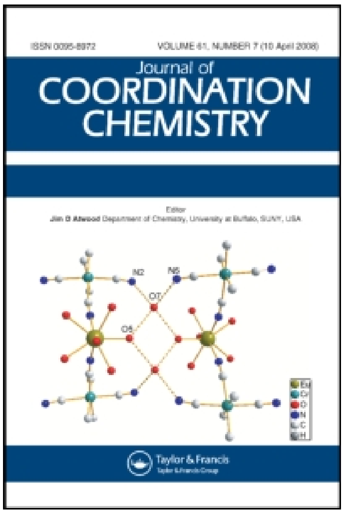

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Review: Coordination Chemistry of o -Quinone Complexes

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To cite this Article Kharisov, B. I. , Méndez-Rojas, M. A. , Garnovskii, A. D. , Ivakhnenko, E. P. and Ortiz-Méndez, U.(2002) 'Review: Coordination Chemistry of o -Quinone Complexes', Journal of Coordination Chemistry, 55: 7, 745 — 770

To link to this Article: DOI: 10.1080/0095897022000001511

URL: http://dx.doi.org/10.1080/0095897022000001511

J. Coord. Chem., 2002, Vol. 55(7), pp. 745–770

REVIEW: COORDINATION CHEMISTRY OF *o*-QUINONE COMPLEXES

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(Received 20 June 2000; Revised 7 December 2000; In final form 27 August 2001)

The structural and tautomeric peculiarities, as well as physical/chemical properties of transition metal complexes with *o*-quinones are reviewed. Synthetic routes for obtaining these complexes starting from different sources (elemental metals, metal carbonyls, salts, and metal complexes) are described and tabulated. The free-radical properties of metal-*o*-quinone complexes are discussed.

Keywords: *o*-quinones; *o*-semiquinones; Coordination chemistry; Free-radical processes

INTRODUCTION

A number of coordination compounds containing ligands able to participate in easy and reversible one-electron redox processes are known. Nitroxyl radicals, spatially hindered *o*-quinones, quinoneimines, and phenoxazinone systems are examples of such ligands.

Compounds of this type, obtained for all transition metals, have intriguing and unique structural, magnetic, and electronic properties [1] and are of considerable interest because the oxidation state of the ligands in these systems, leading to paramagnetism, mimics biochemical processes such as respiration and photosynthesis. Other fields of application include their use as medicinal chemotherapeutic (antitumor) [2,3] and organ-imaging [4,5] agents, in biological intercalation studies [6], and as solid-state materials [7].

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ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/0095897022000001511

As far back as 1931 Mikhaelis suggested the formation of an active form (radical particles) of some ferments from quinones [8]. The coordination chemistry of catechols and semiquinones has developed dramatically over the past 20 years, and, at present, extensive experimental data, dedicated to element-organic *o*-semiquinone complexes, have been accumulated and reviewed in papers by Pierpont [1,9], Tuck [10] Abakumov [11,12] and Kabachnik [13]. In this respect, a recent review [1], which represents an excellent generalization of achievements in this area, should be especially noted.

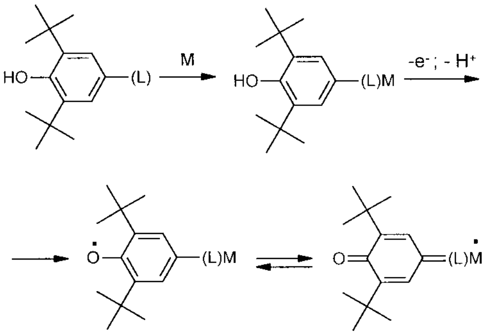
Due to some structural and magnetic peculiarities, the quinone ligands and their metal complexes are different from other classes of coordination compounds [1], as will be shown below. Here we present an overview of the main methods for synthesis of complexes containing benzoquinone, semiquinone, and catecholate ligands, and chemical peculiarities of these products found in recent literature (1994–present). A definite emphasis is given to Russian research results, which, in our opinion, are insufficiently covered in English-language literature during the last 20 years.

