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Complexes of diamagnetic cations with radical anion ligands

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The review summarizes and analyzes the currently know data on the synthesis, molecular and electronic structures and magnetic properties of bi-, tri- and tetraradical complexes containing a diamagnetic metal ion and redox-active ligands in the paramagnetic form.
The bibliography includes 193 references.

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1. Introduction

Studies of metal complexes with redox-active ligands is an actively developing field of coordination chemistry.[1–18] The most widely encountered redox-active ligands are *o*-quinones, *o*-iminobenzoquinones, α-diimines and their numerous derivatives. An interesting feature of the above ligands is the ability to exist in metal complexes in the radical form. This enables the use of compounds based on the radical form of redox-active ligands in spin electronic devices and molecular magnets. The magnetic properties of transition metal complexes with redox-active ligands in the paramagnetic state have now been studied in detail.[18–20] Compounds of this type are characterized by the presence of superexchange pathways, which provide for the strong magnetic exchange between the organic radical ligand and the paramagnetic complexing ion. Meanwhile, before this review, no attempts were made to integrate and systematize the existing data on the nature of magnetic exchange between the radical redox-active ligands in the coordination sphere of a diamagnetic complexing ion. In turn, studying multispin systems consisting of a main group ion (or a diamagnetic transition metal ion) and redox-active ligands in the paramagnetic state often reveals weak magnetic exchange between organic radicals, not camouflaged by the strong superexchange involving the magnetic orbitals of the transition metal ion.

Study of these multispin systems is of particular interest in view of the considerable research attention to possible applications of multiradical compounds in organic electronics.[21,22] Biradicals possess high chemical and electrochemical activities, a narrow HOMO–LUMO energy gap, low-energy absorption in the electronic spectrum, magnetism and EPR activity. The above properties determine the interest in organic biradicals as potential components of molecular electronics and spintronics,[23–27] lithium fuel cells,[28] organic redox flow batteries,[29–31] non-linear optics[32–34] and magnetic materials.[1,29,35–40]

There are a multitude of numerous classes of organic biradicals suitable for the above-listed applications: polycyclic aromatic hydrocarbons,[26,41–43] trimethylenemethanes,[44] bis-nitroxides,[45–47] bis-phenoxyls,[48] benzotriazinyls,[49] biradical bis(triarylamine) salts,[50] *etc*. However, the instability inherent in these compounds and the synthetic difficulties hamper further research, while the synthesis of compounds containing radical ligands in the coordination sphere of a diamagnetic metal ion is free from the above drawbacks.

The review summarizes data on the synthesis, molecular and electronic structures and magnetic properties of multispin systems containing a diamagnetic metal ion. Note that this review addresses bi- and triradical metal complexes in which several paramagnetic redox-active ligands are attached to one metal centre. The coordination and organoelement compounds in which two central ions are linked by a covalent metal–metal bond are also discussed. An extensive class of compounds in which monoradical moieties of a multispin system are connected by a bridging organic ligand[51–56] are beyond the scope of this review.

The following designations and abbreviations are used in the review:

AP — *o*-amidophenolate,
APH_2 — *o*-aminophenol,
BA — benzylideneacetone,

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BIAN — bis(imino)acenaphthene,
bipy — 2,2′-bipyridine,
Cat — catecholate,
3,5-$CatH_2$ — 3,5-di-*tert*-butylcatechol,
C.N. — coordination number,
DABCO — 1,4-diazabicyclo[2.2.0]octane,
DAD — 1,4-diazabuta-1,3-diene,
DFT — density functional theory,
dipp — 2,6-di-*iso*-propylphenyl,
disq — 1,2-diiminosemiquinone,
DME — 1,2-dimethoxyethane,
dmp — 2,6-dimethylphenyl,
dmp′ — 3,5-dimethylphenyl,
dtb — 2,5-di-*tert*-butylphenyl,
Hal-Q — 3,4,5,6-tetrahalocyclohexa-3,5-diene-1,2-dione,
HOMO — highest occupied molecular orbital,
imQ — *o*-iminobenzoquinone,
imSQ — *o*-iminobenzosemiquinone,
IP — α-iminopyridine,
J — magnetic exchange parameter,
l.s. — low spin,
LUMO — lowest unoccupied molecular orbital,
μ_B — Bohr magneton,
μ_{eff} — effective magnetic moment,
MePhen — 2,9-dimethyl-1,10-phenanthroline,
NMI — 1-methylimidazole,
NN-3,6-Q — 5,8-di-*tert*-butyl-2,3-dihydro-1,4-ethanoquinoxaline-6,7-dione,
NQ — 1,2-naphthoquinone,
ONO — 3,5-di-*tert*-butyl-1,2-quinone-1-(2-hydroxy-3,5-di-*tert*-butylphenyl)imine,
pda — *o*-phenylenediamine,
Phen — 1,10-phenanthroline,
Phenox — 2,6,4,6,8-tetra(*tert*-butyl)phenoxazin-1-one radical anion,
PhenQ — 1,2-phenanthrenequinone,
Py — pyridine,
Q — *o*-quinone,
3,5-Q — 3,5-di-*tert*-butyl-*o*-benzoquinone,
3,6-Q — 3,6-di-*tert*-butyl-*o*-benzoquinone,
r — distance between the radical centres,
Solv — solvent,
SOMO — singly occupied molecular orbital,
SQ — *o*-semiquinone,
(3,6-SQ)Na — sodium 3,6-di-*tert*-butyl-*o*-benzosemiquinonate,
S_t — ground spin state of the complex,
τ — geometric parameter for evaluation of the coordination geometry,
TEMPO — (2,2,6,6-tetramethylpiperidin-1-yl)oxyl,
TMEDA — *N*,*N*,*N*′,*N*′-tetramethylethylenediamine,
zJ' — intermolecular magnetic exchange parameter.

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Translation: Z.P.Svitanko

2. Metal complexes with *o*-quinone ligands

Most of the currently known metal complexes of bi- and triradical *o*-semiquinones containing a diamagnetic central ion are based on the *o*-quinone ligands depicted in Fig. 1.

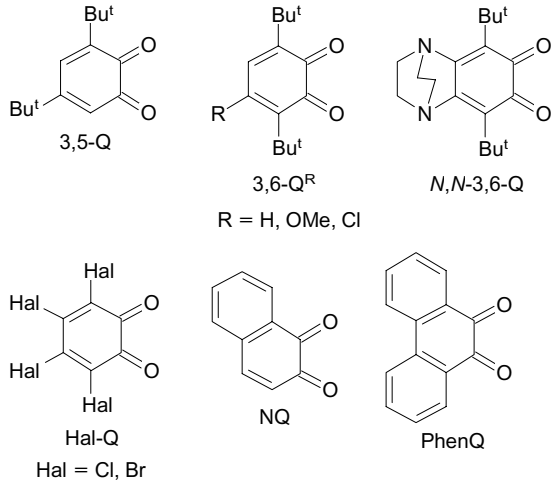
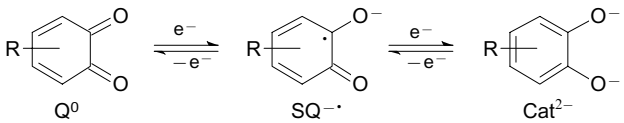


Figure 1. Structures of *o*-quinone ligands.

Quinone in the neutral form (Q^0) is capable of reversible stepwise addition of two electrons to give singly reduced radical anion (*o*-semiquinonate, $SQ^{-\bullet}$) and doubly reduced dianion (catecholate, Cat^{2-}) species (Scheme 1).

Scheme 1



Depending on the number of radical anion SQ ligands coordinated to the metal centre and on the geometry of the resulting metal complex, the whole diversity of known multispin systems can be conventionally divided into several groups: biradical complexes with coordination numbers (C.N.) of 4, 5 and 6 and triradical complexes with C.N. = 6. In addition, there are a few examples of metal *o*-semiquinone derivatives with higher C.N.

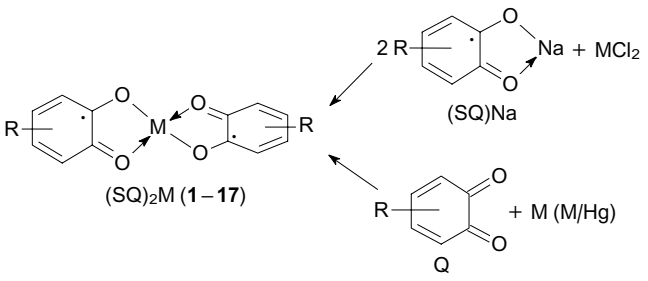
2.1 *o*-Semiquinone complexes with C.N. = 4

It is evident that the simplest system containing a diamagnetic central ion and *o*-quinone ligands is a divalent metal ion coordinated by two ligands in the singly reduced state: $(SQ)_2M^{II}$. Currently, bis-*o*-semiquinonates are known for

divalent metals of Group 2 (Mg, Ca, Sr, Ba), Group 12 (Zn, Cd, Hg) and Group 14 (Pb) of the Periodic Table.

Bis-*o*-semiquinone complexes $(SQ)_2M^{II}$ are formed either upon exchange reaction between sodium *o*-semiquinonate [(SQ)Na] (or *o*-semiquinonate of another alkali metal) and metal chloride MCl_2 (M is Group 2 or 12 metal) or upon direct oxidation of the metal or the metal amalgam with *o*-quinone Q (Scheme 2).

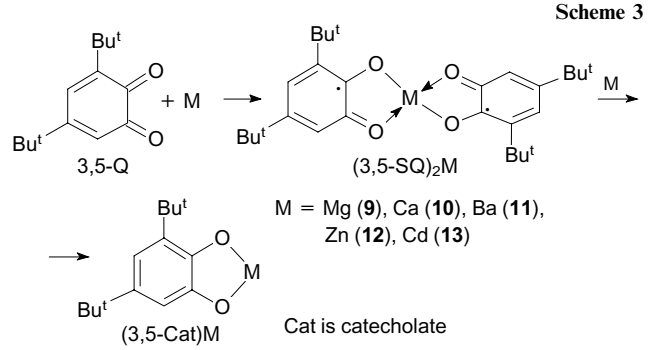
Scheme 2



However, despite the seeming simplicity of the reactions shown in Scheme 2, the synthesis and identification of four-coordinate $(SQ)_2M$ derivatives are faced with some difficulties. Malysheva *et al.*[57] assumed a tetrahedral structure for the biradical products $(3,6\text{-}SQ)_2M$ (**1** – **7**), formed upon the reactions between Group 2 metals and the 3,6-Q ligand in solvating solvents, relying on EPR parameters (D, E) of reaction mixtures recorded in a frozen solvent matrix. However, the observed nearly zero value of the parameter E is typical of not only tetrahedral, but also octahedral metal complexes; furthermore, the latter are most likely to be formed in a solvating solvent such as THF. This assumption is also supported by the fact that the reaction of zinc or cadmium amalgam with 3,6-Q in toluene instead of THF gives insoluble products exhibiting a single broad EPR line, which attests to oligomerization of the arising four-coordinate complexes $(3,6\text{-}SQ)_2M$ in non-coordinating solvents.[58] Oligomeric bis-*o*-semiquinone complexes $(3,6\text{-}SQ)_2M$ [M = Zn (**5**), Cd (**6**)] were also obtained upon the mechanochemical treatment of a solid mixture of *o*-quinone and a metal.[59]

Similarly, metals react with 3,5-Q in solvating solvents even at room temperature; however, with excess of the metal, complexes $(3,5\text{-}SQ)_2M$ (**9** – **13**) are further reduced to catecholate derivatives (3,5-Cat)M (Scheme 3).[60 – 62] Meanwhile, the reaction of Ca or Ba with 3,5-Q in hydrocarbon solvents stops after the formation of bis-*o*-benzosemiquinonates **10** and **11**, even when the metals are taken in excess.[62]

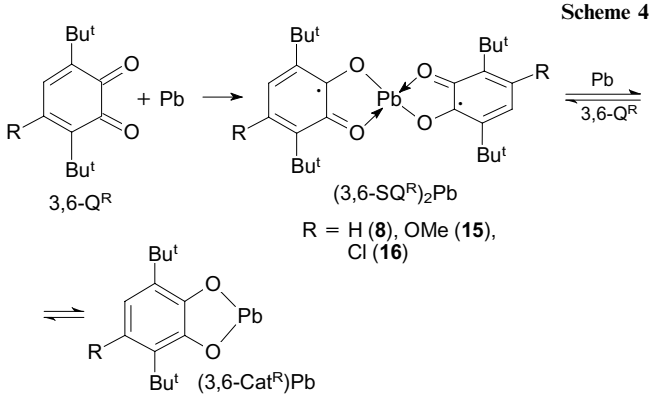
Scheme 3



Like in the case of the 3,6-Q, refluxing of its analogue 3,5-Q with metal powders in toluene leads to oligomerization of the complexes $(3,5\text{-}SQ)_2M$ (**9**, **11** – **13**) *via* the formation of bridging bonds involving the *o*-benzoquinone oxygen atoms.[63] Beryllium and mercury do not react with 3,5-Q even on prolonged intense heating, irrespective of the nature of the solvent.[62, 63]

Metallic lead also reduces *o*-benzoquinones $3,6\text{-}Q^R$ (R = H, OMe, Cl) to catecholate derivatives *via* the intermediate oxidation products $(3,6\text{-}SQ^R)_2Pb$ (**8**, **15** – **16**), which can be intentionally synthesized by the reaction of metal catecholate $(3,6\text{-}Cat^R)Pb^{II}$ with an equimolar amount of the appropriate *o*-benzoquinone (Scheme 4).[64]

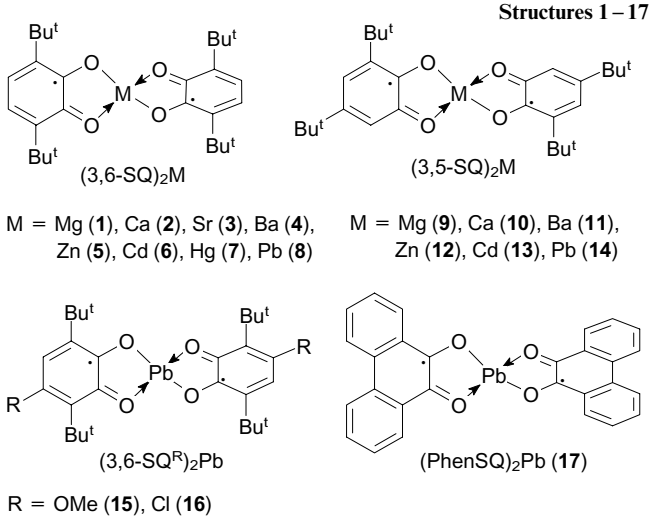
Scheme 4



When metallic lead reacts with 3,5-Q, the equilibrium shown in Scheme 4 shifts to the right: unstable lead(II) bis-*o*-benzosemiquinonate $(3,5\text{-}SQ)_2Pb$ (**14**) is symmetrized to give oligomeric lead(II) catecholate and the starting quinone.[65, 66] Meanwhile, the bis-*o*-semiquinone complex $(PhenSQ)_2Pb$ (**17**) is the final oxidation product of metallic lead with 1,2-phenanthrenequinone (PhenQ) in hexane irrespective of the reactant ratio (1 : 2, 1 : 3, 1 : 4).[66]

Thus, at present there are no data on structurally characterized four-coordinate bis-*o*-semiquinone complexes of Group 2, 12 and 14 metals. Most of $(SQ)_2M$ derivatives of these metals either contain coordinated solvent molecules in the metal coordination sphere or, in the absence of a solvent, are insoluble oligomerization products formed *via* bridging bonds involving *o*-benzoquinone oxygen atoms.

Structures 1 – 17



2.2. *o*-Semiquinone complexes with C.N. = 5

Bis-*o*-semiquinone derivatives with C.N. = 5 are known for metals of Groups 12 (Zn, Cd) and 13 (Ga, In) of the Periodic Table.

Piskunov *et al.*[67] isolated and comprehensively characterized crystalline five-coordinate zinc(II) complexes (3,6-SQ)$_2$Zn(Solv) (**18**–**21**), which were earlier found to form in donor solvents by EPR spectroscopy.[57,58] Easy replacement of a diethyl ether molecule in the metal coordination sphere of complex **18** accounts for the choice of this compound as the starting reactant for the synthesis of a broad range of zinc bis-*o*-semiquinonates **22**–**29** with neutral ligands L^{I}–L^{VIII} (the coordinating atom of the neutral ligand L is typed in bold).[68–70]

The molecular structures of mononuclear (**20**–**24**, **26**) and binuclear (**28**, **29**) zinc complexes were established by X-ray diffraction analysis. The geometry of five-coordinate complexes and the degree of distortion are often analyzed using the geometric parameter τ, which is zero for an ideal tetragonal pyramid and is unity for an ideal trigonal bipyramid.[71] In the considered zinc complexes, the ideal tetragonal pyramidal geometry [τ = 0 (**24** and **26**), 0.03 (**21**), 0.04 (**29**)] is considerably distorted upon metal coordination of a pyridine molecule and molecules of sterically crowded ligands L^{I}, L^{II} and L^{VII} [τ = 0.22 (**20**), 0.26 (**22**), 0.3 (**23**), 0.18 (**28**)].

Magnetic susceptibility measurements for the crystalline samples of **20** and **22**–**29** attest to the presence of antiferromagnetic exchange between unpaired electrons of the *o*-semiquinone ligands. For all of these complexes, high-temperature effective magnetic moments (μ_{eff}) are close to spin-only values: 2.45 μ_B for biradical mononuclear complexes **20**, **22**–**24**, **26** and **27**; 3.00 μ_B for triradical complex **25** containing nitronyl nitroxide L^{IV}; 3.46 μ_B for binuclear complexes **28** and **29** containing four radical anion ligands (where μ_B is the Bohr magneton). As the samples are cooled, μ_{eff} decreases: at 5 K, it is close to zero for the bi- and tetraradical complexes and to 1.73 μ_B for the triradical complex, which attests to the singlet and doublet ground states of the complexes, respectively. The dependence $\mu_{eff}(T)$ for complexes **20**, **22**–**24**, **26** and **27** is adequately described in terms of the exchange-coupled dimer model ($H = -2JS_1S_2$). The same model describes the dependences $\mu_{eff}(T)$ for binuclear complexes **28** and **29**, because two (3,6-SQ)$_2$Zn moieties are fairly remote from each other and there is no any noticeable magnetic exchange between them. In triradical complex **25**, the magnetic exchange between SQ and the nitronyl nitroxide moiety is weak because of a considerable distance between these radical centres. The magnetic exchange parameters J are −69 (**20**), −107 (**22**), −37 (**23**), −36 (**24**), −55 (**25**), −45 (**26**), −121 (**27**), −59 (**28**) and −95 cm^{-1} (**29**). For compounds that were characterized by X-ray diffraction, Piskunov *et al.*[69,70] proposed a magnetic structure correlation between the strength of magnetic exchange and the distance between the radical centres r: a decrease in the distance r results in an increase in the exchange parameter J (Fig. 2). This fact is indicative of the predominance of direct magnetic exchange between the singly occupied orbitals of the SQ ligands in the considered complexes.

One-step mechanochemical synthesis (liquid-assisted grinding, LAG) is a convenient waste-free method for the preparation of zinc bis-*o*-semiquinone derivatives.[72] Depending on the nature of the *N*-donor ligand introduced

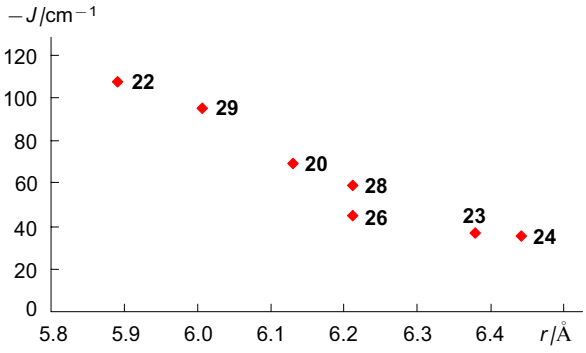
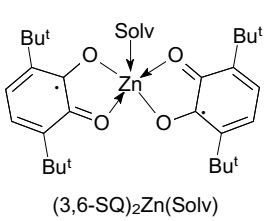


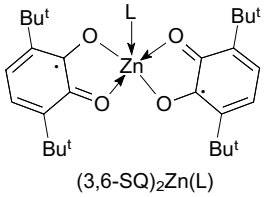
Figure 2. Exchange parameter J as a function of distance between the radical centres in five-coordinate zinc bis-*o*-semiquinonates (**20**, **22**–**24**, **26**, **28**, **29**). Adapted from Ref. 70.

