because the central metal atom can have a strong effect on the electronic structure of the ligand, if there is a strong mixing of the ligand and metal orbitals. Examples are known, where a free ligand is irreversibly reduced (a radical anion is unstable), but reduction of the ligand in a complex becomes reversible (the radical-anionic ligand becomes stable). Due to charge transfer between the metal and the ligand, the valence of the metal in the complex can vary even with changes in the temperature of the sample.

Electrochemical and spectroelectrochemical methods, X-ray diffraction analysis, low-temperature ESR and ENDOR, UV-Vis and near-IR spectroscopy are most informative and are most widely used to study the nature of bonding in non-innocent complexes. After the synthesis of new complexes, for example, of neutral $[ML]^{0}$, they are usually studied by a combination of the above-mentioned methods and also by quantum-chemical calculations (primarily, the geometry and usually with the use of the DFT method). Electrochemical methods allow generation of the ions and radical ions, $[ML]^{2+}$, $[ML]^{+}$, $[ML]^{-}$ and $[ML]^{2-}$. If these species are stable, their structures are studied by appropriate spectroscopic methods. For example, the paramagnetic singly-charged anion in the nickel bis(dithiolenes) $[Ni(S_2C_2R_2)_2]^{z}$ ($z = 2-, 1-, 0$; R = H, Me, CF_3, CN, *etc.*), which are stable in three redox states,[96, 208] was studied by ESR. The delocalisation of the spin predominantly on the ligand is direct evidence for its non-innocent nature. Calculations and UV-Vis spectra provide information on the structures of diamagnetic complexes. These data demonstrated that doubly-charged anions in nickel complexes with dithiolenes can be considered as normal Ni^{II} complexes with two doubly-charged anionic 1,2-dithiolate ligands. Bonding in neutral complexes remains an open question. One description assumes the biradical structure of the ground state of complexes with unpaired electrons localised on the ligands (primarily on the α-C atoms bound to the S atoms). An alternative description is based on a delocalised structure including the resonance enedithiolate and diketone forms of the ligand. X-ray diffraction analysis allows one to determine the structural characteristics of the ligand in complexes {for example, for $[Ni(S_2C_2Me_2)_2]$ in the redox states of $2-$, $1-$ and 0} [85] and draw conclusions about their electronic structures. This gives a better insight into the electronic structures and the nature of metal–ligand bonding in non-innocent complexes.

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