PECULIARITIES OF METAL-*o*-QUINONE AND RELATED COMPLEXES

Metal Oxidation Number and Redox Isomers

In general, the introduction of spatially hindered phenols into coordination compounds produces stable free-radical forms [14–16]. A series of metal complexes with redox-ligands, containing derivatives of 2,6-di-*t*-butylphenols π- or σ-connected, or vicinal fragments in the coordination environment of the central metal atom, were synthesized this way: π-aryl [17] and π-σ-allyl [18] compounds, nitrile complexes [19], metal glyoximates [20] salicylaldiminates [21,22], porphyrines [23–25], and phthalocyanines [26,27].

Spatially hindered phenols can exist in different redox-forms: diamagnetic phenol, paramagnetic phenoxyl, phenolate, and quinolate. These forms are interrelated by reversible transitions, including electron, proton and hydrogen transport (Scheme 1).

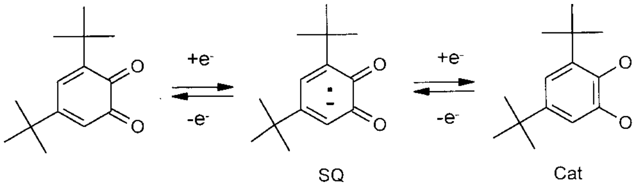


SCHEME 1

A detailed study of a series of coordination and organometallic compounds with ligands containing redox-groups was carried out [17–27] using EPR, electronic absorption spectroscopy, electrochemical methods, and quantum-mechanic calculations. On the basis of these data, some experimental rules were established for redox transformations, depending on the nature of the metal–ligand bond, the distance between the redox-fragment and the metal, and the nature of the metal. It was shown that introduction of a metal atom into organic radicals is an effective way to stabilize them. Moreover, the transformation of ligands into their free-radical form leads to a change of the reactivity of organic and organometallic compounds. This influence is transmitted by an inner-molecular mechanism [28].

Studies on a series of transformations of complexes containing 2,6,di-*t*-butylphenols or corresponding phenoxyl radicals, established that a change in the nature of the organic ligands in metal complexes, leading to their transition from diamagnetic to paramagnetic, is a method of molecule activation. Phthalocyanines [28] containing spatially hindered phenol groups are polyfunctional homogeneous redox-catalysts, whose activity is determined by various redox transformation routes.

In recent years, a number of investigations have been carried out on the coordination chemistry of *o*-quinones, mainly ligands based on 3,6-di-*t*-butyl-1,2-benzoquinone and its analogues. These compounds are capable of taking part in one-electron redox-processes according to Scheme 2 [13]:



SCHEME 2

The capacity to form chelating ligands having different oxidation states explains the variety of coordination compounds formed [9–12]. Several novel synthetic methods for *o*-semiquinolate (SQ) and catecholate complexes of both transition and non-transition metals (Mn, Re, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Tl, Hg) in various oxidation states and ligand environments have been developed (see below). Application of EPR spectroscopy and x-ray single crystal diffraction has demonstrated the influence of electronic and spatial factors on the stability of such complexes [29–31].

For the thallium SQ-complex [32], complex-formation with *o*-quinones as neutral ligands was described, where an inner-molecular electron transition "ligand–ligand" takes place. Highly interesting redox-isometry was reported [33,34]. A series of mono-*o*-semiquinone complexes of rhodium, iridium, and copper, exist in two equilibrium isomers, differing by the place of localization of the non-paired electron (metal or SQ-ligand) (Scheme 3). The necessary conditions for such isomers were formulated and the factors influencing the equilibrium were studied.

$$\mathrm{(COD)Rh^{I}\,SQ(AsEt_3)} \rightleftharpoons \mathrm{(COD)Rh^{II}\,(Cat)(AsEt_3)}$$