Structures 18–29



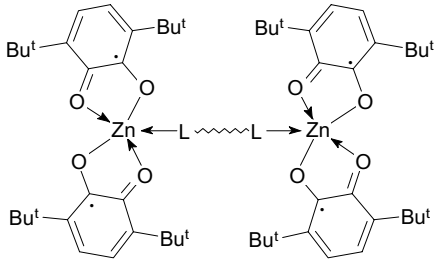
(3,6-SQ)$_2$Zn(Solv)

Solv = Et_2O (**18**), THF (**19**), Py (**20**), H_2O (**21**)



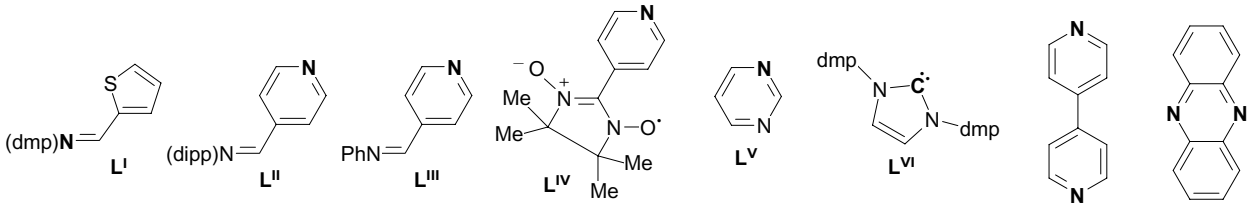
(3,6-SQ)$_2$Zn(L)

L = L^{I} (**22**), L^{II} (**23**), L^{III} (**24**), L^{IV} (**25**), L^{V} (**26**), L^{VI} (**27**)



[(3,6-SQ)$_2$Zn]$_2$(L〰L)

L〰L = L^{VII} (**28**), L^{VIII} (**29**)



dmp is 2,6-dimethylphenyl, dipp is diisopropylphenyl, Py is pyridine

into the reaction mixture containing 3,5-Q, ZnO and 3,5-CatH_2, the formation of mono- (**30**), bi- (**31**) and trinuclear (**32**) complexes is possible.

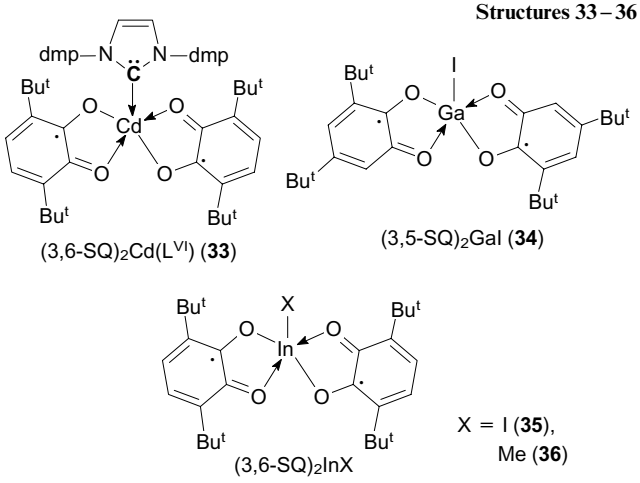
As opposed to 3,6-Q-based derivatives, the metal in complexes **30** – **32** exists in a distorted trigonal bipyramidal environment ($\tau = 0.82 - 0.93$).

Compound **33** containing a metal-coordinated *N*-heterocyclic carbene L^{VI} is the only five-coordinate cadmium bis-*o*-semiquinone complex.[73] In the case of complex **33**, like in analogous zinc derivative **27**, the ground state is a singlet with a thermally accessible triplet state. On going from Zn to Cd, which has a greater covalent radius, the magnetic exchange between two SQ ligands is weakened. In complex **33**, $J = -66$ cm^{-1}.

Biradical *o*-semiquinone derivatives of Group 13 metals are less typical, and only a few examples of five-coordinate gallium and indium bis-*o*-semiquinonates (**34** – **36**) are currently known. In the EPR spectra of the GaI_3 + 3,5-Q reaction mixture, signals of both mono- [(3,5-SQ)GaI_2] and biradical [(3,5-SQ)$_2$GaI (**34**)] compounds were observed;[74] however, only the monoradical complex was isolated in a pure form. Analogous indium derivatives (3,6-SQ)$_2$InI (**35**) and (3,6-SQ)$_2$InMe (**36**) are formed upon the oxidation of metal catecholate complexes; however, only **35** was isolated and characterized, whereas **36** decomposed in solution.[75]

To summarize this Section, one can conclude that the formation of five-coordinate bis-*o*-semiquinone derivatives is typical of Group 12 metals, first of all of Zn, whereas Group 13 metals very rarely form such derivatives. Zinc and cadmium compounds based on 3,6-Q have an ideal or distorted tetragonal pyramidal coordination geometry, respectively, which accounts for the existence of an efficient pathway for direct antiferromagnetic exchange between the unpaired electrons of the SQ ligands. A decrease in the distance between the radical centres leads to a considerable increase in the exchange parameter *J*, which reaches a value of -107 cm^{-1}. Going from 3,6-Q to 3,5-Q is accompanied by a change in the metal coordination geometry from a tetragonal pyramid to a trigonal bipyramid.

Structures 33 – 36



(3,6-SQ)$_2$Cd(L^{VI}) (**33**)

(3,5-SQ)$_2$GaI (**34**)

(3,6-SQ)$_2$InX

X = I (**35**), Me (**36**)

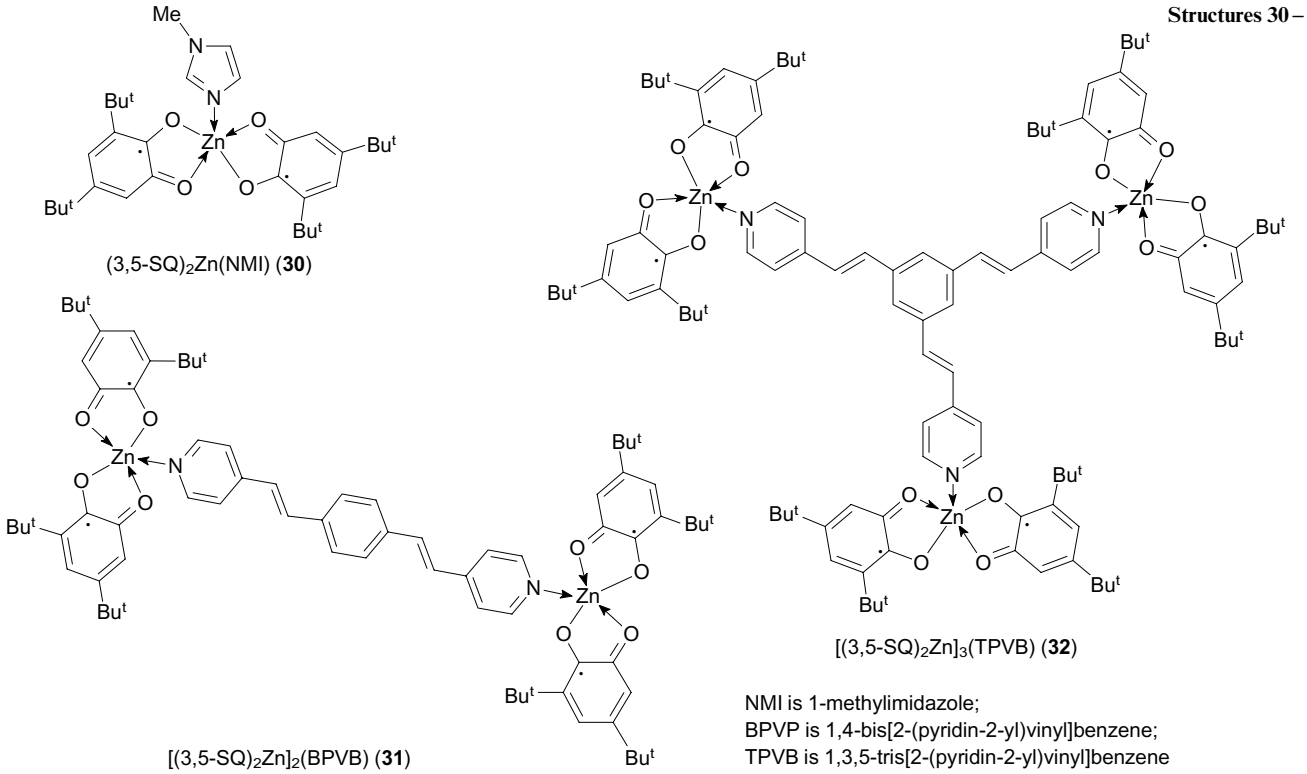
2.3. *o*-Semiquinone complexes with C.N. = 6

2.3.1. Biradical complexes of Group 2 and 12 metals

The six-coordinate bis-*o*-semiquinone complexes of divalent magnesium and zinc in which the SQ moieties are located in *trans*-positions relative to each other are formed upon metal coordination to two monodentate neutral ligands (complexes **37** – **41**)[70, 76, 77] and upon the formation of coordination polymers $[(SQ)_2ZnL]_n$ (complexes **42** – **45**).[67, 70, 72]

The derivatives (3,6-SQ)$_2$Mg(Solv)$_2$ (**37** – **39**) are prepared by reduction of 3,6-Q with magnesium amalgam in Et_2O, THF and Py, respectively. However, only in Et_2O, complex **37** is the final reaction product, whereas in stronger donor solvents, compounds **38** and **39** are further reduced to catecholate derivatives.[76] Complexes **40** – **44** are formed

Structures 30 – 32



(3,5-SQ)$_2$Zn(NMI) (**30**)

[(3,5-SQ)$_2$Zn]$_2$(BPVB) (**31**)

[(3,5-SQ)$_2$Zn]$_3$(TPVB) (**32**)

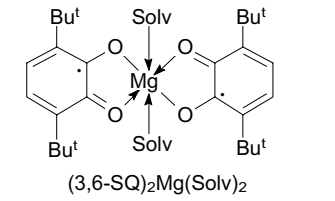
NMI is 1-methylimidazole;
BPVP is 1,4-bis[2-(pyridin-2-yl)vinyl]benzene;
TPVB is 1,3,5-tris[2-(pyridin-2-yl)vinyl]benzene

when the Et_2O molecules in bis-*o*-semiquinonates **18** and **37** are replaced by *N*-donor ligands.[67, 70, 77] When the SQ ligands in the octahedral complexes exist in the *trans*-configuration, the radical centres are most remote from each other. The *r* values found from the X-ray diffraction data for complexes **39**–**41**, **43**–**44** are in the range of 6.49–6.66 Å. In the crystal packing of molecules **39** and **40**, there are two sorts of intermolecular contacts: π–π stacking between the aromatic moieties of the *N*-donor ligands and short contacts between the SQ moieties of two neighbouring molecules.[77] In complex **39**, the short intermolecular SQ–SQ contacts (3.984 Å) form a ferromagnetic exchange pathway between the unpaired electrons of the SQ ligands: the dependence $\mu_{eff}(T)$ is adequately described in terms of the four-spin exchange cluster model $[H = -2J_1(S_1S_2 + S_3S_4) - 2J_2S_2S_3]$, where $J_1 = 0.93$ cm^{-1}, $J_2 = 0.11$ cm^{-1}. In compound **40**, the SQ–SQ contacts are relatively long (5.949 Å); hence, it is appropriate to consider only the intramolecular exchange interaction ($H = -2JS_1S_2$): the value $J = -2.42$ cm^{-1} indicates the presence of weak antiferromagnetic exchange between the spins of the SQ ligands.

Since the dependence $J = f(r)$ holds for five-coordinate zinc complexes, like for compounds **41**, **43** and **44**, Piskunov *et al.*[70] assumed that the pathway for direct (antiferromagnetic) exchange between the SQ ligands predominates in the complexes ($H = -2JS_1S_2$): $J = -20.3$ and -12.3 cm^{-1} for compounds **41** and **43**, respectively. Depending on the conditions, compound **44** crystallizes as two polymorphs (**44a**,**b**), which differ in the relative arrangement of polymer chains. In both polymorphs, the intermolecular exchange parameter between the chains (zJ') is comparable with the *J* value: for **44a**, $J = -17.5$ cm^{-1}, $zJ' = -24.1$ cm^{-1} and for **44b**, $J = -32.5$ cm^{-1}, $zJ' = -10$ cm^{-1}. Much lower *J* values of the considered complexes compared with five-coordinate zinc bis-*o*-semiquinonates are due to the change in the coordination geometry of the complexes, namely, the tetragonal pyramidal structure of compounds with C.N. = 5 facilitates more efficient overlap of the magnetic orbitals localized on the *o*-semiquinone ligands.

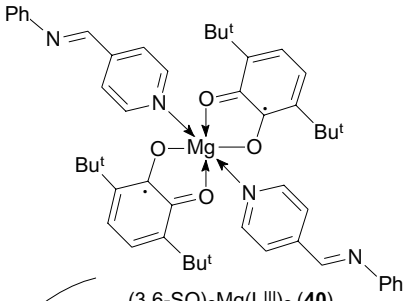
The coordination of two monodentate *N*-donor ligands (Py, NMI) to the structural group $(3,5\text{-SQ})_2M$ yields six-coordinate derivatives **46**–**49** with *cis*-configuration of the SQ ligands.[63, 72]

Structures 37–45

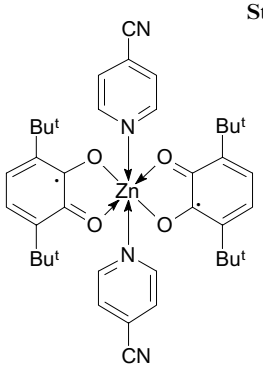


$(3,6\text{-SQ})_2Mg(Solv)_2$

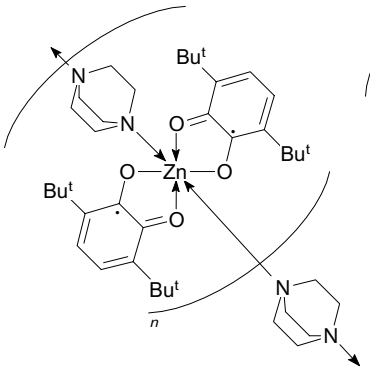
Solv = Et_2O (**37**), THF (**38**), Py (**39**)



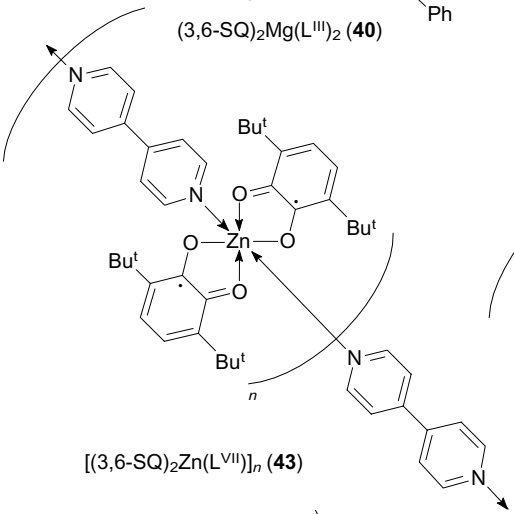
$(3,6\text{-SQ})_2Mg(L^{III})_2$ (**40**)



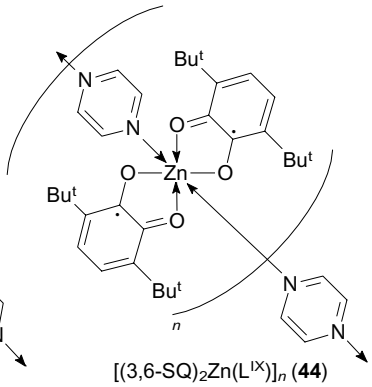
$(3,6\text{-SQ})_2Zn(PyCN\text{-}4)_2$ (**41**)



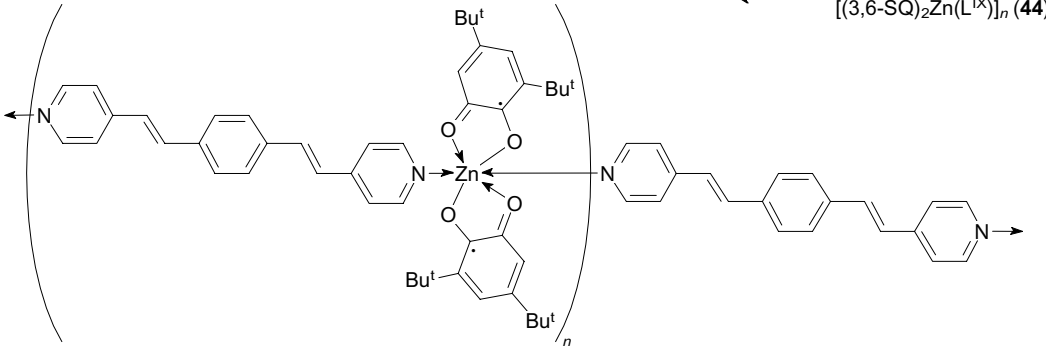
$[(3,6\text{-SQ})_2Zn(DABCO)]_n$ (**42**)



$[(3,6\text{-SQ})_2Zn(L^{VII})]_n$ (**43**)



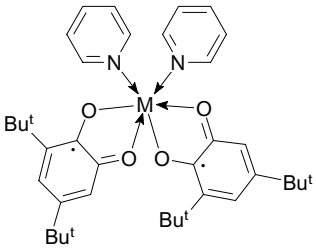
$[(3,6\text{-SQ})_2Zn(L^{IX})]_n$ (**44**)



DABCO is 1,4-diazabicyclo[2.2.0]octane

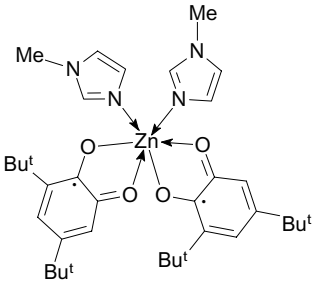
$[(3,5\text{-SQ})_2Zn(BPVB)]_n$ (**45**)

Structures 46 – 49



$(3,5\text{-SQ})_2M(Py)_2$

M = Mg (**46**), Zn (**47**), Cd (**48**)



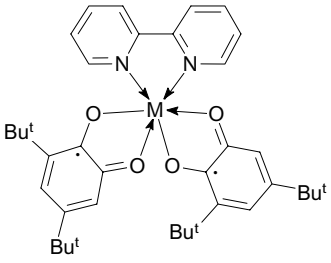
$(3,5\text{-SQ})_2Zn(NMI)_2$ (**49**)

In the case of $(SQ)_2M^{II}$ coordination to bidentate neutral ligands such as 2,2′-bipyridine (bipy), 1,2-dimethoxyethane (DME), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), 1,10-phenanthroline (Phen), 2,9-dimethyl-1,10-phenanthroline (MePhen) and 3,6-Q, only the *cis*-configuration of the SQ ligands in the resulting complexes (**50** – **67**) is possible.[63, 67, 72, 73, 76 – 79]

Magnesium complex **57** is formed upon the reduction of 3,6-Q with magnesium amalgam in DME. This reaction conducted in toluene affords bis-*o*-semiquinone complex **59**, which contains a coordinated 3,6-Q molecule.[76] Magnesium complexes **61**, **64** and **66** are formed upon the addition of *N*-donor ligands to a solution of $(3,6\text{-SQ})_2Mg(Et_2O)_2$ (**37**).[77] As compared with derivatives **39** and **40**, in which the SQ ligands have a *trans*-configuration, complexes **57**, **61**, **64** and **66** have a highly distorted octahedral geometry. The distance between the radical centres *r* in the *cis*-complexes is markedly shorter than that in **39** or **40** ($r \approx 6.6$ Å) and varies in the range of 5.25 – 5.36 Å. Meanwhile, the crystal packing of complexes contains both types of intermolecular contacts considered above for **39** and **40**: the distance between the SQ moieties of neighbouring molecules is approximately 4 Å, which gives rise to an intermolecular antiferromagnetic exchange pathway (J_2, J_3) (unlike **39** in which a ferromagnetic exchange pathway occurs), which is comparable in strength with the intramolecular SQ – SQ ferromagnetic exchange (J_1). The values of the exchange parameters J_1, J_2 and J_3 determined using the four-spin exchange cluster model [$H = -2J_1(S_1S_2 + S_3S_4) - 2J_2S_2S_3 - 2J_3(S_1S_3 + S_2S_4)$] are 2.79, −6.06 and −0.02 cm^{-1} (**57**); 4.93, −13.7 and −0.032 cm^{-1} (**61**); 3.96, −0.85 and −0.50 cm^{-1} (**64**); and 3.57, −4.44 and −0.50 cm^{-1} (**66**).

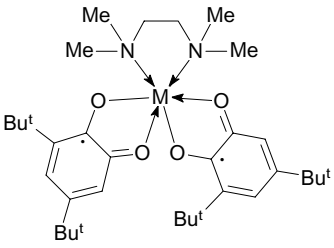
The molecular structure, crystal packing and nature of magnetic exchange are retained on going from magnesium derivatives **61**, **64** and **66** to analogous zinc derivatives **62**, **65** and **67**.[79] Since neither the *r* value [5.072 Å (**65**), 5.295 Å (**67**)] nor the distance between the SQ moieties of neighbouring molecules [3.869 Å (**65**), 4.005 Å **67**)] change significantly on going from Mg to Zn, the sign and the strength of intra- and intermolecular SQ – SQ exchange in both series of complexes differ little: apart from the weak intramolecular ferromagnetic exchange (J_1), there is intermolecular antiferromagnetic SQ – SQ exchange (J_2) with a comparable strength. The J_1 and J_2 values determined

Structures 50 – 67



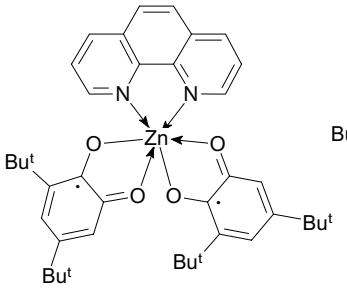
$(3,5\text{-SQ})_2M(bipy)$

M = Mg (**50**), Zn (**51**), Cd (**52**)

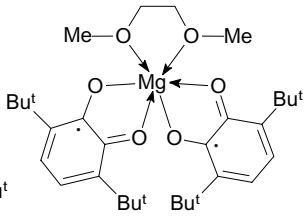


$(3,5\text{-SQ})_2M(TMEDA)$

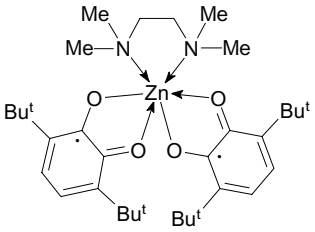
M = Mg (**53**), Zn (**54**), Cd (**55**)



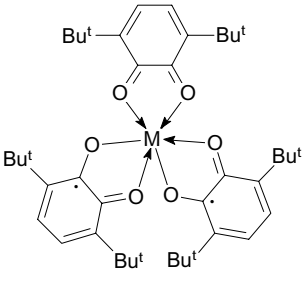
$(3,5\text{-SQ})_2Zn(Phen)$ (**56**)



$(3,6\text{-SQ})_2Mg(DME)$ (**57**)

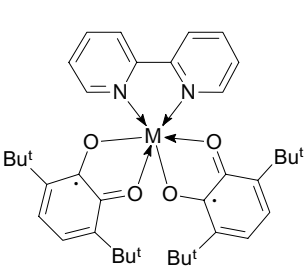


$(3,6\text{-SQ})_2Zn(TMEDA)$ (**58**)



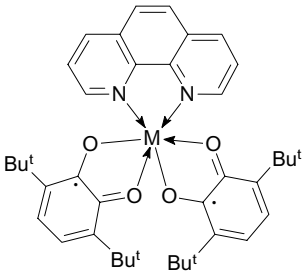
$(3,6\text{-SQ})_2M(3,6\text{-Q})$

M = Mg (**59**), Cd (**60**)



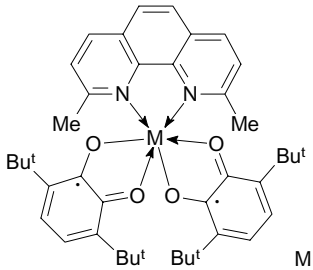
$(3,6\text{-SQ})_2M(bipy)$

M = Mg (**61**), Zn (**62**), Cd (**63**)



$(3,6\text{-SQ})_2M(Phen)$

M = Mg (**64**), Zn (**65**)



$(3,6\text{-SQ})_2M(MePhen)$

M = Mg (**66**), Zn (**67**)

bipy is 2,2′-bipyridine, TMEDA is *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, DME is 1,2-dimethoxyethane

within the framework of the tetramer model ($H = -2J_1S_1S_2 - 2J_2S_2S_3 - 2J_1S_3S_4$) are 8.6 and −14.7 (**62**), 8.4 and −9.7 (**65**), and 4.4 and −4.1 cm^{-1} (**67**).

At the same time, the considerable distortion of the octahedral geometry in the complex (3,6-SQ)$_2$Zn(TMEDA) (**58**) induces a change in the nature and strength of the intramolecular magnetic exchange ($J = -33.7$ cm^{-1}, $H = -2JS_1S_2$). Lange *et al.*[78] assumed that the exchange interaction between the organic radicals is propagated by filled Zn^{II} 3*d* orbitals, and particularly the presence of the superexchange pathway in **58** is responsible for the fairly strong antiferromagnetic SQ−SQ exchange.

Weak antiferromagnetic SQ−SQ exchange ($J = -4$ cm^{-1}) takes place in the distorted-octahedral cadmium complex (3,6-SQ)$_2$Cd(3,6-Q) (**60**), which contains a coordinated neutral *o*-quinone.[73] A much stronger antiferromagnetic SQ−SQ exchange was found in (3,6-SQ)$_2$Cd(bipy) (**63**) ($J = -46$ cm^{-1}).[67] The fact that the exchange parameter *J* is higher by an order of magnitude for **63** than for **60** is attributable to different geometry of the complexes: in molecule **63**, the metal atom exists in a distorted trigonal prismatic environment, which is favourable for more efficient overlap of the magnetic orbitals of the SQ ligands.

A theoretical study of bis-*o*-semiquinone complexes of Group 2 and 12 metals [80] is fully confirmed by obtained experimental data. The ground state multiplicity of the considered systems depends on the relative efficiency of two exchange pathways: direct exchange between the magnetic orbitals of *o*-semiquinone ligands and the superexchange pathway through vacant *p* orbitals of the central metal ion. In the case of the tetrahedral configuration, both exchange pathways are ferromagnetic, which gives rise to a triplet ground state for (SQ)$_2$M^{II}. Conversely, in the case of the octahedral *trans*-configuration, both of these pathways are antiferromagnetic, which corresponds to the singlet ground state. In the case of the octahedral *cis*-configuration of the SQ ligands, the direct exchange is antiferromagnetic because of the effective overlap of the magnetic orbitals of the SQ ligands, whereas the superexchange interaction is ferromagnetic due to the overlap of the ligand orbitals with various mutually orthogonal *p* orbitals of the metal ion. For the *cis*-configuration, the crucial role belongs to superexchange, which results in a triplet ground state. The considerable distortion of the *cis*-configuration in (3,6-SQ)$_2$Zn(TMEDA) (**58**) (the angle between the SQ ligands, which is 90° for the ideal *cis*-configuration, decreases to 55°) increases the efficiency of the direct overlap between the SQ orbitals and, as a consequence, $S_t = 0$.

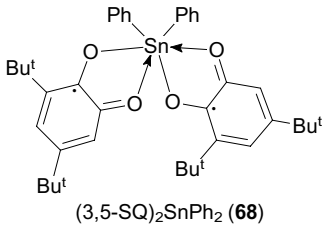
2.3.2. Biradical complexes of Group 14 metals

Most of the currently known *o*-quinone complexes of Group 14 metals are diamagnetic catecholate derivatives. Compounds containing *o*-semiquinone moieties are much more rarely encountered. The number of reliably characterized Si^{IV}, Ge^{IV}, Sn^{IV} and Pb^{IV} bis-*o*-semiquinonates isolated in a pure form is particular; in particular, compounds **68**–**78** have been reported.

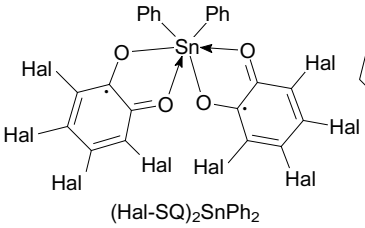
Complexes (SQ)$_2$SnPh$_2$ (**68**–**71**), which are formed upon the reactions of organotin compounds (Ph_6Sn_2, Ph_4Sn, Ph_3SnCl, Ph_2SnCl_2) with various substituted *o*-quinones, were characterized only by EPR spectroscopy in solution.[81] Batsanov *et al.*[82] were able to prepare the crystals of **71** in an amount sufficient only for their X-ray diffraction study. Conversely, analogous compounds (3,6-SQ)$_2$SnX$_2$ (**72**–**74**) based on 3,6-Q, which are formed upon oxidation of catecholate derivatives or $SnHal_2$ with two equivalents of 3,6-Q, are the major products of the indicated reactions and have been characterized in detail not only in solution, but also in the crystalline state.[83] According to the X-ray diffraction data, *o*-semiquinone ligands in distorted octahedral complexes **71**, **73** and **74** have a *cis*-configuration.

The reaction of Cl-Q and SiI_4 (3 : 1) in non-donor solvents affords biradical silicon complex (Cl-SQ)$_2$Si(Cl-Cat) (**75**).[84] The slightly distorted octahedral geometry of complex **75** implies the orthogonal arrange-

Structures 68–79

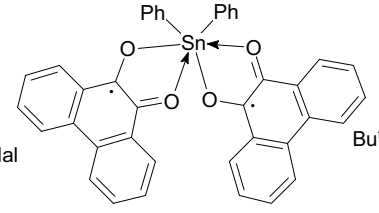


(3,5-SQ)$_2$SnPh$_2$ (**68**)

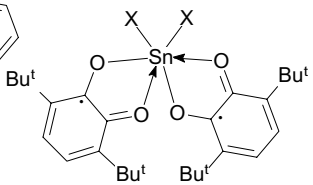


(Hal-SQ)$_2$SnPh$_2$

Hal = Cl (**69**), Br (**70**)

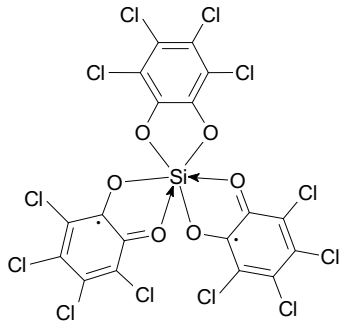


(PhenSQ)$_2$SnPh$_2$ (**71**)

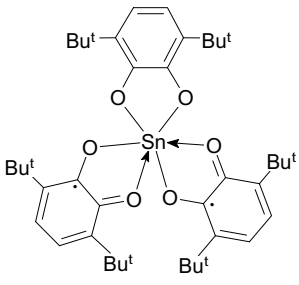


(3,6-SQ)$_2$SnX$_2$

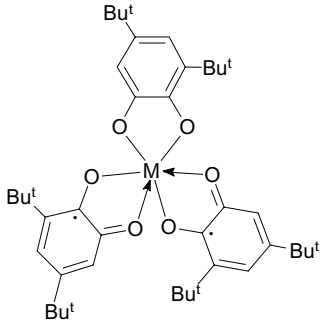
X = Cl (**72**), Br (**73**), Ph (**74**)



(Cl-SQ)$_2$Si(Cl-Cat) (**75**)

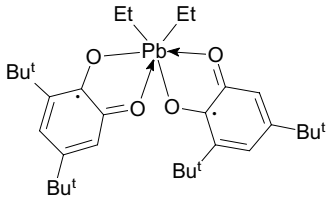


(3,6-SQ)$_2$Sn(3,6-Cat) (**76**)



(3,5-SQ)$_2$M(3,5-Cat)

M = Sn (**77**), Ge (**78**)



(3,5-SQ)$_2$PbEt$_2$ (**79**)

ment of the SQ magnetic orbitals and silicon(IV) 3*p* orbitals, which accounts for the triplet ground state $S_t = 1$ for **75**. The calculated exchange parameter ($J_{calc} = 317$ cm^{-1}) attests to strong ferromagnetic SQ–SQ exchange; however, experimental determination of this parameter is hampered by the presence of π–π stacking between the SQ ligands of neighbouring molecules in the crystal packing of **75**, resulting in strong intermolecular antiferromagnetic exchange between them.

A signal corresponding to mixed-ligand Sn^{IV} derivatives $(SQ)_2Sn(Cat)$ (**76**, **77**) was detected by EPR both upon oxidation of tin amalgam with 3,6-Q [85] and upon oxidation of the metal with 3,5-Q.[86] Lado *et al.*[87] isolated and characterized complex **76**, which can be obtained by oxidation of $(3,6\text{-Cat})Sn^{II}$ with two equivalents of 3,6-Q and by the reaction of tin with 3,6-Q (1 : 3). According to calculations,[88] the triplet ground state of biradical tin(IV) complexes $(SQ)_2Sn(Cat)$ is due to the predominant contribution of the ferromagnetic superexchange *via* the vacant *p* orbitals of the metal ion.

The only biradical germanium(IV) *o*-semiquinone complex that was characterized in the crystalline state is mixed-ligand compound **78**, formed upon the reaction of germanium metal with 3,5-Q taken in 1 : 3 molar ratio.[89]

Like germanium(IV), lead(IV) is not prone to form biradical compounds. To date, the only known bis-*o*-semiquinone complex of lead(IV) is $(3,5\text{-SQ})_2PbEt_2$ (**79**), which can be obtained both by oxidation of Et_4Pb with quinone in saturated hydrocarbon solvents and by the reaction of $(3,5\text{-Cat})PbEt_2$ with an equivalent of 3,5-Q.[90]

Thus, Group 14 metals do not tend to form bis-*o*-semiquinone derivatives, because the SQ radical anions in the coordination spheres of Si^{IV}, Ge^{IV}, Sn^{IV} and Pb^{IV} are prone to undergo further reduction to the dianion state (Cat^{2-}). Most of the few known bis-*o*-semiquinone derivatives of Group 14 metals are Sn^{IV} complexes the coordination geometry of which implies a triplet ground spin state, because of the predominance of superexchange mechanism of the interaction between the SQ ligands.

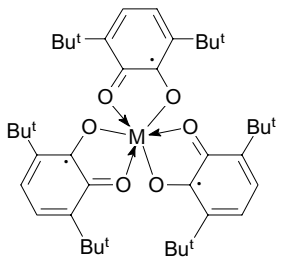
2.3.3. Bi- and triradical complexes of trivalent metals

The formation of triradical tris-*o*-semiquinone derivatives is most typical of Group 13 metals. Apart from main group metals (Al, Ga, In), the low-spin cobalt(III) ion ($3d^6$, $S_{Co} = 0$) can also serve as a complexing agent in $(SQ)_3M$.

The synthetic routes to $(SQ)_3M$ include both direct reduction of the corresponding *o*-quinone (3,6-Q, NN-3,6-Q, PhenQ, 3,5-Q) with excess metal (or its amalgam) [74,91–96] and the exchange between Na or Tl *o*-semiquinonate and $MHal_3$ (M = Al, Ga, In) taken in 3 : 1 ratio.[78,96–98] The complex $(3,6\text{-SQ})_3Co$ (**83**) was obtained by the reaction of $Co_2(CO)_8$ with 3,6-Q.[78]

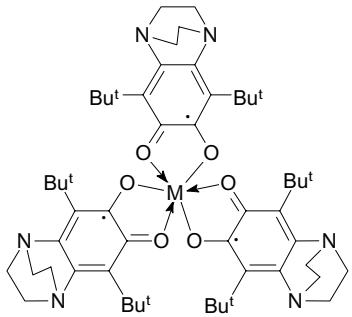
According to the X-ray diffraction data, tris-*o*-semiquinone complexes of Al (**84**)[96] and Ga (**81**,[78] **85**,[96] **88**[97,98]) have a distorted octahedral coordination geometry, whereas the metal coordination geometry in analogous In derivatives (**82**,[94] **86**[96]) is a trigonal prism. These details of the molecular structure of $(SQ)_3M$ (M = Al, Ga, In) are responsible for basically different magnetic properties of complexes within this series. In the octahedral Al and Ga derivatives, the ground spin state is a quadruplet ($S_t = 3/2$) because of the prevailing superexchange (ferromagnetic) interaction between the unpaired electrons of the SQ ligands *via* the orthogonal vacant *p* orbitals of the metal ion.[88,92] The exchange parameters *J* determined using the exchange-coupled trimer model [$H = -2J(S_1S_2 + S_1S_3 + S_2S_3)$] amount to 6.2 cm^{-1} (**80**),[78] 8.6 cm^{-1} (**81**)[78] and 7.8 cm^{-1} (17.63 cm^{-1}) (**88**).[92,98] The short intermolecular C–H contacts in the crystalline samples of $(NN\text{-}3,6\text{-SQ})_3M$ [M = Al (**84**), Ga (**85**)] give rise to an intermolecular exchange pathway (zJ'); however, its contribution to the magnetic behaviour of complexes is insignificant:

Structures 80 – 90



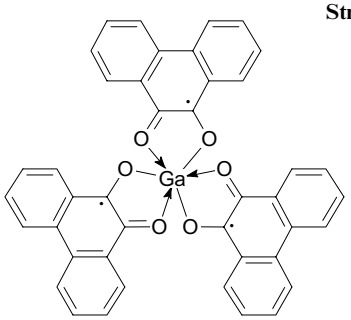
$(3,6\text{-SQ})_3M$

M = Al (**80**), Ga (**81**), In (**82**), Co (**83**)

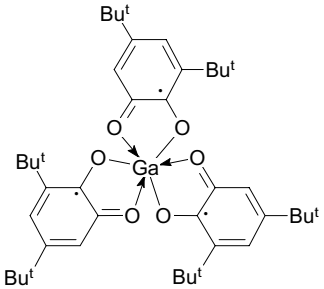


$(NN\text{-}3,6\text{-SQ})_3M$

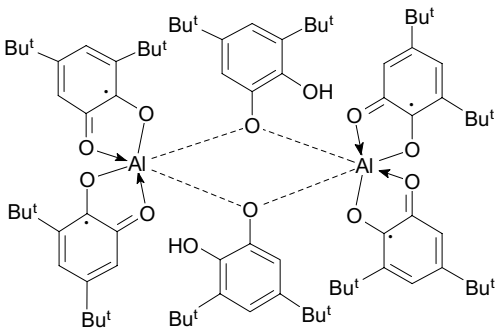
M = Al (**84**), Ga (**85**), In (**86**)



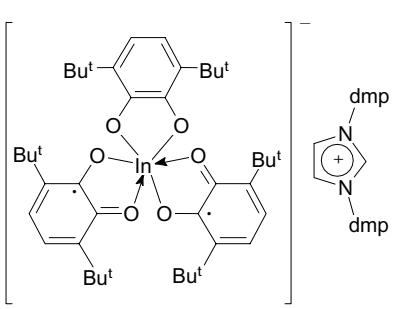
$(PhenSQ)_3Ga$ (**87**)



$(3,5\text{-SQ})_3Ga$ (**88**)



$[Al_2(\mu\text{-}3,5\text{-CatH})_2(3,5\text{-SQ})_4]$ (**89**)



$[(3,6\text{-SQ})_2In(3,6\text{-Cat})]^-[LH^{VI}]^+$ (**90**)

$J = 18.5\ cm^{-1}$, $zJ' = -2.2\ cm^{-1}$ (**84**); $J = 10.6\ cm^{-1}$, $zJ' = -0.4\ cm^{-1}$ (**85**).[96]

Unlike octahedral Al and Ga derivatives, in the trigonal prismatic derivatives of $(SQ)_3In$ (**82**, **86**), the dihedral angle between the planes of the SQ ligands is close to 60°, which ensures efficient overlap between the magnetic orbitals localized on the SQ ligands. Thus, in these complexes, direct (antiferromagnetic) exchange predominates ($J = -28.1\ cm^{-1}$, $zJ' = -6\ cm^{-1}$) and the ground state is a doublet ($S_t = 1/2$).[94,96]

Meanwhile, although the cobalt complex $(3,6\text{-SQ})_3Co$ (**83**) is isostructural to the analogous gallium complex $(3,6\text{-SQ})_3Ga$ (**81**), there is fairly strong antiferromagnetic exchange interaction ($J = -39\ cm^{-1}$) between the unpaired electrons of the SQ ligands in **83**.[78] A fundamental difference between the magnetic behaviours of compounds **81** and **83** is due to the presence of the filled 3*d* level in the Co^{III} ion; the 3*d* orbitals with appropriate symmetry efficiently overlap with the π orbitals of the SQ ligands.

Biradical complexes of Group 13 metals with C.N. = 6 are very rarely encountered. The dimeric aluminium complex (**89**) comprising two $(3,5\text{-SQ})_2Al$ moieties connected *via* the oxygen atoms of two bridging dioxolene ligands was isolated[98] as a product of the exchange reaction between (3,5-SQ)Na and $AlCl_3$. Both metal atoms in dimer **89** have a distorted octahedral geometry; there is ferromagnetic exchange interaction ($J = 18\ cm^{-1}$) between the spins of the orthogonal SQ ligands in the $(3,5\text{-SQ})_2Al$ moieties, while the magnetic exchange between the SQ radicals linked to different coordination centres of the dimer is very weak.