SCHEME 3

Equilibrium between metal-quinone redox isomers is extremely sensitive to the properties of nitrogen-donor co-ligands. Redox isomers exist (Scheme 4) in cobalt complexes containing semiquinolate (SQ) and catecholate (Cat) ligands derived from 3,5-di-*t*-butyl-1,2-benzoquinone (3,5-DBBQ) [35]:

$$\mathrm{Co^{III}(bipy)(3,5\text{-}DBSQ)(3,5\text{-}DBCat)} \rightarrow \mathrm{Co^{II}(bipy)(3,5\text{-}DBSQ)_2}$$

SCHEME 4

This observation was extended to include complexes containing various N-donor ligands and complexes prepared with 3,6-DBBQ [36–39]. The complexes undergo a valence tautomeric transformation from low spin at low temperatures, to high spin at high temperatures. Equilibrium occurs in separate electron transfer (Scheme 5) and spin transition (Scheme 6) steps [40,41]:

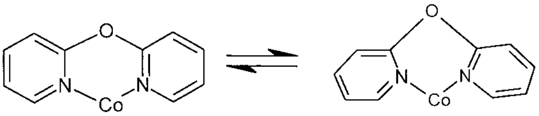
$$\underset{(d\pi)^6(d\sigma)^0(\pi_{Q1})^2(\pi_{Q2})^1}{\mathrm{Co^{III}(N\text{-}N)(SQ)(Cat)}} \rightarrow \underset{(d\pi)^6(d\sigma)^1(\pi_{Q1})^1(\pi_{Q2})^1}{\mathrm{Co^{II}(N\text{-}N)(SQ)_2}}$$

SCHEME 5

$$\underset{(d\pi)^6(d\sigma)^1(\pi_{Q1})^1(\pi_{Q2})^1}{\mathrm{Co^{III}(N\text{-}N)(SQ)_2}} \rightarrow \underset{(d\pi)^5(d\sigma)^2(\pi_{Q1})^1(\pi_{Q2})^1}{\mathrm{Co^{II}(N\text{-}N)(SQ)_2}}$$

SCHEME 6

As a result, low-spin Co(III) is converted to high-spin Co(II). This process may be viewed as a charge-transfer-induced spin transition [40a]. Valence tautomerism driven by pressure was found for the $[\mathrm{Co(SQ)_2(phen)}] \cdot n\mathrm{C_6H_5CH_3}$ ($n = 0,1$) complex, with pressures within 0.075–0.700 GPa for the toluene solvate and 0.10–2.5 GPa for the non-solvated complex [40b]. The complexes $\mathrm{Co(Py_2}X\mathrm{)(3,6\text{-}DBQ)_2}$ ($X = \mathrm{S}$, Se, Te; 3,6-DBQ is 3,6-di-*t*-butyl-1,2-benzoquinone), reported here, at temperatures below 150 K are all in the $\mathrm{Co^{III}(Py_2}X\mathrm{)(3,6\text{-}DBSQ)(3,6\text{-}DBCat)}$ isomeric form with magnetic moments $S = 1/2$ due to the radical semiquinone ligand. As the sample temperature is increased, shifts to the high-spin $\mathrm{Co^{II}(Py_2}X\mathrm{)(3,6\text{-}DBSQ)_2}$ redox isomer are observed with transition temperatures of 370, 290, and 210 K for the ligands containing S, Se, and Te bridging atoms, respectively [40a]. A similar complex with $X = \mathrm{O}$, reported in the same work [40a] and obtained from toluene, contains the $\mathrm{Co^{II}(Py_2O)(3,6\text{-}DBSQ)_2}$ redox isomer with magnetic moment 3.5–4.0 μ_B and space group $P2_1/c$. The switching properties of this compound appear to be associated with the planar/folded change in conformation of the $\mathrm{Py_2O}$ ligand associated with electron transfer between the metal and quinone ligands (Scheme 7):