Ionic indium complex **90** containing differently charged *o*-quinone ligands (two of which are in the singly reduced state and one is in the doubly reduced state) is formed when $(3,6\text{-SQ})_3In$ (**82**) reacts with *N*-heterocyclic carbene, which acts in this reaction as the reducing agent.[68] In **90**, the indium atom has a typical trigonal prismatic coordination geometry.

To summarize the above, one can conclude that triradical complexes $(SQ)_3M$ are preferably formed in the *o*-quinone–trivalent metal systems. The direct antiferromagnetic exchange pathway predominates in the case of trigonal prismatic coordination geometry of the complexes, while the nature of superexchange in octahedral derivatives depends on the nature of the metal ion orbitals: ferromagnetic exchange occurs *via* the vacant *p* orbitals of Al^{III} and Ga^{III}, whereas the filled Co^{III} 3*d* orbitals give rise to the antiferromagnetic exchange interaction pathway.

2.4. *o*-Semiquinone complexes with C.N. > 6

The currently known multispin *o*-semiquinone complexes containing diamagnetic complexing ions with C.N. exceeding six were prepared using Ca^{II}, La^{III} ($3d^06s^0$) and Ce^{IV} ($4f^05d^06s^0$).

The mononuclear bis-*o*-semiquinone complex $(3,6\text{-SQ})_2Ca(THF)_3$ (**91**) is formed upon the oxidation of polynuclear calcium catecholate with 3,6-Q.[99] The Ca^{II} coordination environment of **91** is a pentagonal bipyramid (C.N. = 7), the equatorial plane of which is formed by two SQ ligands and the oxygen atom of one of the three coordinated THF molecules, whereas the other two molecules occupy apical positions.

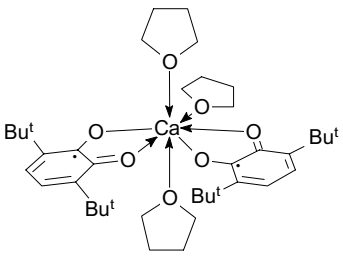
Complexes **92**–**94** were prepared by the exchange reaction between (3,6-SQ)Na and the corresponding lanthanide nitrate.[100] The Ce^{IV} ion in **92** is coordinated in the bidentate fashion by four SQ ligands (C.N. = 8). In bimetallic complex **93**, the La^{III} coordination environment (C.N. = 8) is a distorted square antiprism formed by oxygen atoms of four SQ ligands, two of which are bridging between the La and Na atoms. The presence of the THF molecule in the metal coordination sphere of **94**, which contains three SQ ligands and a bidentate 3,6-Q molecule, gives rise to a monocapped square antiprism as the La coordination geometry (C.N. = 9).

The spins of the SQ ligands in complexes **92** and **94** are involved in strong antiferromagnetic exchange interaction, resulting in the singlet $S_t = 0$ (in **92**) or doublet $S_t = 1/2$ (in **94**) ground state. For compound **92**, the dependence $\mu_{eff}(T)$ was analyzed within the framework of the four-spin exchange cluster model $[H = -2J_1(S_1S_2 + S_2S_3 + S_3S_4 + S_1S_4) - 2J_2(S_1S_3 + S_2S_4)]$; the optimal values of the exchange parameters are $J_1 = -152\ cm^{-1}$ and $J_2 = 0.2\ cm^{-1}$. The dependence $\mu_{eff}(T)$ for complex **94** is adequately described by the three-spin exchange cluster model ($H = -2J_{12}S_1S_2 - 2J_{23}S_2S_3$); the exchange parameters J_{12} and J_{23} are -100 and $-9\ cm^{-1}$, respectively.

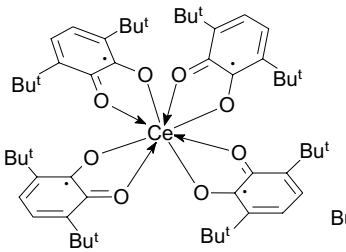
3. Metal complexes with bidentate *N*,*N*-chelating redox-active ligands

The bidentate ligands containing the N=C–C=N backbone are widely used as redox-active ligands in the coordination chemistry and catalysis, as they can also undergo one- and two-electron transfer to give the radical anion and dianion forms, respectively (Scheme 5).[8,17]

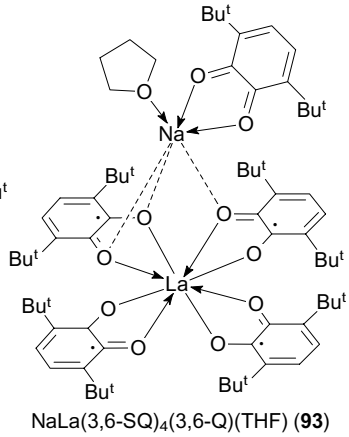
Structures 91–94



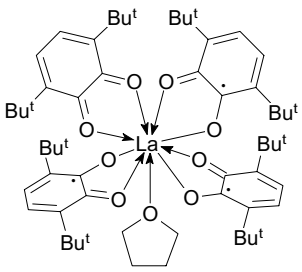
$(3,6\text{-SQ})_2Ca(THF)_3$ (**91**)



$(3,6\text{-SQ})_4Ce$ (**92**)

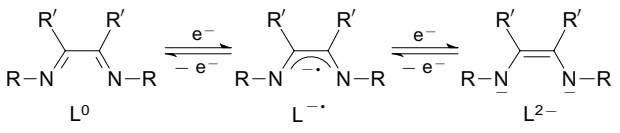


$NaLa(3,6\text{-SQ})_4(3,6\text{-Q})(THF)$ (**93**)



$La(3,6\text{-SQ})_3(3,6\text{-Q})(THF)$ (**94**)

Scheme 5



R = Alk, Ar; R′ = H, Alk, Ar, fused 1,2-arylenes

This Section covers the data on bi- and triradical complexes in which the coordination sphere of a diamagnetic ion includes *o*-phenylenediamine (pda), 2,2′-bipyridine (bipy), 1,4-diazabutadiene (DAD), bis(imino)acenaphthene (BIAN) or α-iminopyridine (IP) ligands in the radical anion form.

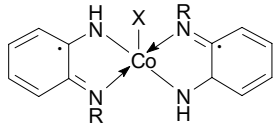
3.1. Complexes based on pda ligands

The coordination geometry of *o*-phenylenediamine type ligands is similar to that of *o*-quinones; however, as opposed to the latter, steric control is possible in the former by means of functionalization of nitrogen atoms; therefore, these ligands can serve for the preparation of monomeric low-coordinate metal complexes.

Using unsubstituted and *N*-phenyl-substituted *o*-phenylenediamines, a series of five-coordinate cobalt(III) complexes (d^6, $S_{Co} = 0$) $(disq^R)_2CoX$ (R = H, Ph; X = Hal, SCN) (**95**–**98**) have been prepared.

The complexes $(disq^R)_2CoX$ (**95**–**98**) are obtained by the oxidation of $(disq^H)_2Co^{II}$ with air or iodine, with halide anions being present in the reaction mixture (**95**–**97**),[101,102] or by the reaction of the corresponding *o*-phenylenediamine with cobalt(II) salts (2 : 1) in the presence of a base (**95**, **98**).[103,104] The coordination geometry of the metal in **95** and **98** is a tetragonal pyramid.[103,104] Complexes **95**–**98** are diamagnetic and, at room temperature, they exhibit well-resolved NMR spectra, which is indicative of a strong antiferromagnetic exchange interaction between two 1,2-diiminosemiquinone (disq) radical anion ligands, resulting in the singlet ground state for the complexes.

Structures 95 – 98



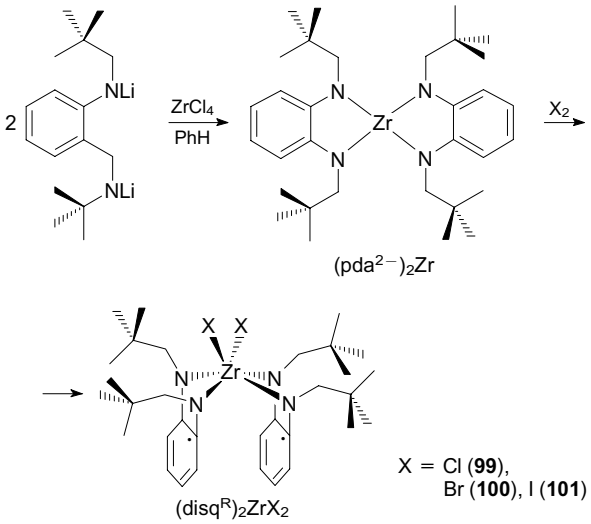
95–**98**

R = H: $(disq^H)_2CoX$
X = Cl (**95**), I (**96**), SCN (**97**);
R = Ph: $(disq^{Ph})_2CoI$ (**98**)
X = I

A series of compounds $(disq^R)_2ZrX_2$ [R = neopentyl, X = Cl (**99**), Br (**100**), I (**101**)], containing a diamagnetic Zr^{IV} ion ($4d^0 5s^0$) and two disq radical anions, was prepared by the reaction of the zirconium bis-*o*-phenylenediamide complex $(pda^{2-})_2Zr$ with halogens and halogen-containing oxidants ($PhICl_2$, Br_2, I_2) (Scheme 6).[105]

According to the X-ray diffraction data, the Zr^{IV} ion in complexes **99**–**101** has a trigonal prismatic coordination geometry, with the disq ligands being arranged in such a way that the benzene groups are virtually parallel to each other (the angles between the ring planes are 12.8°, 13.3° and 15.2° for **99**–**101**, respectively). The centroid – centroid distances between the benzene rings are approximately 3.4 Å, which is favourable for the intramolecular π – π stacking in the molecules of **99**–**101**. These features of molecular structure stabilize the singlet ground state for

Scheme 6



complexes **99**–**101**: on temperature rise to 350 K, μ_{eff} increases only to 1.6 μ_B, which is markedly lower than the value of 2.45 μ_B, calculated theoretically for a system consisting of two non-interacting unpaired electrons located in different centres. Density functional theory calculations point to the presence of binding interaction between the SOMO of two disq ligands, which gives rise to a unique HOMO, whereas the antibonding linear combination forms a unique LUMO. This configuration of orbitals delocalized over both disq ligands results in the closed-shell singlet ground state. Thus, because of molecular structure details, the ground state of **99**–**101** is not biradical, as the singly occupied molecular orbitals (SOMO) of the two disq ligands directly overlap.

3.2. Complexes based on bipy ligands

2,2′-Bipyridine and its derivatives are the most widely used bidentate nitrogen donor ligands in the coordination chemistry.[106] Quite a number of transition and main group metal complexes containing redox-active bipy ligands in various oxidation states have been prepared back by the mid-20th century.[107] Meanwhile, there are only a few known complexes containing a diamagnetic central ion and two or more bipy ligands in the radical anion form. Moreover, since most of compounds **102**–**112** were synthesized and characterized in the 1960–1970s, no X-ray diffraction data are available for them, which complicates deriving structure – magnetic property relationships.

The biradical beryllium complex (**102**) can be prepared both by the exchange reaction between $BeCl_2$ and $(bipy^-)Li$ (1 : 2) and by the reaction of the beryllium complex $Cl_2Be(bipy^0)$, containing a neutral bipy ligand, with $(bipy^{2-})Li_2$ (1 : 1).[108] According to the results of magnetic susceptibility measurements, compound **102** consists of a Be^{II} ion and two bipy ligands as radical anions. The singlet ground state ($S_t = 0$) of complex **102** is implemented as a result of antiferromagnetic exchange interaction between the $bipy^-$ ligands ($J = -8$ cm^{-1}).[109,110]

The reaction of iodine-activated magnesium powder with $bipy^0$ in THF affords complex **103** containing in the coordination sphere a solvent molecule as well as two $bipy^-$ ligands. Refluxing **103** with excess $bipy^0$ in benzene results in the formation of compound **104** in which magnesium is coordinated by bipy ligands in the radical anion and neutral

forms.[111] According to the data of magnetochemistry, in $(bipy^{-})_2Mg(THF)$ (**103**) [like in $(bipy^{-})_2Be$ (**102**)], the radical centres of the $bipy^{-}$ ligand are antiferromagnetically coupled ($J = -5.2$ cm^{-1}), but the exchange parameter is lower than that in **102**, which was attributed[112] to different Mg–N and Be–N bond ionicities and to increasing distance between the radical centres due to the greater covalent radius of Mg^{II}.

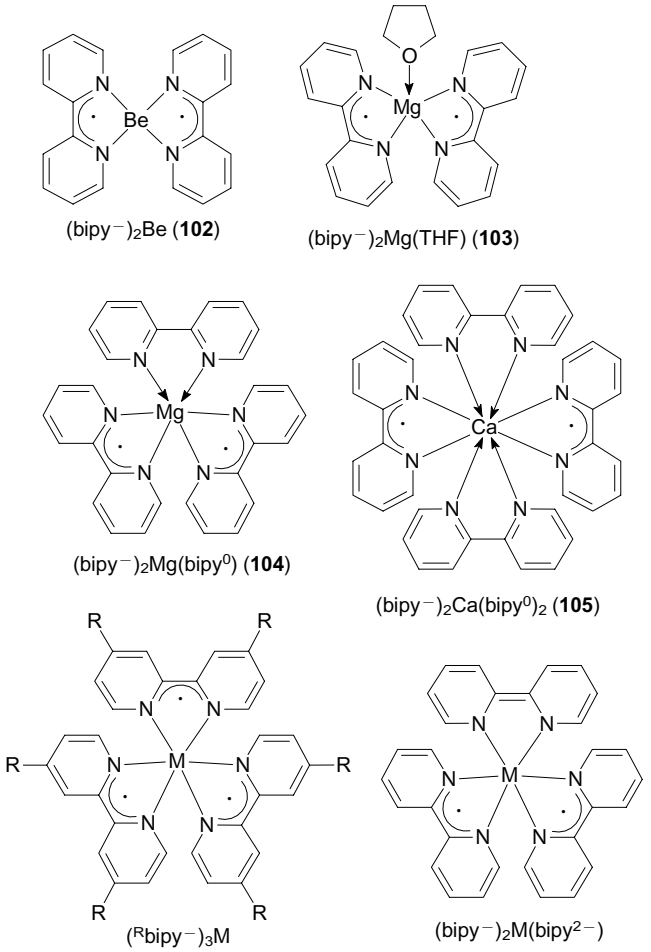
Calcium complex $(bipy^{-})_2Ca(bipy^{0})_2$ (**105**) contains two neutral and two organic radical anion ligands. In complex **105** (C.N. = 8), like in **102** (C.N. = 4), the singlet ground state is due to the antiferromagnetic exchange interaction between the $bipy^{-}$ ligands.[109]

The homoleptic aluminium tris-bipyridine complex $(bipy^{-})_3Al$ (**106**) was prepared by the reaction of $bipy^{0}$ with $LiAlH_4$ (3 : 1) and by the exchange reaction between $(bipy^{-})Li$ and $AlCl_3$ (3 : 1).[113] The magnetic susceptibility measurements for **106** attest to antiferromagnetic exchange between the $bipy^{-}$ ligands.[109,114] The doublet ground state ($S_t = 1/2$) in **106** is implemented due to the presence of an antiferromagnetic superexchange pathway ($J = -79$ cm^{-1}) between the spins of two of the three $bipy^{-}$ ligands *via* the vacant Al^{III} 3*d* orbitals.[114] A similar electronic structure is inherent in the tris-bipyridine compounds of scandium $(bipy^{-})_3Sc$ (**107**)[109] and yttrium $(bipy^{-})_3Y$ (**108**).[115] A higher contribution of the Sc^{III} 3*d* orbitals to the metal–nitrogen bond results in a higher exchange parameter for **107** ($J = -139$ cm^{-1}) compared to aluminium analogue **106**. A theoretical study of $(bipy)_3M$ (M = Al, Sc, Y) also attests to the presence of antiferromagnetic superexchange between two $bipy^{-}$ ligands with participation of vacant t_{2g} orbitals of the metal ($J_{calc} = -51$, -159, -108 cm^{-1} for **106**–**108**, respectively), while the remaining unpaired electron is located in the ligand-centred SOMO π* orbital.[116,117]

Aluminium complexes $(^{R}bipy^{-})_3Al$ [R = Me (**109**), Bu^t (**110**)] are formed upon disproportionation of $AlBr\cdot(Et_3N)_n$ in the presence of the desired substituted $^{R}bipy$ ligands.[118] According to the X-ray diffraction data, the aluminium atom in **109** and **110** has a slightly distorted octahedral environment. In addition, the arrangement of molecules in the crystal lattice of **109** gives rise to π–π stacking between the $^{Me}bipy$ ligands of neighbouring molecules. Like complex **106**, analogues **109** and **110** have a doublet ground state ($S_t = 1/2$) and a thermally accessible quadruplet state ($S_t = 3/2$) ($J_{calc} = -35$ and -40 cm^{-1} for **109** and **110**, respectively). Apart from strong antiferromagnetic exchange interaction, complex **109** also experiences weak 3D magnetic interactions at 19 K. Crystalline **109** and **110** exist in a quadruplet excited state at room temperature; however, in solution, both complexes exist in a doublet spin state at the same temperature. This may be due to either stabilization of the ground state or destabilization of the excited state by solvation (or both factors).

Tris-bipyridine complexes $(bipy^{-})_2M(bipy^{2-})$ [M = Zr (**111**), Hf (**112**)] are formed upon the reaction of bipy with appropriate metal tetrachlorides (3 : 1) in the presence of sodium amalgam.[119] According to DFT calculations, **111** and **112** contain a diamagnetic M^{IV} metal ion. The electronic structure of the compounds is described most adequately by the formula $[(bipy^{-})_2M^{IV}(bipy^{2-})]^0$, while the singlet ground state is due to the strong antiferromagnetic coupling between the unpaired electrons of two $bipy^{-}$ ligands [$J_{calc} = -1012$ (**111**) and -940 cm^{-1} (**112**)].[117] However, the energy difference between the resonance

Structures 102 – 112



$(bipy^{-})_2Be$ (**102**)

$(bipy^{-})_2Mg(THF)$ (**103**)

$(bipy^{-})_2Mg(bipy^{0})$ (**104**)

$(bipy^{-})_2Ca(bipy^{0})_2$ (**105**)

$(^{R}bipy^{-})_3M$

R = H; M = Al (**106**), Sc (**107**), Y (**108**)
M = Al; R = Me (**109**), Bu^t (**110**)

$(bipy^{-})_2M(bipy^{2-})$

M = Zr (**111**), Hf (**112**)

forms $(bipy^{-})_2M^{IV}(bipy^{2-})$ and $(bipy^{2-})_2M^{IV}(bipy^{0})$ containing no radical ligands is very small, namely, 0.3 (**111**) and 0.5 kcal mol^{-1} (**112**).

In all of the considered cases, the magnetic exchange between the $bipy^{-}$ radical anion ligands is antiferromagnetic, irrespective of the coordination environment of the central ion. Out of compounds **102**–**112**, tris-bipyridine derivatives of Group 3 and 13 metals $(bipy^{-})_3M$ (M = Al, Sc, Y) have now been studied in most detail. In these compounds, the antiferromagnetic superexchange pathway is formed with participation of the vacant *d* orbitals, unlike the $(SQ)_3Al$ derivatives in which the magnetic exchange between the SQ ligands is ferromagnetic and occurs *via* the vacant *p* orbitals of the metal.

3.3. Complexes based on DAD ligands

The weak shielding of the SQ oxygen atoms results in oligo- and polymerization of $(SQ)_2M$ type compounds of the considered metals, which hampers the possibility of preparing biradical derivatives with C.N. = 4. The presence of substituents at the DAD nitrogen atoms is favourable for stabilization of four-coordinate $(DAD^{-})_2M^{II}$ derivatives (where M is Group 2 or 12 metal).

The complex $(p\text{-Tol-DAD}^{Ph-})_2Be$ (**113**) was prepared by the reaction of $BeCl_2$ with the appropriate diazabutadiene (1 : 2) in the presence of two equivalents of sodium in

toluene.[120] The beryllium atom in **113** has a distorted tetrahedral geometry. Analysis of the bond lengths in the ligands is indicative of charge delocalization over the N–C–C–N moieties of DAD^-. Both crystalline **113** and its solutions in non-polar solvents exhibit an intense EPR signal, but no half-field signal characteristic of triplet species is present.

The derivatives (Bu^t-$DAD^-)_2M$ [M = Mg (**114**), Ca (**115**), Zn (**116**), Sr (**117**)] are obtained by the reduction of (Bu^t-DAD^0) with metal amalgam [121] and by the exchange reaction between MCl_2 and (Bu^t-DAD^-)Li (**114**, **116**).[122] Complex **114** can also be prepared *via* the reaction of (Bu^t-DAD^0), $MgCl_2$ and Mg (2 : 1 : 1).[123] The EPR spectra of the series of complexes **114**–**117** recorded in a frozen solvent matrix are typical of randomly oriented triplet species with trigonal or higher symmetry and indicate orthogonal positions of the two DAD^- ligands,[121] which was later confirmed by X-ray diffraction analysis for compounds **114** and **117**.[122]

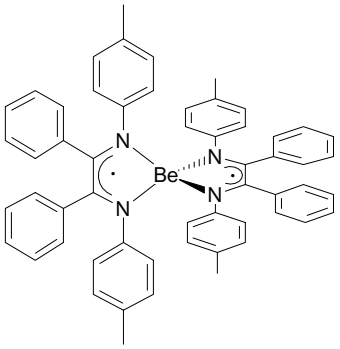
The reaction of DAD^0 with $ZnCl_2$ leads to coordination of the neutral ligand to the metal atom to give $(DAD^0)ZnCl_2$, which is subsequently reduced by alkali metals[124] or zinc[125] to give biradical complexes ($DAD^-)_2Zn$ (**118**, **119**). Complex **119** can also be prepared by the direct reaction of an excess of granulated zinc with DAD and I_2 (2 : 2 : 1) in THF.[125] Bulky substituents at the nitrogen atom induce a considerable distortion of the tetrahedral geometry of **118** and **119**: the dihedral angles between the planes of the DAD^- ligands are 53° and 57°, respectively.

Unlike *o*-quinone derivatives, $(DAD^-)_2M$ do not tend to increase the metal C.N. by coordinating solvating solvents, *N*-donor ligands or DAD^0. This is due to the presence of steric hindrance brought about by bulky substituents at the DAD^- nitrogen atoms. Nevertheless, in the products of reactions between *N*-aryl-substituted diazabutadienes and Mg in DME (compounds **120**–**122**), the magnesium atom has a distorted octahedral rather than tetrahedral environment (the angle between the planes of the DAD^- ligands is 74°), because of coordination of the metal to a DME molecule.[126]

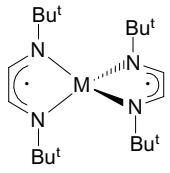
A series of studies[127–130] reports the synthesis of binuclear biradical diazabutadiene complexes **123**–**127** containing the metal–metal bond; however, in solution, these compounds dissociate to monoradical fragments.

Zinc complex **123** was obtained by the reaction of $ZnCl_2$ with the complex Na_2(dipp-DAD^{Me2-}) generated *in situ*.[130] The zinc atoms have a distorted planar trigonal environ-

Structures 113–127

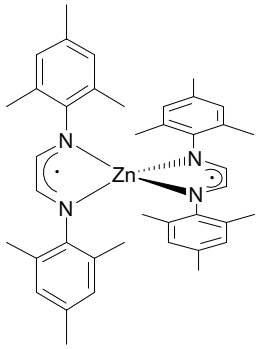


(p-Tol-DAD^{Ph-})$_2$Be (**113**)

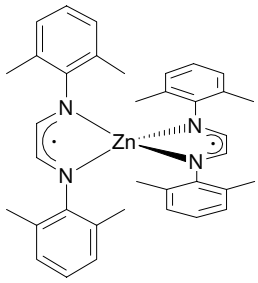


(Bu^t-DAD^-)$_2$M

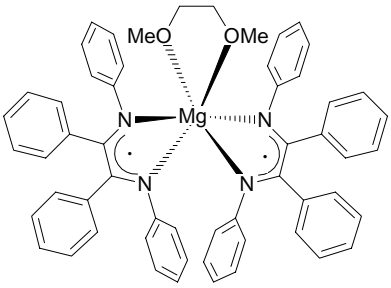
M = Mg (**114**), Ca (**115**), Zn (**116**), Sr (**117**)



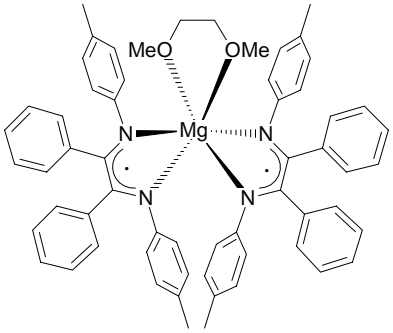
(Mes-DAD^-)$_2$Zn (**118**)



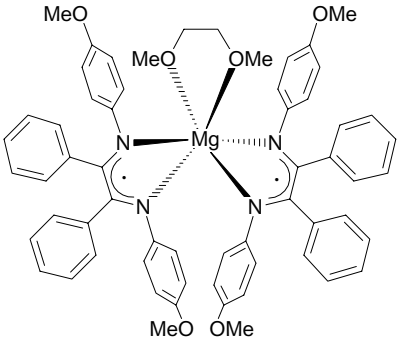
(dmp-DAD^-)$_2$Zn (**119**)



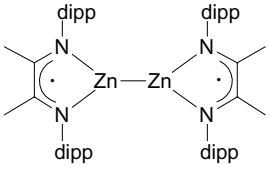
[(Ph-DAD^{Ph-})$_2$Mg(DME) (**120**)



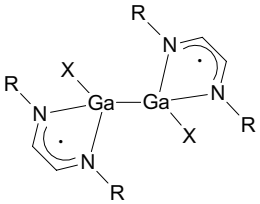
[(p-Tol-DAD^{Ph-})$_2$Mg(DME) (**121**)



[(p-MeOPh-DAD^{Ph-})$_2$Mg(DME) (**122**)

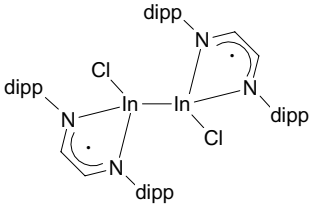


[(dipp-DAD^{Me-})Zn]$_2$ (**123**)



[(R-DAD^-)GaX]$_2$

R = Bu^t, X = I (**124**);
R = dipp, X = Br (**125**), I (**126**)



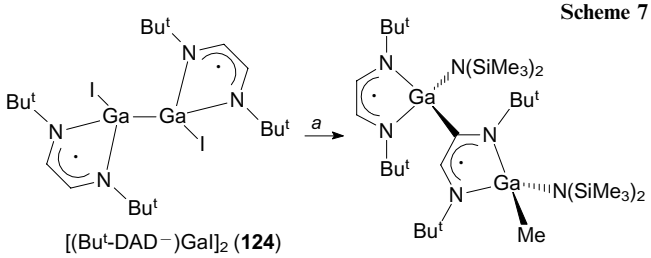
[(dipp-DAD^-)InCl]$_2$ (**127**)

ment (C.N. = 3), and the angle between the C_2N_2Zn planes is 46.4°.

Complexes $[(Bu^t\text{-}DAD^-)GaI]_2$ (**124**) and $[(dipp\text{-}DAD^-)InCl]_2$ (**127**) are formed upon the reaction of DAD^0 with low-valence metal halides (Ga^II, In^ICl) in toluene.[127,128] Compounds $[(dipp\text{-}DAD^-)GaX]_2$ [X = Br (**125**), I (**126**)] were prepared by the reaction of the anionic *N*-heterocyclic gallium carbene analogue $[K(TMEDA)][:Ga^I(dipp\text{-}DAD^0)]$ with $[MoBr_2(CO)_2(PPh_3)_2]$ and Ga^II, respectively.[129] Complexes **124**–**127** are isostructural and are centrosymmetric dimers, in which M^{II} centres exist in a distorted tetrahedral environment.

An unusual biradical product **128** was prepared by the reaction of $[(Bu^t\text{-}DAD^-)GaI]_2$ (**124**) with four equivalents of sodium bis-trimethylsilylamide in diethyl ether (Scheme 7).[131]

Scheme 7



$[(Bu^t\text{-}DAD^-)GaI]_2$ (**124**)

(*a*) 4 $NaN(SiMe_3)_2$

$[(Bu^t\text{-}DAD^-)Ga\{N(SiMe_3)_2\}.\{CC(H)N_2(Bu^t)_2]-Ga[N(SiMe_3)_2]Me\}]$ (**128**)

According to the X-ray diffraction data, the two heterocycles in **128** have similar geometry in which the gallium atoms are located in a distorted tetrahedral environment. The angle between the planes of two radical ligands is 84°. However, like the initial complex **124**, product **128** dissociates in solution into two monoradical fragments.

In addition, there are known binuclear biradical gallium diazabutadiene complexes **129** and **130** containing bridging groups between two metal centres.[132,133]

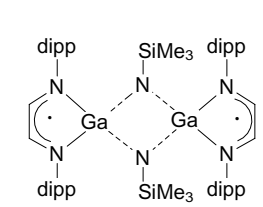
Complex **129** with μ-$NSiMe_3$ bridging groups is the major product of the reaction between the dimer $[(dipp\text{-}DAD^{2-})Ga^{II}]_2$ and excess Me_3SiN_3 in hexane.[133] The metal–metal bond is not retained in **129**, although the Ga···Ga distance [2.654(3) Å] is shorter than twice the van der Waals radius (3.8 Å). The Ga atoms in **129** have a distorted tetrahedral coordination geometry. The structure of binuclear dimer **129** is retained in a toluene solution.

The crystals of **130** were prepared, in an amount sufficient only for X-ray diffraction study, by oxidation of $[(Pr^i\text{-}DAD^{2-})GaC(SiMe_3)_3]$ with atmospheric oxygen.[132] In compound **130**, the central peroxide group is terminally coordinated to two gallium atoms.

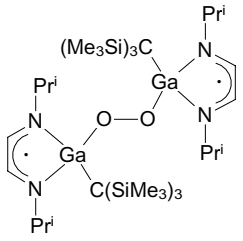
The reaction of indium(I) triflate (InOTf) with *N*,*N*′-dimesityldiazabutadiene affords indium(II) complex **131**, which undergoes reversible oligomerization (Scheme 8).[134]

At room temperature, the solid-state EPR spectrum of complex **131** exhibits a half-field signal, which implies the presence of a biradical; as the sample is cooled to 273 K, this signal almost disappears. Thus, the triplet state of **131** is thermally accessible and the transition between the $S = 0$ and $S = 1$ states is accompanied by the reversible phase transition between the low-temperature phase with paired electrons (characterized by X-ray diffraction data at 173 K)

Structures 129, 130

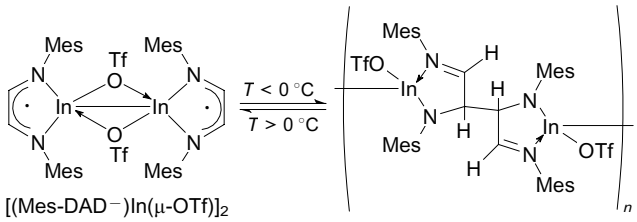


$[(dipp\text{-}DAD^-)Ga(\mu\text{-}N(SiMe_3)]_2$ (**129**)



$[(Pr^i\text{-}DAD^-)Ga(C(SiMe_3)_3O]_2$ (**130**)

Scheme 8



$[(Mes\text{-}DAD^-)In(\mu\text{-}OTf)]_2$ (**131**)

Mes is 2,4,6-trimethylphenyl; Tf = CF_3SO_2

and the paramagnetic phase as a result of C–C bond cleavage in the polymer structure. Moreover, the reversibility of phase transition may be indicative of structural similarity of the high- and low-temperature phases and, hence, close proximity of radicals formed upon the C–C bond cleavage, which accounts for strong antiferromagnetic exchange between them.

Thus, two types of biradical complexes based on diazabutadienes can be conventionally distinguished. The first group includes complexes of divalent Group 2 and 12 metals $(DAD^-)_2M^{II}$ (M = Be, Mg, Ca, Sr, Zn), which have a more or less distorted tetrahedral geometry. The second group is comprised of Group 13 metal complexes $[(DAD^-)M^{II}X]_2$ (M = Ga, In), in which two monoradical moieties are linked by a metal–metal covalent bond.

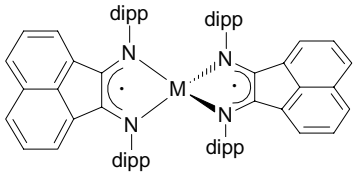
3.4. Complexes based on BIAN ligands

Another type of redox-active *N*,*N*-bidentate α-diimine ligands are sterically crowded bis(imino)acenaphthenes possessing a high-capacity conjugated π-electron system because of the presence of not only diazabutadiene, but also an annulated naphthalene moiety in the molecule.

Complexes **132**–**137** containing two $BIAN^-$ ligands coordinated to the metal centre were prepared for Group 2 (Mg, Ca) and 12 (Zn) metals.

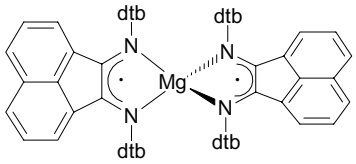
Magnesium and calcium complexes **132**–**135** are formed in the reaction between stoichiometric amounts of $(BIAN^{2-})M(THF)_n$ and $BIAN^0$ (Ref. 135). The synthetic approaches to zinc complexes **136** and **137** include the direct reduction of the $BIAN^0$ ligand with zinc [in the case of Mg and Ca, this reaction affords $(BIAN^{2-})M(THF)_n$] and the exchange reaction between $(CF_3-BIAN^{2-})Na_2$ and $ZnCl_2$.[136] The degree of distortion of the tetrahedral coordination geometry in compounds **132**, **133** and **136** depends on the steric crowding of aryl substituents in the $BIAN^-$ ligand: the considerable deviation of the angle between the ligands from 90° in **132** (49°)[137] and **133** (48°)[135] is caused by minimization of the steric repulsion of the Pr^i groups in

Structures 132 – 137

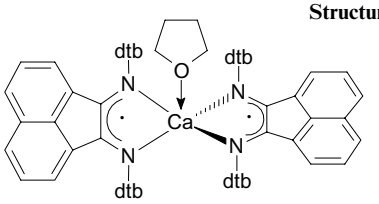


(dipp – BIAN$^-$)$_2$M

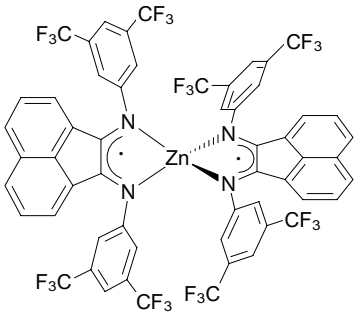
M = Mg (**132**), Ca (**133**)



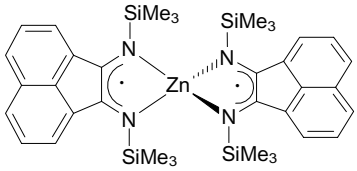
(dtb – BIAN$^-$)$_2$Mg (**134**)



(dtb – BIAN$^-$)$_2$Ca(THF) (**135**)



(CF$_3$ – BIAN$^-$)$_2$Zn (**136**)



(SiMe$_3$ – BIAN$^-$)$_2$Zn (**137**)

dtb is 2,5-di-*tert*-butylphenyl

the *ortho*-positions of the ligands, whereas in **136**, the CF_3 groups in the *meta*-positions of BIAN$^-$ do not induce such a substantial structure distortion, and the angle between the ligands is 83°.[136] According to EPR data, the radical centres in (BIAN$^-$)$_2$M (M = Mg, Zn) are localized on the ligands and the distance between them is approximately 5.5 Å.

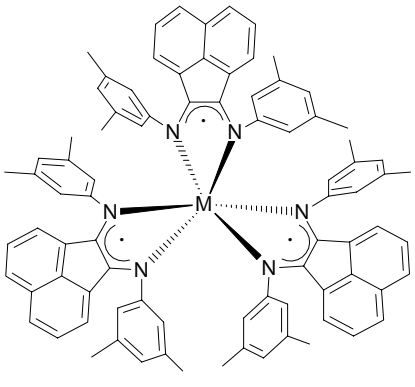
Unlike DAD$^-$ derivatives, there are known examples of complexes where a Group 13 metal (Al, Ga) is coordinated by three BIAN$^-$ ligands.

The complexes (BIAN$^-$)$_3$Ga (**139**, **140**) are formed upon the reaction of BIAN^0 with gallium[136] (or gallium amalgam)[138] on heating; the synthesis of aluminium complex **138** includes the reduction of BIAN^0 with a stoichiometric amount of KC_8 and the subsequent exchange reaction of the obtained intermediate with $AlCl_3$ (3 : 1).[138] Complexes **138** – **140** have a slightly distorted octahedral geometry. The exchange parameters J calculated from the temperature dependence of the EPR spectra are −3.2 (**138**) and −2.1 cm^{-1} (**139**) [$H = -2J(S_1S_2 + S_2S_3 + S_1S_3)$]. According to DFT calculations, weak antiferromagnetic coupling in **138** and **139** is due to the direct magnetic exchange between the p orbitals of nitrogen of adjacent dmp′ – BIAN$^-$ ligands, with the exchange strength being dependent on the distance between nitrogen atoms. Due to the smaller radius of the Al^{III} ion, the N – N distances in **138** are shorter (2.9 Å) than in gallium complex **139** (> 3.0 Å), which is reflected in the magnetic exchange energy. This small difference between the energies of the doublet and quadruplet states implies that both these states would be present in **138** and **139** at room temperature. The μ_{eff} values [2.76 μ_B (**138**) and 2.71 μ_B (**139**)] measured by the Evans method at 298 K in solution are intermediate between the theoretical spin-only values of 1.73 μ_B ($S = 1/2$) and 3.0 μ_B ($S = 3/2$) and thus confirm this assumption.[138] Meanwhile, the μ_{eff} value of the crystalline sample of **140** in the 300 – 20 K range is only slightly higher than the spin-only value of 3.0 μ_B calculated for a system of three non-interacting spins $S_R = 1/2$ and amounts to 3.2 μ_B.[136]

As opposed to rather widely represented diazabutadiene analogues [(DAD$^-$)M^{II}(X)]$_2$, only a few examples of biradical binuclear BIAN complexes **141** – **144** containing a metal – metal bond are known.

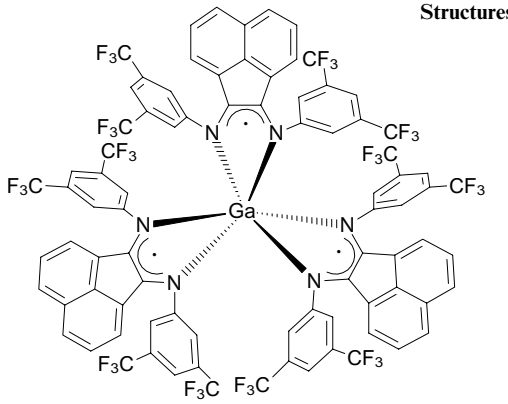
The complex [(dipp – BIAN$^-$)Zn]$_2$ (**141**) was prepared by the exchange reaction between (dipp – BIAN^{2-})Na$_2$ and $ZnCl_2$.[139] The rotation of two BIAN$^-$ ligands relative to the Zn – Zn bond (the dihedral angle between the C_2N_2Zn planes is approximately 42°) is due to steric repulsion between the Pr^i groups of the *N*-aryl substituents. Unlike [(dipp – DAD^{Me-})Zn]$_2$ (**123**), complex **141** retains its structure in solution: the distance between the unpaired electrons

Structures 138 – 140



M = Al (**138**), Ga (**139**)

(dmp′ – BIAN$^-$)$_3$M



(CF$_3$ – BIAN$^-$)$_3$Ga (**140**)

calculated from EPR data in the point dipole approximation [140] is 7.57 Å, which is in good agreement with the distance of 7.67 Å between the centroids constructed on the imine carbon atoms of the radical anion ligands in the molecular structure of the complex.

The complex [(dipp–BIAN$^-$)GaI]$_2$ (**142**) is formed upon the oxidation of digallane [(dipp-BIAN^{2-})Ga^{II}]$_2$ with one equivalent of iodine in toluene.[141] According to the X-ray diffraction data, both Ga atoms in **142** have a slightly distorted tetrahedral geometry, and molecules of the complex are packed in such a way that acenaphthene moieties are exactly parallel to each other (the distance between the planes is 3.4 Å). The relatively high exchange parameter J (-38 cm^{-1}, $H = -2JS_1S_2$) attests to efficient magnetic exchange through the digallane bridge. In addition, rather strong intermolecular magnetic exchange is possible in the crystalline sample of **142** due to the $\pi-\pi$ stacking between the aromatic rings of neighbouring molecules.

The reaction of digallane [(dipp–BIAN^{2-})Ga]$_2$ with benzylideneacetone gives complex **143**, containing two BIAN$^-$ ligands, a Ga–Ga bond and a 4,5-diphenyloctа-2,6-diene-2,7-diolate moiety.[141] The diolate ligand in complex **143** is *cis*-coordinated to Ga, while in the complex [(dipp–BIAN$^-$)GaI]$_2$ (**142**), iodine atoms occupy *trans*-positions. As a result, the planes of diimine ligands both within the molecule and between the molecules of **143** in the crystal cell are not parallel to each other. Unlike **142**, compound **143** is readily soluble in organic solvents and its structure is retained in solution.