$\mathrm{Co^{II}(py_2O)(3,6\text{-}DBSQ)_2}$ $\mathrm{Co^{III}(py_2O)(3,6\text{-}DBSQ)(3,6\text{-}DBCat)}$

SCHEME 7

For the analogous nickel complex [42], one-electron reduction (Scheme 8) of the complex leads to one-electron oxidation of the metal.

$$\mathrm{Ni^{II}(3,6\text{-}DBSQ)_2 + e \rightarrow [Ni^{II}(3,6\text{-}DBSQ)(3,6\text{-}DBCat]^- \rightarrow [Ni^{III}(3,6\text{-}DBSQ)_2]^-}$$

SCHEME 8

For other metal complexes with the same ligands, such change of metal oxidation number has also been reported: $\mathrm{Mn^{II}(SQ)_2 \rightarrow [Mn^{IV}(Cat)_2]^-}$ [43], $\mathrm{V^{III}(SQ)_3} \rightarrow$

$[V^{V}(Cat)_3]^-$ [44]. In all these cases reduction occurs initially at SQ ligand [42]. Other examples are cationic porphyrin complexes of nickel which can exist as either $[Ni^{III}(porph)]^+$ or $[Ni^{II}(porph^\bullet)]^+$ charge-localized redox isomers [45]. The oxidation state of manganese in its semiquinone and catecholate complexes is typically lower, and metal and quinone orbital energies are quite similar [1]. A redox series of ruthenium complexes can be represented as follows (Scheme 9) [46]:

$$[Ru^{II}(bipy)_2Q]^{3+} \xrightarrow{e^-} [Ru^{II}(bipy)_2Q]^{2+} \xrightarrow{e^-} [Ru^{II}(bipy)_2SQ]^{+} \xrightarrow{e^-} (Ru^{II}(bipy)_2Cat]$$

SCHEME 9

It is noted [42] that the similarity in energy between metal and quinone electronic levels is responsible for shifts in charge distribution between metal and ligands. These shifts result from change in the donor character of the ligand with reduction from SQ to Cat and the consequent inversion in the order of localized metal and quinone electronic levels.

The metal oxidation number in quinone complexes can also be changed by electrochemical methods. For example, the electrochemical oxidation (Schemes 10, 11) of $[M^{IV}(DBCat)_3]^{2-}$ ($M = $ Mn, Tc, Re) results in products having different oxidation state on the central atom [47,48]:

$$M^{IV}(DBCAT)_3]^{2-} - e^- \rightarrow [M^{III}(DBCat)_2]^- + DBBQ \quad M = Mn$$

SCHEME 10

$$[M^{IV}(DBCat)_3]^{2+} - e^- \Leftrightarrow [M^{V}(DBCat)_3]^- \quad M = Tc,\ Re$$

SCHEME 11

Photochemistry of quinone (1,4-benzoquinone, duroquinone, 2,6-di-*t*-butylbenzoquinone, etc.) radical anions was studied in detail [49]. Cyclic voltammetry data in various solvents show typical reversible two-wave voltammograms for, the quinines corresponding to two successive one-electron transfers (Schemes 12, 13) to the radical anion then to the dianion:

$$Q + e^- \rightarrow Q^{\bullet -}$$

SCHEME 12

$$Q^{\bullet -} + e^- \rightarrow Q^{2-}$$

SCHEME 13

Charge Distribution

Charge distribution related to the balance in energy between frontier quinone and metal orbitals is described in Fig. 1 (adapted from [1]) with permission.