Aluminium complex **144** formed upon oxidation of (dipp–BIAN^{2-})Al(I)(Et$_2$O) with benzophenone in diethyl ether has a molecular structure, very similar to the structure of **142**, with the only difference that the metal atoms are linked *via* an oxygen bridge rather than directly (the Al–O–Al moiety is linear).[142] As in the structure of **142**, the BIAN$^-$ planes in **144** are parallel, but no $\pi-\pi$ stacking occurs in the crystal lattice.

Unlike the binuclear derivatives [(dipp–BIAN$^-$)MX]$_2$, the biradical binuclear derivatives [(dipp–BIAN$^-$)M(μ-X)]$_2$ containing bridging groups between the two metal centres are a rather widely known type of compounds.

Zinc dimers are formed in THF under the following conditions: oxidation of BIAN^0 with excess Zn in the presence of I$_2$ (complex **145**),[139] the reaction of **145** with two equivalents of KH (complex **146**),[143] the reaction of [(dipp–BIAN$^-$)Zn]$_2$ (**141**) with phenylacetylene (1 : 1) (complex **147**).[143] According to the X-ray diffraction data, the Zn atoms in compounds **145**–**147** have a distorted tetrahedral coordination environment, while the Zn···Zn distances are substantially different, depending on the nature of the bridging ligand [2.4785(6) Å (**146**), 2.7816(3) Å (**145**), 3.346(2) Å (**147**)]; however, all these values exceed the range for the Zn–Zn bond (2.29–2.40 Å).[144] In nonpolar solvents, the dimeric structure of **146** and **147** is retained; conversely, in coordinating 2-methyltetrahydrofuran, compound **145** dissociates into the monoradical moieties (dipp-BIAN$^-$)ZnI(THF).

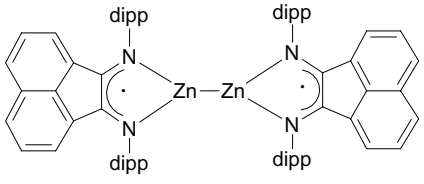
Magnesium complex **148** is the product of the reaction of BIAN^0 with MgMe$_2$,[145] while **149** and **150** are formed in the reactions of (BIAN^{2-})Mg(THF)$_3$ with halogen-containing reagents.[146] In compound **148**, magnesium atoms have a considerably distorted tetrahedral environment (C.N. = 4), whereas in compounds **149** and **150**, C.N. = 5 because of a metal-coordinated THF molecule, and the coordination environment of Mg is a trigonal bipyramid. In solution, the dimeric structure of complexes **148**–**150** is not retained.

The binuclear aluminium complex **151** with bridging ethylene ligands is formed on refluxing of the product of phenylacetylene addition to dialane [dipp–BIAN(μ-C(H)CPh)Al]$_2$.[147] The structure of **151** in solution and in the crystalline state is the same: the distance between the unpaired electrons calculated from parameters of the EPR spectrum is approximately 8.5 Å, which is in good agreement with the X-ray diffraction data (the distance between the centroids constructed on imine carbon atoms of the radical anion ligand in the molecular structure of the complex is 8.52 Å).

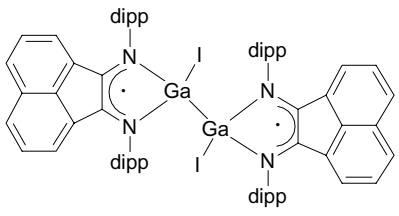
Binuclear complex **152** was isolated from the reaction mixture upon the reaction of (dipp–BIAN^{2-})Mg(THF)$_3$ with benzophenone. In **152**, two (dipp-BIAN$^-$)Mg moieties are linked by a pinacolate unit, resulting from dimerization of two benzophenone ketyl radicals.[148] In a toluene solution, the phenylpinacolate bridge undergoes homolytic cleavage, which is accompanied by transformation of binuclear homo-biradical complex **152** into mononuclear hetero-biradical complex **153** (Scheme 9).

The chemistry of bi- and triradical complexes of main group metals with BIAN$^-$ ligands includes the abundance of diverse structures: apart from mononuclear [(BIAN$^-$)$_2$M^{II} and (BIAN$^-$)$_3$M^{III}] derivatives, there are quite a few binuclear compounds containing either a metal–metal bond ([(BIAN$^-$)M]$_2$) or some bridging groups

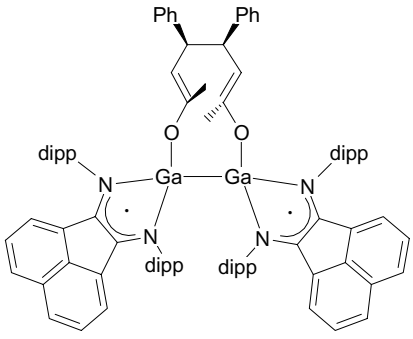
Structures 141–144



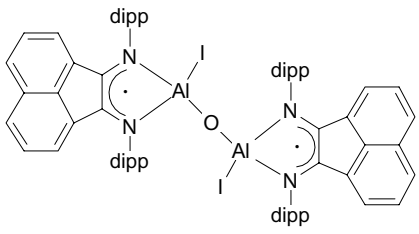
[(dipp–BIAN$^-$)Zn]$_2$ (**141**)



[(dipp–BIAN$^-$)GaI]$_2$ (**142**)

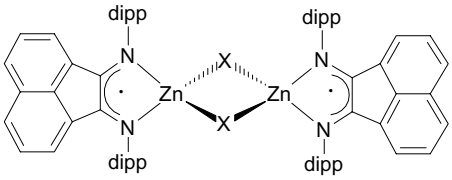


[(dipp–BIAN$^-$)Ga(BA-BA)-Ga(dipp–BIAN$^-$)]$_2$ (**143**)



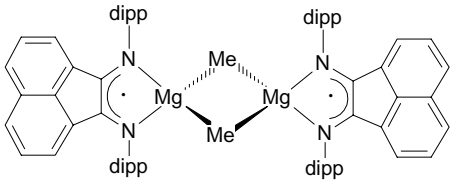
[(dipp–BIAN$^-$)Al(I)]$_2$O (**144**)

Structures 145–151

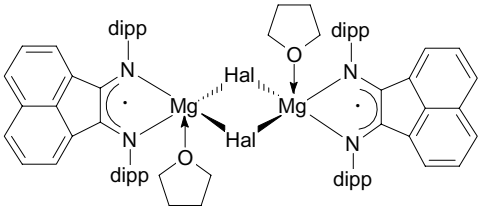


$[(dipp-BIAN^-)Zn(\mu\text{-}X)]_2$

X = I (**145**), H (**146**), CCPh (**147**)

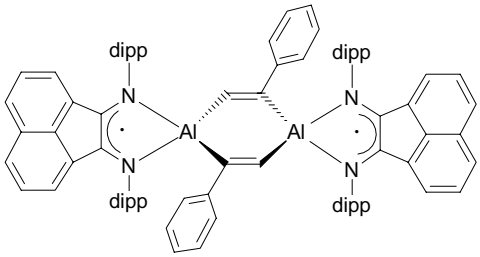


$[(dipp-BIAN^-)Mg(\mu\text{-}Me)]_2$ (**148**)



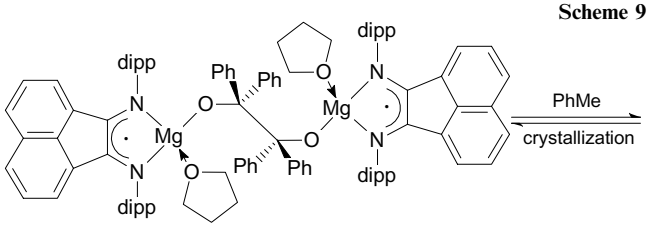
$[(dipp-BIAN^-)Mg(\mu\text{-}Hal)(THF)]_2$

Hal = Cl (**149**), Br (**150**)

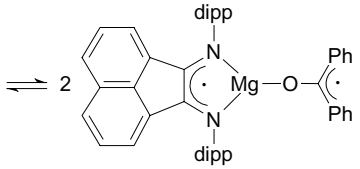


$[(dipp-BIAN^-)Al(\mu\text{-}C(H)CPh)]_2$ (**151**)

Scheme 9



$[\{(dipp-BIAN^-)Mg(THF)\}_2\{\mu\text{-}O_2C_2Ph_4\}]$ (**152**)



$[(dipp-BIAN^-)Mg(OCPh_2)]$ (**153**)

($[(BIAN^-)M(\mu\text{-}X)]_2$). The latter type of compounds is of particular interest, since the nature of bridging (μ-X) groups makes it possible to vary the distance between the radical centres of the $BIAN^-$ ligands.

3.5. Complexes based on IP ligands

The biradical bis-iminopyridyl derivatives containing a diamagnetic metal ion and two IP^- ligands are mainly represented by five-coordinate Group 13 metal complexes $(IP^-)_2MX$ (M = Al, Ga), with only a few examples of compounds with C.N. ≠ 5 and compounds formed by metals of other groups of the Periodic Table.

The four-coordinate zinc complex $(IP^-)_2Zn$ (**154**) was synthesized by the reaction of $ZnCl_2$ with a neutral IP^0 ligand in the presence of Na (1 : 2 : 2).[149] The metal atom in compound **154** has a slightly distorted tetrahedral geometry (the angle between the planes of the IP^- ligands is 85°), which leads to a virtually zero spatial overlap of the SOMO orbitals of the IP^- ligands and, as a consequence, weak magnetic exchange between the two radicals ($J = -32$ cm^{-1}). According to spectral data [EPR and electron nuclear double resonance (ENDOR)] and DFT calculations, the spin density is concentrated almost entirely on the ligands, between which the dipole–dipole coupling occurs, but no effective superexchange pathway is present.[150]

The two-electron outer-sphere oxidation of $(Bu_4N)^+[(IP^{2-})_2Ga]^-$ with two equivalents of ferricinium salt $[Cp_2Fe]^+[B(C_6H_3\text{-}3,5\text{-}CF_3)_4]^-$ gives the cationic complex $[(IP^-)_2Ga]^+$ (**155**), containing the $[B(C_6H_3\text{-}3,5\text{-}CF_3)_4]^-$ anion in the outer sphere.[151] The Ga coordination geometry in **155** is a distorted tetrahedron. The radicals of the IP^- ligands are antiferromagnetically coupled ($J = -77$ cm^{-1}).

Conversely, the cationic aluminium complexes $[(IP^-)_2Al(Solv)]^+$ [Solv = THF (**156**), Et_2O (**157**)] are five-coordinate because of the presence of a solvent molecule coordinated to the metal atoms. These complexes were obtained by oxidation of $[(IP^{2-})_2Al]^-$ and $(IP^-)_2AlMe$ (**164**), respectively.[152]

The neutral complexes $(IP^-)_2AlX$ are formed in the reaction of AlX_3 with IP^0 in the presence of Na (1 : 2 : 2) [X = Cl (**158**), OTf (**159**)];[153] they are also obtained by reactions of $[(IP^{2-})_2Al]^-$ with ZnX_2 [X = Cl (**158**), C≡CPh (**161**), N_3 (**162**), SPh (**163**), NHPh (**166**)],[154] pyridine oxide [X = OH (**160**)][155] and dimethyl sulfide [X = SMe (**165**)].[154] Complex **164** was obtained by the exchange reaction between **158** and MeLi.[154] The aluminium atom in **156**–**166** exists in a distorted trigonal-bipyramidal coordination environment ($\tau = 0.67-0.86$); the degree of deviation of the geometry of the complex from the ideal trigonal bipyramid increases with increasing electronegativity of the ligand X.[154] The spins of the IP^- ligands in $(IP^-)_2AlX$ are coupled by strong antiferromagnetic superexchange interaction [$H = -2JS_1S_2$, $J = -212$ (**158**), -370 (**160**), -99 (**161**), -100 (**162**), -95 (**163**), -118 (**164**), -94 (**165**) and -121 cm^{-1} (**166**)].[154,155] The most pronounced superexchange is observed at the smallest angle between the IP^- planes, probably due to the most efficient overlap of the magnetic orbitals of organic IP^- ligands with the Al–X σ* orbitals.

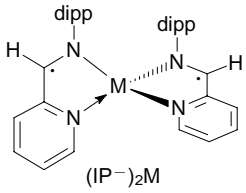
The approaches to the synthesis of gallium complexes $(IP^-)_2GaX$ are similar to those considered above and include the direct reaction of two equivalents of IP^0 with $GaCl_3$ in the presence of two moles of sodium metal [X = Cl (**167**)] [156] or the reaction of $[(IP^{2-})_2Ga]^-$ with dimethyl sulfide [X = SMe (**168**)],[156] pyridine oxide [X = OH (**169**)] and TEMPO (**170**).[151] Complexes **167**–**170** are isostructural

and have a substantially distorted trigonal-bipyramidal geometry ($\tau = 0.66-0.78$). The magnetic exchange in aluminium $(IP^-)_2AlX$ (**158**–**166**) and gallium $(IP^-)_2GaX$ (**167**–**170**) complexes has a similar nature; however, the antiferromagnetic exchange parameter between the unpaired electrons of the IP^- ligands is much lower in **167**–**170** and does not exceed 100 cm^{-1} [$H = -2JS_1S_2$, $J = -100$ (**167**), -79 (**168**), -79 cm^{-1} (**169**)]. While comparing the geometric parameters of gallium and aluminium complexes $(IP^-)_2MX$, note that, because of the greater ionic radius of Ga^{III}, the dihedral angles between the IP^- planes are greater in the $(IP^-)_2GaX$ complexes than in the corresponding aluminium compounds. In turn, the increase in the dihedral angles between the IP^- π-systems in five-coordinate gallium(III) complexes impairs the overlap between them and the E–X σ* orbital compared to that in aluminium complexes.[151]

The only six-coordinate bis-iminopyidine complex $(IP^-)_2Al(SC(S)NMe_2)$ (**171**) is formed upon the oxidation of $[(IP^{2-})_2Al]^-$ with tetramethylthiuram disulfide.[154] The increase in the C.N. in **171** compared to **158**–**166** does not induce a significant change in the nature and strength of the antiferromagnetic exchange between the IP^- ligands ($J = -105$ cm^{-1}).

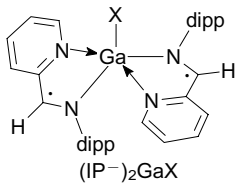
The cobalt complex $(IP^-)_2Co^{III}Me$ (**172**) is formed upon the reduction of $(IP^-)_2Co^{II}$ with sodium metal followed by the addition of MeI to the intermediate.[157] As in the case of $(IP^-)_2MX$ (M = Al, Ga), the metal atom in **172** has a distorted trigonal-bipyramidal coordination geometry ($\tau = 0.76$). Despite the presence of two radical IP^- ligands, compound **172** is diamagnetic and gives rise to a well-resolved NMR spectrum, which is invariable in the temperature range from -20 to 40 °C, indicating that **172** exists as a singlet biradical.

Structures 154–172



$(IP^-)_2M$

M = Zn (**154**), Ga (**155**)

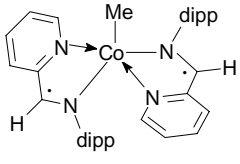


$(IP^-)_2GaX$

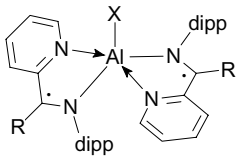
X = Cl (**167**), SMe (**168**), OH (**169**), TEMPO (**170**);

TEMPO =



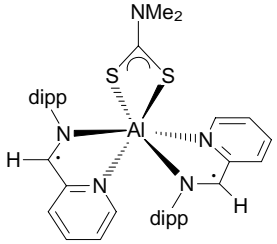


$(IP^-)_2CoMe$ (**172**)



$(^RIP^-)_2AlX$

R = H; X = THF (**156**), Et_2O (**157**), Cl (**158**), OTf (**159**), OH (**160**), C≡CPh (**161**), N_3 (**162**), SPh (**163**), Me (**164**), SMe (**165**); R = Me; X = NHPh (**166**)



$(IP^-)_2Al(SC(S)NMe_2)$ (**171**)

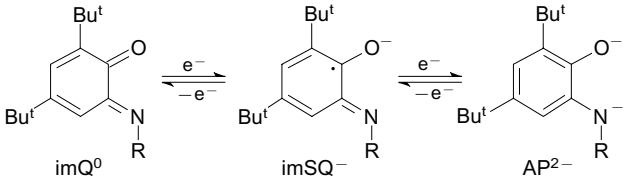
The above can be summarized by concluding that in the series of trigonal-bipyramidal complexes of Group 13 metals $(IP^-)_2MX$ (M = Al, Ga), strong antiferromagnetic exchange between the unpaired electrons of IP^- is due to the superexchange interaction caused by overlap between the π-system of IP^- and the M–X σ* orbital.

4. Metal complexes with *o*-iminoquinone ligands

o-Iminobenzoquinones, which are structurally analogous to both *o*-quinones and α-diimines, occupy an intermediate position between them both in the degree of shielding of the coordination centre and in the oxidative ability. Therefore, *o*-iminobenzoquinones allow not only the preparation of monomeric metal complexes, but also, unlike sterically overcrowded α-diimines, variation of the number of redox-active ligands in the complexes.

In the metal coordination sphere, *o*-iminobenzoquinones, like *o*-quinones, can exist in neutral (imQ^0), radical anion (*o*-iminobenzosemiquinonate, $imSQ^-$) and dianion (*o*-amidophenolate, AP^{2-}) forms (Scheme 10).

Scheme 10



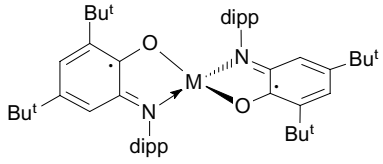
imQ^0 $imSQ^-$ AP^{2-}

Biradical complexes with C.N. of 4, 5 and 6 and triradical complexes with C.N. of 6 were prepared using *o*-iminoquinone type ligands, similarly to *o*-quinone complexes.

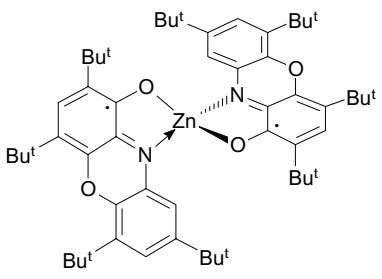
4.1. *o*-Iminosemiquinone complexes with C.N. = 4

The few four-coordinate bis-*o*-iminobenzosemiquinone complexes **173**–**175** known by now are based on Group 12 metals.

Structures 173–175



$(dipp-imSQ)_2M$ M = Zn (**173**), Cd (**174**)



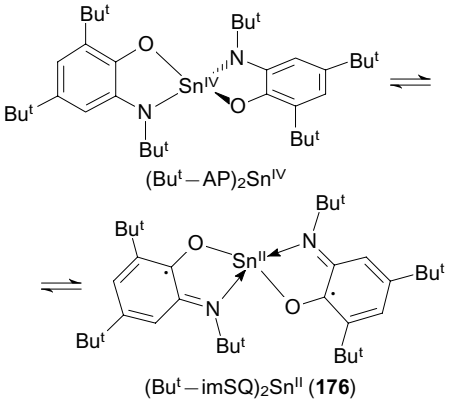
$(Phenox)_2Zn$ (**175**)

The complexes (dipp–imSQ)$_2$M [M = Zn (**173**), Cd (**174**)] were obtained by direct reduction of the imQ^0 ligand with the amalgam of the required metal in pyridine.[158] Zinc complex **173** was isolated from the reaction mixture, whereas cadmium complex **174** was generated and studied by EPR spectroscopy *in situ*. According to EPR data, complexes **173** and **174** in solution have a distorted tetrahedral geometry; the distances between the radical centres are 5.3 and 5.4 Å, respectively. The structure of **173** in the crystalline state is similar to that observed in solution: the Zn atom is located in a slightly distorted tetrahedral environment (the dihedral angle between the imSQ planes is 92.5°). According to magnetochemical measurements, weak antiferromagnetic exchange ($J = -41$ cm^{-1}) occurs between two radical centres of **173**, the ground state is singlet, and the triplet state is thermally accessible.

The zinc complex (Phenox)$_2$Zn (**175**) is formed upon the addition of $ZnCl_2$ to the reduced phenoxazine ligand under aerobic conditions.[159] The Zn atom in **175** has a pseudotetrahedral configuration; the dihedral angle between the phenoxazine ligands is 78.1°. Meanwhile, despite the more pronounced distortion of the coordination polyhedron in **175** than in **173**, the magnetic exchange between the radical centres of the Phenox ligands is weak ferromagnetic ($H = -2JS_1S_2$, $J = 6.5$ cm^{-1}, $zJ' = -0.6$ cm^{-1}), while the ground state of the complex is a triplet ($S = 1$). According to DFT calculations, the spin density of **175** in the ground state is mainly localized on the nitrogen atoms of the phenoxazine ligands ($J_{calc} = 16$ cm^{-1}).