In situations where the metal orbital energy is high relative to the quinone π level, the ligand bonds as a reduced catecholate to an oxidized form of the metal. When

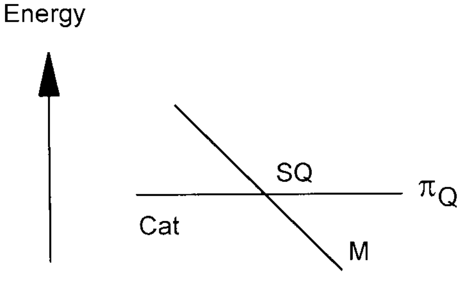
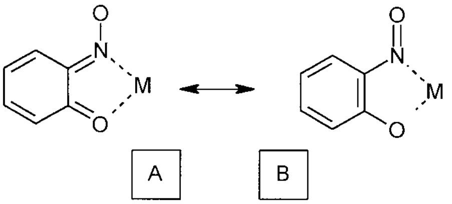


FIGURE 1

the metal orbital energy is low, charge is located in the metal-localized levels with ligands coordinated as partially reduced semiquinones [1].

Periodic trends in charge distribution for transition-metal complexes containing catecholate and semiquinone ligands are discussed in detail [50,51]. It was noted that "the most straightforward factor influencing charge distribution in the neutral $M(\mathrm{DBQ})_2$ and $M(\mathrm{DMQ})_3$ complexes is the periodic dependence of metal orbital energy [50]." For a congeneric group of metals, charge distribution may shift from $M^{\mathrm{III}}(\mathrm{SQ})_3$ for a first-row metal to $M^{\mathrm{VI}}(\mathrm{Cat})_3$ for the corresponding third-row metal. This shift appears clearly in the properties of the neutral complexes formed by members of the Cr, Mn, and Fe triads [1]. A comparison of charge distribution for $M^{\mathrm{II}}(\mathrm{DBSQ})_2$ ($M=$ Mn, Co, Ni, Cu), $M^{\mathrm{III}}(\mathrm{DBSQ})_3$ ($M=$ V, Cr, Fe), $M^{\mathrm{VI}}(\mathrm{DBCat})_3$ ($M=$ Mo, W, Tc, Re) and other metal complexes has been reported [50].

For some metal complexes of *o*-quinone monooximes, an analysis of the charge distribution within the *o*-quinone monooxime ligands through crystallographic data is reported [52]. Intermediate structures between the forms (A) and (B) can exist within these compounds (Scheme 14) [53]:

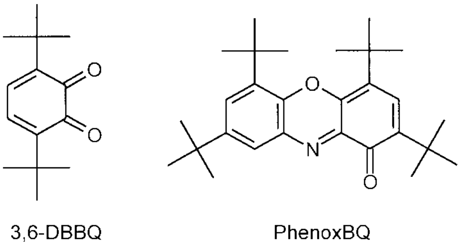


SCHEME 14

The data obtained [53] indicate that the ligands are always in an intermediate state between thee limiting forms; complexation to a *d*-metal influences the mesomeric equilibrium between these forms, causing a shift to the right.

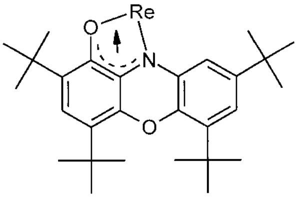
STRUCTURAL PECULIARITIES

As mentioned above, metal-quinone complexes frequently have some peculiarities in their structure due to the possibility that the ligands exist in different forms: quinone, semiquinone, and catecholate (Scheme 2). The presence of substituents also affects the structures. Thus, in the reactions between $Ru_3(CO)_{12}$ with 3,6-di-*t*-butyl-1,2-benzoquinone (3,6-DBBQ) or 2,4,6,8-tetra-*t*-butylphenoxazin-1-one (*L*), leading to $Ru(CO)_2L_2$, the presence of bulky substituents at the ring positions adjacent to the quinone oxygen atoms reduces the tendency for bridging interactions of both types and simplifies product isolation. *t*-Butyl substituents of the iminoquinone 2,4,6,8-tetra-*t*-butylphenoxazin-1-one (PhenoxBQ) may similarly block bridging interactions [54], and with the availability of these two ligands (Scheme 15), simple quinone and iminoquinone ruthenium complexes are formed from $Ru_3(CO)_{12}$ in relatively simple reactions [55].