The tin complex containing two *o*-iminoquinone ligands can exist in non-polar solvents as two redox forms: tin(IV) bis-*o*-amidophenolate and tin(II) bis-*o*-iminobenzosemiquinonate (**176**) (Scheme 11).[160]

Scheme 11



Since the transition from one equilibrium form to the other is accompanied by a considerable change in the geometry [the tetrahedron in (Bu^t–AP)$_2$Sn^{IV} turns into the tetragonal pyramid in (Bu^t–imSQ)$_2$Sn^{II} (**176**)], this transition is possible only in solution. The equilibrium shown in Scheme 11 is a unique example of redox isomerism in the series of main group metal derivatives.

4.2. *o*-Iminosemiquinone complexes with C.N. = 5

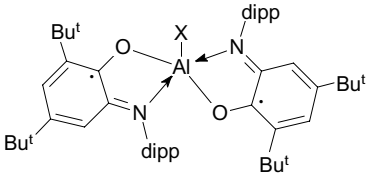
Five-coordinate bis-*o*-iminobenzosemiquinone complexes (imSQ)$_2$MX are widely represented by trivalent Group 13 metal (Al, Ga, In) derivatives **177**–**194** and diamagnetic Co^{III} (l.s. Co^{III}, $3d^6$, $S_{Co} = 0$) compounds **195**–**214**.

Methods for the synthesis of (imSQ)$_2$MX (M = Al, Ga, In) (**177**–**194**) include the oxidation of *o*-amidophenolates of these metals (**171**, **183**–**185**, **191**–**194**),[161–164] exchange reactions of (imSQ)Na with MX_3 (**177**, **184**–**185**, **194**)[162,165,166] or $AlkMI_2$ (**182**, **190**).[164,167] Compounds **178**–**180**, **186**–**189** were prepared by the exchange reaction between (imSQ)$_2$MI and excess inorganic salts M′X (X = N_3, NCS, NCO, OPh).[164,166,167] The coordination geometry of the structurally characterized complexes of the (imSQ)$_2$MX series is intermediate between the trigonal bipyramid and tetragonal pyramid ($\tau = 0.43–0.56$). Aluminium complexes **179** and **180**, in which the metal atom has only a slightly distorted tetragonal-pyramidal coordination geometry ($\tau = 0.1$), form an exception. In (imSQ)$_2$MX (**177**–**194**), the nature of the magnetic exchange between the unpaired electrons of the imSQ ligands depends on the nature of the apical substituent X. When X = Alk, there is weak ferromagnetic exchange interaction between the imSQ ligands propagated by vacant metal *p* orbitals. The introduction into the apical position of a substituent containing a heteroatom directly linked to the metal gives rise to superexchange between the radical ligands as a result of coupling of oxygen and nitrogen *p* orbitals of the imSQ ligands with the *p* or π orbitals of the heteroatoms of the apical substituent X.[167] The efficiency of superexchange increases with decreasing Ga–X bond length in (imSQ)$_2$GaX (**183**–**189**).[164] The increase in the covalent radius of the metal in the series Al–Ga–In is accompanied by a substantial decrease in the magnetic exchange strength, because of the greater distance between the radical centres. The exchange parameter *J* calculated using the exchange-coupled dimer model ($H = -2JS_1S_2$) amounts to −121.8 (**177**), −184.7 (**178**), −178.6 (**179**) and −152.8 cm^{-1} (**180**) for (imSQ)$_2$AlX; −92.3 (**183**), −87.1 (**184**), −68.6 (**185**), −72.6 (**186**), −121.7 (**187**), −85 (**188**) and −139.3 cm^{-1} (**189**) for (imSQ)$_2$GaX; and 8.6 (**190**), 8.8 (**191**), −28.5 (**192**), −27.3 (**193**) and −27.5 cm^{-1} (**194**) for (imSQ)$_2$InX.

Five-coordinate cobalt(III) bis-*o*-iminobenzosemiquinone derivatives (imSQ)$_2$CoX (**195**–**214**) are obtained by the reaction of imQ^0 with (imSQ)Tl or $CoCl_2$ (**195**, **197**),[168,169] by the addition of iodine (**198**)[169] or NO (**196**, **199**)[170] to (imSQ)$_2$Co^{II}, by the exchange reaction between **197** and KSCN (**200**),[169] and by the reaction of *o*-aminophenols APH_2 with Co^{II} salts in the presence of Et_3N and atmospheric oxygen (**201**–**215**).[104,171–175] Unlike (imSQ)$_2$MX (M = Al, Ga, In), cobalt compounds **195**–**214** contain the metal in a distorted tetragonal-pyramidal environment ($\tau = 0–0.39$). An exception is complex **215**, possessing a distorted tetragonal-bipyramidal geometry ($\tau = 0.72$).[173] Despite the presence of two radical centres, complexes **195**–**214** are actually diamagnetic, because of the strong antiferromagnetic superexchange between the imSQ unpaired electrons *via* completely filled atomic orbitals of the low-spin cobalt(III) ion (d^6, $S_{Co} = 0$), while the paramagnetism of **215** is caused by the presence of the vinyl group in the molecule ($S_R = 1/2$).

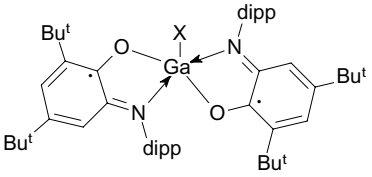
While comparing the five-coordinate Group 13 metal complexes with bis-iminopyridine and bis-*o*-iminobenzosemiquinone ligands, one can conclude that in both series of complexes, the apical substituent participates in the formation of an antiferromagnetic superexchange pathway between the ligand radical centres. However, whereas the formation of the exchange pathway in (IP$^-$)$_2$MX (M = Al, Ga) involves the M–X σ* orbital (*i.e.*, the nature of the substituent X does not play a role), in (imSQ)$_2$MX (M = Al,

Structures 177–215



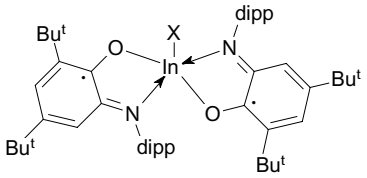
(dipp–imSQ)$_2$AlX

X = I (**177**), N_3 (**178**), NCS (**179**), NCO (**180**)



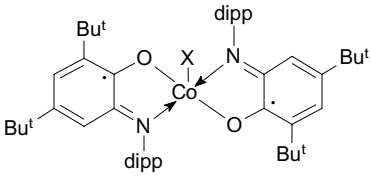
(dipp–imSQ)$_2$GaX

X = Me (**181**), Et (**182**), Cl (**183**), Br (**184**), I (**185**), N_3 (**186**), NCS (**187**), NCO (**188**), OPh (**189**)



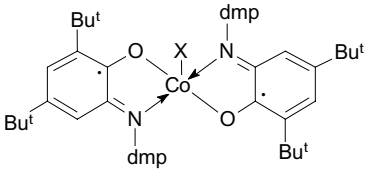
(dipp–imSQ)$_2$InX

X = Me (**190**), Et (**191**), Cl (**192**), Br (**193**), I (**194**)



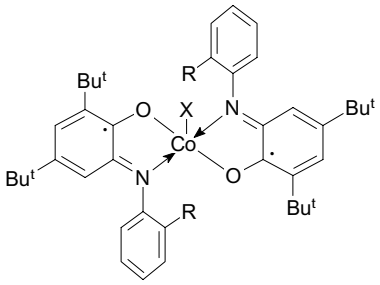
(dipp–imSQ)$_2$CoX

X = Cl (**195**), NO (**196**)



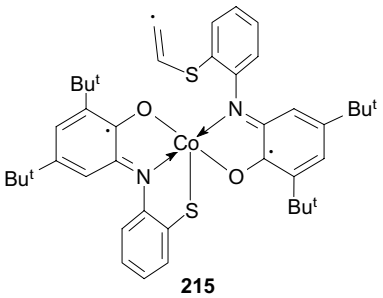
(dmp–imSQ)$_2$CoX

X = Cl (**197**), I (**198**), NO (**199**), SCN (**200**)



(R–imSQ)$_2$CoX

R = H: X = Cl (**201**), I (**202**);
R = CF_3: X = CH_2CN (**203**);
R = Me: X = SPh (**204**), SePh (**205**);
R = Ph: X = Cl (**206**), SPh (**207**);
R = SPh: X = Cl (**208**), SCN (**209**), N_3 (**210**), NO_2 (**211**), I_3 (**212**);
X = Cl: R = OMe (**213**), C(O)OMe (**214**)



215

Ga, In), the exchange pathway involves the *p*-(π) orbitals of heteroatoms of the apical substituent X and, as a consequence, this superexchange pathway between the imSQ spins is absent in the complexes with apical alkyl substituents.

4.3. *o*-Iminosemiquinone complexes with C.N. = 6

4.3.1. Biradical complexes

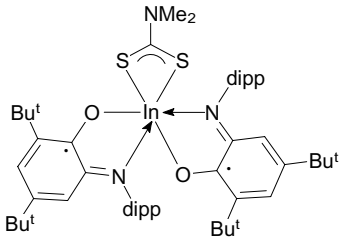
Currently, six-coordinate bis-*o*-iminosemiquinone derivatives are known for indium(III) (**216**, **217**), tin(IV) (**218**–**234**), and Group 4 metals (Zr^{IV}, Hf^{IV}) (**235**–**239**). All compounds are characterized by *cis*-orientation of the imSQ ligands.

Indium complex **216** is formed upon oxidation of [(AP)In(I)(TMEDA)] with tetramethylthiuram dusulfide,[163] and complex **217** is obtained by addition of excess pyridine to (dipp-imSQ)$_2$InI (**194**).[164] It is noteworthy that the oxidation of gallium *o*-amidophenolates with tetramethylthiuram disulfide does not give a six-coordinate complex such as **216**, because of the smaller covalent radius of the metal.[162] The indium atom in **216** and **217** has a distorted octahedral coordination environment. In both complexes, there is a weak antiferromagnetic exchange between the spins of imSQ: $J = -5.5$ cm^{-1} ($H = -2J\Sigma S_iS_{i+1}$) for **216** and $J = -9.9$ cm^{-1} ($H = -2JS_1S_2$) for **217**. The markedly lower exchange parameters J for **216** and **217** compared to (dipp–imSQ)$_2$InX (**192**–**194**) ($\approx$30 cm^{-1}) attest to a change in the mechanism of magnetic exchange between the unpaired electrons of imSQ as the C.N. changes from 5 to 6, in particular, predominance of the direct antiferromagnetic exchange pathway through direct overlap of the molecular orbitals of the imSQ ligands, in the case of six-coordinate complexes.

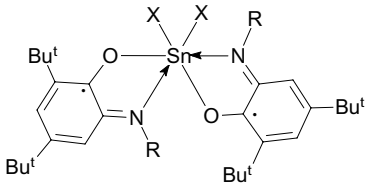
Methods for the synthesis of the series (imSQ)$_2$SnX$_2$ (**218**–**232**) include the exchange reaction between (imSQ)Li and R_2SnCl_2 (**218**–**221**),[176] oxidative addition of $SnCl_2$ to imQ (**222**, **229**),[177,178] oxidation of (AP)$_2$Sn(THF) with bromine or iodine (2 : 1) (**223**, **224**),[179] the exchange between (imSQ)$_2$SnCl$_2$ (**222**, **229**) and excess inorganic salts M′X (**226**–**228**, **230**–**232**),[178] and oxidation of tin *o*-amidophenolates (AP)SnX$_2$ and the mixed-ligand complex (imSQ)$_2$Sn(AP) (**233**) with oxygen (**219**, **221**, **225**).[180,181] According to the X-ray diffraction data, the tin atom in (imSQ)$_2$SnX$_2$ (**218**, **221**–**228**, **230**–**232**) has a distorted octahedral coordination geometry (the angle between the imSQ planes ranges from 49.7° to 69.42°). In this series of complexes, the nature of exchange interaction between the imSQ ligands is also determined by the nature of substituents X. In the complexes with X = Me (**218**) and Ph (**221**), there is rather strong antiferromagnetic coupling between the imSQ ligands due to the predominance of direct magnetic exchange [$J = -51.3$ (**218**) and -29.9 cm^{-1} (**221**)].[178,181] Meanwhile, if X is a halide (pseudohalide), the exchange parameters J are an order of magnitude lower: -3.8 (**222**), -6.5 (**223**), -5.9 (**224**), -5.6 (**226**), -6.9 (**227**), -6.8 (**228**), -6.3 (**229**), -3.6 (**230**), -4.0 (**231**), -0.1 cm^{-1} (**232**).[177,178] In this case, weak antiferromagnetic coupling between the imSQ ligands is a result of two exchange mechanisms with comparable strengths: direct exchange and superexchange.

The biradical tin tris-ligand complex containing differently charged *o*-iminoquinone ligands —

Structures 216 – 239

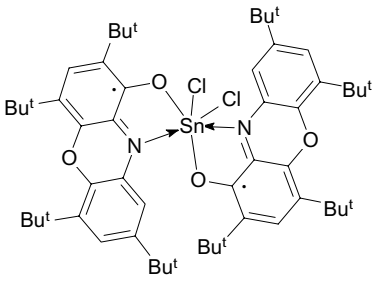


(dipp – imSQ)$_2$In(SC(S)NMe$_2$) (**216**)

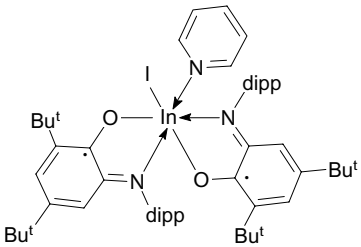


(R – imSQ)$_2$SnX$_2$

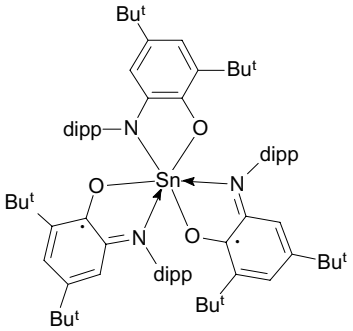
R = dipp: X = Me (**218**), Et (**219**), Bu^n (**220**), Ph (**221**), Cl (**222**), Br (**223**), I (**224**), OH (**225**), N$_3$ (**226**), NCO (**227**), NCS (**228**);
R = dmp: X = Cl (**229**), N$_3$ (**230**), NCO (**231**), NCS (**232**)



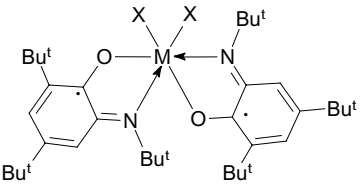
(Phenox)$_2$SnCl$_2$ (**234**)



(dipp – imSQ)$_2$In(I)(Py) (**217**)



(dipp – imSQ)$_2$Sn(dipp – AP) (**233**)



(Bu^t – imSQ)$_2$MX$_2$

M = Zr, X = F (**235**), Cl (**236**), Br (**237**);
M = Hf, X = Cl (**238**), Br (**239**)

(dipp-imSQ)$_2$Sn(dipp-AP) (**233**) — is formed upon the reaction of excess tin amalgam with imQ.[181] According to the X-ray diffraction data, the three ligands are structurally equivalent, which attests to delocalization of four negative charges between them, while the metal atom has a distorted prismatic coordination environment, as opposed to tin derivatives **218** – **232** considered above. The unpaired electrons of imSQ in **233** are coupled by weak ferromagnetic exchange (J = 7.9 cm^{-1}). According to quantum chemical calculations, HOMO is localized on one iminoquinone ligand, whereas HOMO-1 is delocalized over the other two ligands, which ensures the orthogonal arrangement of magnetic orbitals and gives rise to a triplet ground state in **233**.

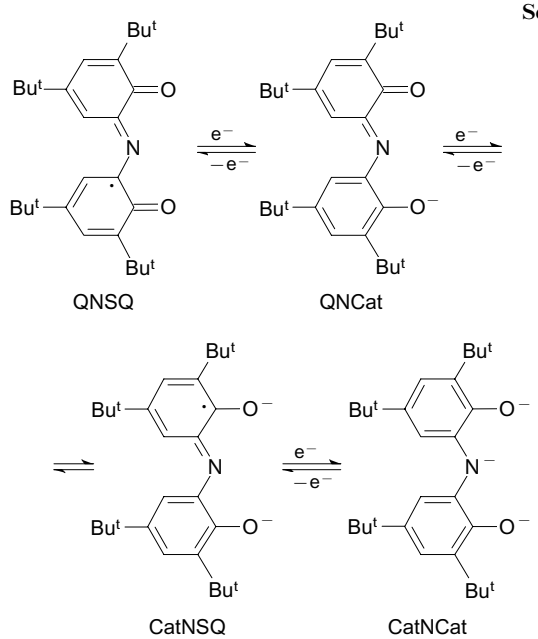
The six-coordinate bis-*o*-iminobenzosemiquinone complex (Phenox)$_2$SnCl$_2$ (**234**) based on the phenoxazine ligand is formed by the reaction of 1-*H*-1-oxo-2,4,6,8-tetra(*tert*-butyl)phenoxazin-1-one with SnCl$_2$.[182] Complex **234** has a distorted octahedral geometry in which weak antiferromagnetic exchange interaction takes place between the imSQ spins (J = −1 cm^{-1}, zJ' = −1.4 cm^{-1}).

Zirconium and hafnium bis-*o*-iminobenzosemiquinone complexes (Bu^t-imSQ)$_2$MX$_2$ (**235** – **239**) are formed upon the two-electron oxidation of the bis-*o*-amidophenolates of the corresponding metals with halogen-containing oxidants.[183,184] Compounds **236** – **239** are structural analogues and have a distorted prismatic geometry. Unlike compounds (disq^R)$_2$ZrX$_2$ **99** – **101**,[105] in which the structural flexibility of the disq^R ligands allows the intramolecular π – π stacking, resulting in overall diamagnetism, in complexes **236** – **239**, the imSQ ligands are arranged at an angle of approximately 70°, which precludes strong direct magnetic exchange. As a consequence, the singlet ground state S_t = 0 in (Bu^t-imSQ)$_2$MX$_2$ is implemented due to strong antiferromagnetic superexchange between the imSQ radicals *via* metal *d* orbitals.

Several biradical six-coordinate complexes were prepared using 3,5-di-*tert*-butyl-1,2-quinone-1-(2-hydroxy-3,5-di-*tert*-butylphenyl)imine (ONO), an *o*-iminoquinone type tridentate ligand. This ligand contains two oxygen atoms in the *ortho*-positions relative to nitrogen and, when complexed with a metal, it can exist in four different redox states (Scheme 12).[185]

Biradical complexes based on ONO ligands are formed by Group 4 (Ti), 14 (Ge, Sn) and 12 (Zn) metals.

Scheme 12



The biradical complexes $(CatNSQ)_2M$ [M = Ge (**240**), Sn (**241**), Ti (**242**)] are obtained by template synthesis from 3,5-$CatH_2$ and MCl_2 or MCl_4 in aqueous ammonia–ethanol solution.[186] The orthogonal positions of the ligands in pseudooctahedral complexes **240**–**242** stabilize the triplet ground state by forming an efficient pathway for ferromagnetic superexchange, with the unpaired electron spin density being delocalized over the ligands and orthogonal metal-centred orbitals.[187] Different superexchange strengths in **240** ($J = 27\ cm^{-1}$), **241** ($J = 23\ cm^{-1}$) and **242** ($J = 56\ cm^{-1}$) are attributable to the nature of metal orbitals participating in the formation of this exchange pathway: the overlap between the ligand orbitals and Ge^{IV} and Sn^{IV} vacant *p* orbitals is less efficient than that in the case of Ti^{IV} 3*d* orbitals.[187]

The complex (CatNCat)Sn(SQNSQ) (**243**), a redox isomer of **241**, is formed upon template synthesis and contains the monoanion form of the QNCat ligand in the triplet state (SQNSQ).[188] The ground state of **243** is also a triplet, but as opposed to **241**, both unpaired electrons are located in one ligand, while the other ligand is diamagnetic.

The zinc bis-ligand complex formed under anaerobic conditions upon the reaction between $(CatNCatH_4)(CF_3CO_2)$ and $Zn(BF_4)_2 \cdot 2H_2O$ in the presence of Et_3N also exists as two redox isomers: diamagnetic green $(CatNQ)_2Zn$ and paramagnetic red (QNCat)Zn(SQNSQ) (**244**).[185] According to DFT calculations, the energy barrier between the two redox-isomers is 8.9 kcal mol^{-1} (Ref. 189).

The complex $(CatNSQ')_2Sn$ (**245**) was prepared by the reaction of tridentate 2,4,6,8-tetra(*tert*-butyl)-9-hydroxyphenoxazin-1-one with tin dichloride in the presence of atmospheric oxygen.[182] Like in the case of $(CatNSQ)_2Sn$ (**241**), the tin atom in **245** has an octahedral coordination environment; however, the ferromagnetic exchange between the radicals is much weaker ($J = 3.5\ cm^{-1}$), which may be due to longer Sn–O bonds in **245** compared to **241**.

Thus, the magnetic exchange between the unpaired electrons of *o*-iminosemiquinone ligands in biradical six-coordinate metal complexes is ferromagnetic, provided that the SOMO of redox-active ligands are strictly orthogonal or that both unpaired electrons are located on the same tridentate ONO ligand. A significant antiferromagnetic exchange is present only in prismatic zirconium(IV) and hafnium(IV) complexes, because of the formation of an efficient pathway for antiferromagnetic superexchange involving metal *d* orbitals. The weak antiferromagnetic imSQ–imSQ exchange in indium(III) and tin(IV) complexes is a consequence of two exchange mechanisms (direct exchange and superexchange) with comparable efficiency. However, the absence of halides or their analogues in the Sn^{IV} coordination sphere results in a considerable decrease in the efficiency of superexchange pathway and predominance of the direct imSQ–imSQ antiferromagnetic exchange.

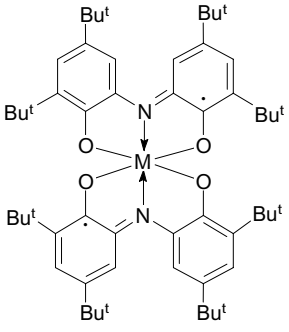
4.3.2. Triradical complexes

Tris-*o*-iminobenzosemiquinone derivatives are known for trivalent gallium and cobalt.

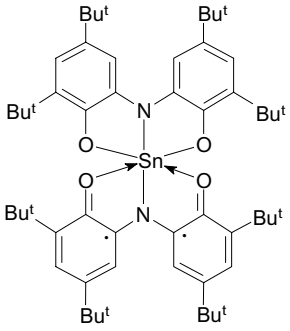
The complexes $(R\text{-}imSQ)_3M$ (M = Ga, Co) **246**–**253** were prepared by the reaction of the corresponding metal salts [$GaCl_3$ or $Co(ClO_4)_2 \cdot 6H_2O$] with three equivalents of substituted *o*-aminophenols $(R\text{-}AP)H_2$ in the presence of Et_3N and atmospheric oxygen.[190–192] The metal atoms in the molecules of **246**–**253** have a distorted octahedral coordination environment, in which the dihedral angles between the planes of three imSQ ligands are virtually equal in gallium derivatives **246** and **248**, whereas in cobalt compounds **249**–**253**, the dihedral angles between the ligand planes within one complex are markedly different.

Irrespective of the nature of substituent R, antiferromagnetic exchange interaction predominates between the spins of the R-imSQ ligands in $(R\text{-}imSQ)_3Ga$ (**246**–**248**): the exchange parameters *J* are −31.8 (**246**), −17.4 (**247**) and −20.7 cm^{-1} (**248**) [$H = -2J(S_1S_2 + S_2S_3) - 2J(S_1S_3)$]. The obtained *J* values attest to predominance of inductive effects of substituents R over steric effects. Conversely, the combination of electronic and steric effects of substituents

Structures 240–245

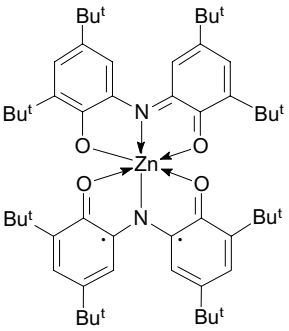


$(CatNSQ)_2M$

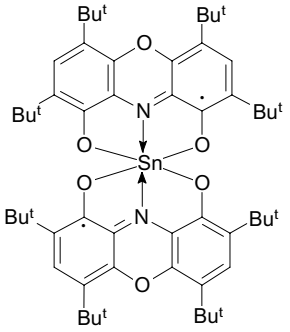


(CatNCat)Sn(SQNSQ) (**243**)

M = Ge (**240**), Sn (**241**), Ti (**242**)

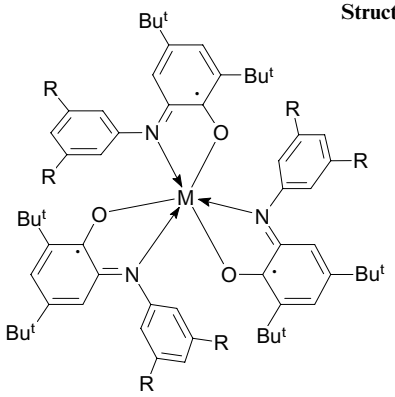


(QNCat)Zn(SQNSQ) (**244**)



$(CatNSQ')_2Sn$ (**245**)

Structures 246–253



M = Ga [$(R\text{–}imSQ)_3Ga$], R = Bu^t (**246**), CF_3 (**247**), Cl (**248**);
M = Co [$(R\text{–}imSQ)_3Co$], R = H (**249**), OMe (**250**), Bu^t (**251**), F (**252**), CF_3 (**253**)

R determines the ground state multiplicity for (R–imSQ)$_3$Co (**249**–**253**): $S_t = 3/2$ for R = H, Bu^t, CF$_3$; $S_t = 1/2$ for R = OMe, F. In view of the considerable difference between the dihedral angles between ligand planes in **249**–**253**, the experimental dependences $\mu_{eff}(T)$ were simulated considering two exchange parameters J and J' [$H = -2J(S_1S_2 + S_2S_3) - 2J'(S_1S_3)$]: $J = 9.1$ cm^{-1}, $J' = 59.5$ cm^{-1} (**249**); $J = 11.0$ cm^{-1}, $J' = -14.0$ cm^{-1} (**250**); $J = 49.0$ cm^{-1}, $J' = 28.7$ cm^{-1} (**251**); $J = -99.0$ cm^{-1}, $J' = 3.4$ cm^{-1} (**252**); $J = 35.6$ cm^{-1}, $J' = -4.8$ cm^{-1} (**253**).[190, 192, 193]

Thus, on going from more symmetrical octahedral gallium tris-*o*-semiquinone complexes to their *o*-iminobenzosemiquinone analogues, the predominant exchange mechanism changes: ferromagnetic superexchange *via* the Ga^{III} vacant *p* orbital predominates in (SQ)$_3$Ga, while in (R–imSQ)$_3$Ga, the doublet ground state is caused by direct imSQ–imSQ antiferromagnetic exchange. The combination of electronic and steric effects of substituents R in (R–imSQ)$_3$Co enables the ferromagnetic exchange interaction between the imSQ ligands, whereas in (SQ)$_3$Co, there is strong antiferromagnetic exchange between the SQ ligands.

5. Conclusion

Analysis of the currently available data on bi- and triradical complexes containing a diamagnetic metal and redox-active ligands in the radical anion form provides the conclusion that in most cases, their preparation is a simple synthetic procedure, which does not require numerous steps or cumbersome operations and gives target compounds in high preparative yields. In addition to the ready availability of precursors, this is a significant advantage over the design of organic biradicals, which is a synthetic challenge. Analysis of the magnitudes and signs of exchange parameters J over series of complexes with *o*-(imino)quinone type ligands (Table 1) prompts the conclusion that varying the natures of the chosen diamagnetic metal ion and the coordination environment allows targeted design of multispin systems with the multiplicity ranging from singlet to quadruplet states and the exchange parameter ranging from –185 to 56 cm^{-1}. The strength of the magnetic exchange between the radical ligands depends on a number of factors such as the distance between the radical centres, coordination geometry, nature of redox-active and extra ligands and the nature of the metal. By structural modification of complexes within a series, it is possible to tune the above parameters and, as a consequence, prepare compounds with a specified singlet–triplet energy gap. Meanwhile, despite the diversity of classes of compounds with *N*,*N*-chelating redox-active ligands, their magnetic properties (except for those of α-iminopyridine derivatives) have been scarcely studied (see Table 1), which opens up extensive prospects for further studies of multispin systems containing a diamagnetic cation and radical redox-active ligands.

Table 1. Complexes of diamagnetic cations with radical anion ligands.

Compound	C.N.	S_t	J/cm^{-1}	Ref.
Metal complexes with o-quinone ligands				
(3,6-SQ)$_2$Zn(Py) (**20**)	5	0	–69 [a]	69
(3,6-SQ)$_2$Zn(L^{I}) (**22**)	5	0	–107 [a]	69
(3,6-SQ)$_2$Zn(L^{II}) (**23**)	5	0	–37 [a]	69
(3,6-SQ)$_2$Zn(L^{III}) (**24**)	5	0	–36 [a]	69
(3,6-SQ)$_2$Zn(L^{IV}) (**25**)	5	1/2	–55 [a]	69
(3,6-SQ)$_2$Zn(L^{V}) (**26**)	5	0	–45 [a]	70
(3,6-SQ)$_2$Zn(L^{VI}) (**27**)	5	0	–121 [a]	68
[(3,6-SQ)$_2$Zn]$_2$(L^{VII}) (**28**)	5	0	–59 [a]	69
[(3,6-SQ)$_2$Zn]$_2$(L^{VIII}) (**29**)	5	0	–95 [a]	70
(3,6-SQ)$_2$Cd(L^{VI}) (**33**)	5	0	–66 [a]	73
(3,6-SQ)$_2$Mg(Py)$_2$ (**39**)	6	1	0.93, 0.11 [e]	77
(3,6-SQ)$_2$Mg(L^{III})$_2$ (**40**)	6	0	–2.42 [a]	77
(3,6-SQ)$_2$Zn(p-CN–Py)$_2$ (**41**)	6	0	–20.3 [a]	70
[(3,6-SQ)$_2$Zn(L^{VII})]$_n$ (**43**)	6	0	–12.3 [a]	70
[(3,6-SQ)$_2$Zn(L^{IX})]$_n$ (**44a**)	6	0	–17.5,[a] $zJ' = -24.1$	70
[(3,6-SQ)$_2$Zn(L^{IX})]$_n$ (**44b**)	6	0	–32.5,[a] $zJ' = -10$	70
(3,6-SQ)$_2$Mg(DME) (**57**)	6	1	2.79, –6.06, –0.02 [f]	77
(3,6-SQ)$_2$Zn(TMEDA) (**58**)	6	0	–33.7 [a]	78
(3,6-SQ)$_2$Cd(3,6-Q) (**60**)	6	0	–4 [a]	73
(3,6-SQ)$_2$Mg(bipy) (**61**)	6	0	4.93, –13.7, –0.032 [c]	77
(3,6-SQ)$_2$Zn(bipy) (**62**)	6	0	8.6, –14.7 [g]	79
(3,6-SQ)$_2$Cd(bipy) (**63**)	6	0	–46 [a]	67
(3,6-SQ)$_2$Mg(Phen) (**64**)	6	1	3.96, –0.85, –0.50 [c]	77
(3,6-SQ)$_2$Zn(Phen) (**65**)	6	0	8.4, –9.7 [d]	79
(3,6-SQ)$_2$Mg(MePhen) (**66**)	6	0	3.57, –4.44, –0.50 [c]	77
(3,6-SQ)$_2$Zn(MePhen) (**67**)	6	1	4.4, –4.1 [d]	79
(3,6-SQ)$_3$Al (**80**)	6	3/2	6.2 [h]	78
(3,6-SQ)$_3$Ga (**81**)	6	3/2	8.6 [e]	78
(3,6-SQ)$_3$Co (**83**)	6	1/2	–39 [e]	78
(NN-3,6-SQ)$_3$Al (**84**)	6	3/2	18.5 [e], $zJ' = -2.2$	96
Metal complexes with o-quinone ligands				
(*N*,*N*-3,6-SQ)$_3$Ga (**85**)	6	3/2	10.6,[e] $zJ' = -0.4$	96
(*N*,*N*-3,6-SQ)$_3$In (**86**)	6	1/2	–28.1,[e] $zJ' = -6$	96
(3,5-SQ)$_3$Ga (**88**)	6	3/2	7.8,[e] 17.6 [e]	92, 98
[Al$_2$(μ-3,5-CatH)$_2$(3,5-SQ)$_4$] (**89**)	6	2	17.79, –0.027 [b]	98
(3,6-SQ)$_4$Ce (**92**)	8	0	–152, 0.2 [c]	100
La(3,6-SQ)$_3$(3,6-Q)(THF) (**94**)	9	1/2	–100, –9 [d]	100
Metal complexes with bipyridyl ligands				
(bipy$^-$)$_2$Be (**102**)	4	0	–8 [a]	110
(bipy$^-$)$_2$Mg(THF) (**103**)	5	0	–5.2 [a]	112
(bipy$^-$)$_3$Al (**106**)	6	1/2	–79 [l]	114
(bipy$^-$)$_3$Sc (**107**)	6	1/2	–139 [l]	114
Metal complexes with bis(imino)acenaphthene ligands				
(dmp′-BIAN$^-$)$_3$Al (**138**)	6	1/2	–3.2 [e]	138
(dmp′-BIAN$^-$)$_3$Ga (**139**)	6	1/2	–2.1 [e]	138
[(dipp-BIAN$^-$)GaI]$_2$ (**142**)	4	0	–38 [a]	141
Metal complexes with iminopyridine ligands				
(IP$^-$)$_2$Zn (**154**)	4	0	–32 [a]	149
[(IP$^-$)$_2$Ga]$^+$ (**155**)	4	0	–77 [a]	151
(IP$^-$)$_2$AlCl (**158**)	5	0	–212 [a]	154
(IP$^-$)$_2$AlOH (**160**)	5	0	–370 [a]	155
(IP$^-$)$_2$Al(CCPh) (**161**)	5	0	–99 [a]	154
(IP$^-$)$_2$AlN$_3$ (**162**)	5	0	–100 [a]	154
(IP$^-$)$_2$AlSPh (**163**)	5	0	–95 [a]	154
(IP$^-$)$_2$AlMe (**164**)	5	0	–118 [a]	154
(IP$^-$)$_2$AlSMe (**165**)	5	0	–94 [a]	154
(^{Me}IP$^-$)$_2$Al(NHPh) (**166**)	5	0	–121 [a]	154
(IP$^-$)$_2$GaCl (**167**)	5	0	–100 [a]	156
(IP$^-$)$_2$GaSMe (**168**)	5	0	–79 [a]	156
(IP$^-$)$_2$GaOH (**169**)	5	0	–79 [a]	151
(IP$^-$)$_2$Al(SC(S)NMe$_2$) (**171**)	6	0	–105 [a]	154

Table 1 (continued).

Compound	C.N.	S_t	J/cm^{-1}	Ref.	Compound	C.N.	S_t	J/cm^{-1}	Ref.
Metal complexes with o-iminoquinone type ligands					*Metal complexes with o-iminoquinone type ligands*				
(dipp-imSQ)$_2$Zn (**173**)	4	0	−41 [a]	158	(dipp-imSQ)$_2$SnBr$_2$ (**223**)	6	0	−6.5 [a]	178
(Phenox)$_2$Zn (**175**)	4	1	6.5,[a] $zJ' = -0.6$	159	(dipp-imSQ)$_2$SnI$_2$ (**224**)	6	0	−5.9 [a]	178
(dipp-imSQ)$_2$AlI (**177**)	5	0	−121.8 [a]	166	(dipp-imSQ)$_2$Sn(N$_3$)$_2$ (**226**)	6	0	−5.6 [a]	178
(dipp-imSQ)$_2$AlN$_3$ (**178**)	5	0	−184.7 [a]	166	(dipp-imSQ)$_2$Sn(NCO)$_2$ (**227**)	6	0	−6.9 [a]	178
(dipp-imSQ)$_2$AlNCS (**179**)	5	0	−178.6 [a]	166	(dipp-imSQ)$_2$Sn(NCS)$_2$ (**228**)	6	0	−6.8 [a]	178
(dipp-imSQ)$_2$AlNCO (**180**)	5	0	−152.8 [a]	164	(dmp-imSQ)$_2$SnCl$_2$ (**229**)	6	0	−6.3 [a]	178
(dipp-imSQ)$_2$GaCl (**183**)	5	0	−92.3 [a]	167	(dmp-imSQ)$_2$Sn(N$_3$)$_2$ (**230**)	6	0	−3.6 [a]	178
(dipp-imSQ)$_2$GaBr (**184**)	5	0	−87.1 [a]	167	(dmp-imSQ)$_2$Sn(NCO)$_2$ (**231**)	6	0	−4.0 [a]	178
(dipp-imSQ)$_2$GaI (**185**)	5	0	−68.6 [a]	167	(dmp-imSQ)$_2$Sn(NCS)$_2$ (**232**)	6	0	−0.1 [a]	178
(dipp-imSQ)$_2$GaN$_3$ (**186**)	5	0	−72.6 [a]	167	(dipp-imSQ)$_2$Sn(dipp-AP) (**233**)	6	1	7.9 [a]	181
(dipp-imSQ)$_2$GaNCS (**187**)	5	0	−121.7 [a]	167	(Phenox)$_2$SnCl$_2$ (**234**)	6	0	−1,[a] $zJ' = -1.4$	182
(dipp-imSQ)$_2$GaNCO (**188**)	5	0	−85 [a]	164	(CatNSQ)$_2$Ge (**240**)	6	1	27 [a]	186
(dipp-imSQ)$_2$Ga(OPh) (**189**)	5	0	−139.3 [a]	164	(CatNSQ)$_2$Sn (**241**)	6	1	23 [a]	186
(dipp-imSQ)$_2$InMe (**190**)	5	1	8.6 [a]	164	(CatNSQ)$_2$Ti (**242**)	6	1	56 [a]	186
(dipp-imSQ)$_2$InEt (**191**)	5	1	8.8 [a]	163	(CatNSQ')$_2$Sn (**245**)	6	1	3.5 [a]	182
(dipp-imSQ)$_2$InCl (**192**)	5	0	−28.5 [a]	164	(Bu^t-imSQ)$_3$Ga (**246**)	6	1/2	−31.8 [h]	192
(dipp-imSQ)$_2$InBr (**193**)	5	0	−27.3 [a]	164	(CF$_3$-imSQ)$_3$Ga (**247**)	6	1/2	−17.4 [h]	192
(dipp-imSQ)$_2$InI (**194**)	5	0	−27.5 [a]	165	(Cl-imSQ)$_3$Ga (**248**)	6	1/2	−20.7 [h]	192
(dipp-imSQ)$_2$In(SC(S)NMe$_2$) (**216**)	6	0	−5.5 [i]	163	(H-imSQ)$_3$Co (**249**)	6	3/2	9.1, 59.5 [j]	190
(dipp-imSQ)$_2$In(I)(Py) (**217**)	6	0	−9.9 [a]	164	(OMe-imSQ)$_3$Co (**250**)	6	1/2	11.0, −14.0 [j]	192
(dipp-imSQ)$_2$SnMe$_2$ (**218**)	6	0	−51.3 [a]	178	(Bu^t-imSQ)$_3$Co (**251**)	6	3/2	49.0, 28.7 [j]	192
(dipp-imSQ)$_2$SnPh$_2$ (**221**)	6	0	−29.9 [a]	181	(F-imSQ)$_3$Co (**252**)	6	1/2	−99.0, 3.4 [j]	192
(dipp-imSQ)$_2$SnCl$_2$ (**222**)	6	0	−3.8 [a]	177	(CF$_3$-imSQ)$_3$Co (**253**)	6	3/2	35.6, −4.8 [j]	192

Note. C.N. is coordination number, S_t is ground spin state of the complex, J is exchange parameter, zJ' is intermolecular exchange parameter. [a] $H = -2JS_1S_2$; [b] $H = -2J_1(S_1S_2 + S_3S_4) - 2J_2(S_1S_3 + S_1S_4 + S_2S_3 + S_2S_4)$; [c] $H = -2J_1(S_1S_2 + S_2S_3 + S_3S_4 + S_1S_4) - 2J_2(S_1S_3 + S_2S_4)$; [d] $H = -2J_{12}S_1S_2 - 2J_{23}S_2S_3$; [e] $H = -2J_1(S_1S_2 + S_3S_4) - 2J_2S_2S_3$; [f] $H = -2J_1(S_1S_2 + S_3S_4) - 2J_2S_2S_3 - 2J_3(S_1S_3 + S_2S_4)$; [g] $H = -2J_1S_1S_2 - 2J_2S_2S_3 - 2J_1S_3S_4$; [h] $H = -2J(S_1S_2 + S_1S_3 + S_2S_3)$; [i] $H = -2J\Sigma S_iS_{i+1}$; [j] $H = -2J(S_1S_2 + S_2S_3) - 2J'(S_1S_3)$; [k] no data on the Hamiltonian are reported.

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