SCHEME 15

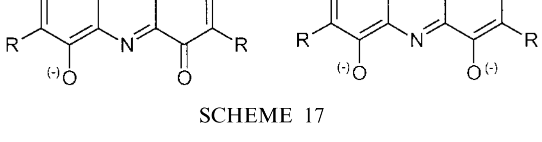
For the rhenium complex $Re(CO)_3(C_{14}H_{21}NO)(C_{28}H_{39}NO_2)$, prepared from $Re(CO)_5Br$ or $Re_2(CO)_{10}$, 3,5-di-*t*-butylcatechol (3,5-DBCat), 3,5-di-*t*-butyl-1,2-benzoquinone (3,5-DBBQ) and ammonium hydroxide [56], bond lengths can be explained by delocalization of the oxygen anion and the phenoxazinyl radical throughout the chelate ring (Scheme 16):



SCHEME 16

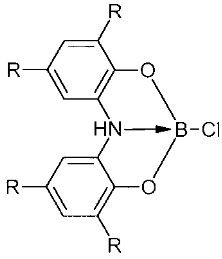
It is noted [56] that "mononuclear complexes of divalent rhenium are rare, and coordination of two different radical ligands to a single metal is also unique".

Template syntheses with the same ligand (3,5-di-*t*-butylcatechol) in the presence of ammonia with boron, aluminium, gallium, or strontium chloride, or with calcium or barium acetate produces, under oxidizing conditions, neutral complexes *ML* (*M* = BCl), ML_2 (*M* = Al, Ga, Ca, Ba), and ML_3H [57]. The ligand *L* {*bis*(3,5-di-*t*-butyl-1-hydroxy-2-phenyl)amine} can be in different oxidation states; the most important ones are the following (Scheme 17):



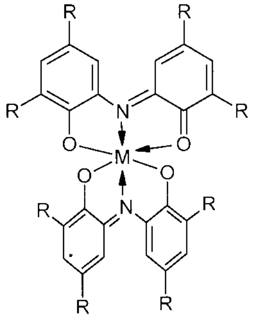
SCHEME 17

The proposed structure for the diamagnetic boron complex is as follows (Scheme 18) [57]:



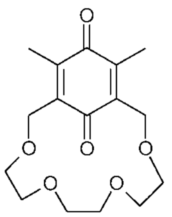
SCHEME 18

The complexes of Al and Ga are proposed to be formed by bonding two ligands in two different oxidation states (Scheme 19):



SCHEME 19

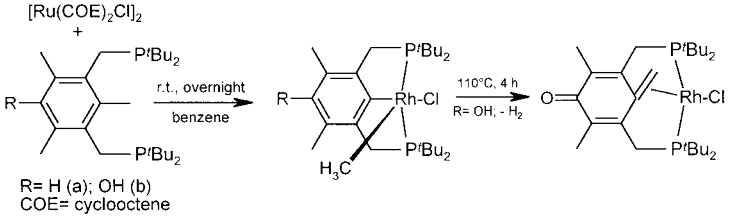
A series of Li and Na complexes with quinone crowns {such as [Li(NCS)(5QC-HQDME)] and [Na(NCS)(5QC-HQDME)] (5QC-HQDME = 15,17-dimethyl-16,18-dimethoxy-3,6,9,12-tetraoxabicyclo-[12.3.1]octadeca(1,14,16)-triene)} were obtained and structurally characterized [58]. The redox-active crown ethers used are illustrated in Scheme 20:



SCHEME 20

EPR studies demonstrated the intermolecular nature of the interaction between the cations and the ligands.

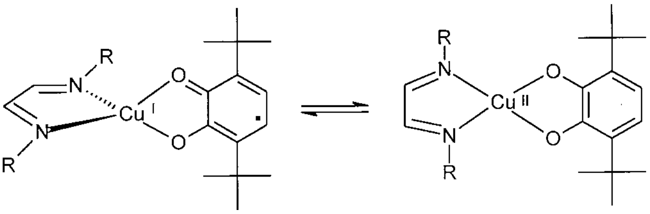
Quinone derivatives such as quinone methides (the monomethylene analogues of quinones) have also been extensively studied [59] (and references therein) because they possess biological activity, particularly as antitumor agents. The first thermally stable quinone methide, having no substituents in the methylene group ("simple quinone methide") was crystallographically characterized [59a]. Stabilization of the quinone methide can be achieved by complexation to a transition metal center (Scheme 21):



SCHEME 21

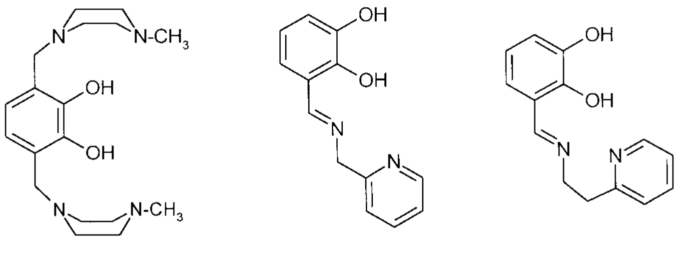
The synthesized complex does not react with air, carbon monoxide, or trimethylphosphine. It is noted [59a] that "the rhodium center is very strongly bound to the quinonoid ligand". Recently, Vaissermann *et al.* synthesized and fully characterized (even by x-ray diffraction) the first o-quinone methide complex, with Ir as the metal center [59b]. This complex is stable at room temperature, a notable difference when compared with the simplest known o-quinone methide that is unstable above -100°C [59c].

Substituted 1,4-diazabutadiene coligands complexed with Cu(3,6-DBQ) give temperature and solvent dependent EPR and electronic spectra that indicate the following equilibrium (Scheme 22) [1,30,60]:



SCHEME 22

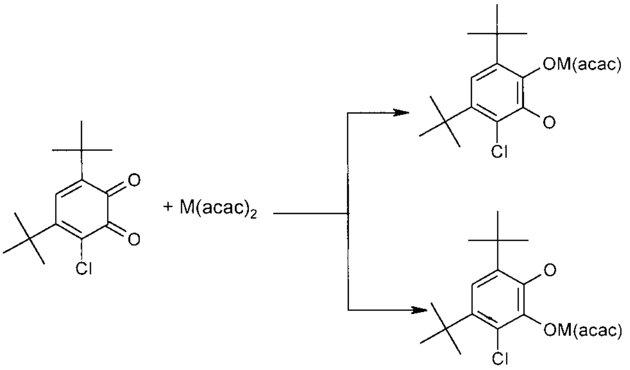
A series of catechol ligands functionalized with N-donor chelating substituents was developed (Scheme 23) [61,62]:



SCHEME 23

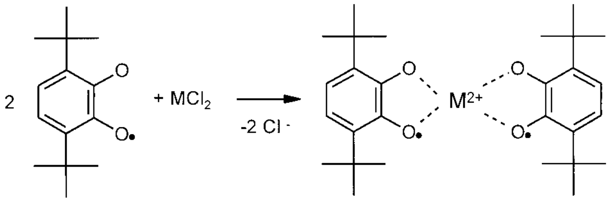
Multimetallic complexes (tetranuclear and pentanuclear with complicated structures) of these ligands which could have unique magnetic properties were prepared and studied. In the copper compex with H_2L,$^1Cu_5(OH)_2(L)_2(NO_3)_4$, all magnetic interactions within the complex unit H_2L appear to be antiferromagnetic, as well as in copper complexes with two other ligands, $\{Cu(HL^1)(NO_3)]_4$ and $[Cu_2(L_2)(OAc)_2]_2$ [63,64].

Cationotropy (migration of alkali metal cations between equivalent positions in the ionic pairs of anion-radicals), takes place because the symmetric position of a cation is not energetically beneficial. The *p*-benzo-semiquinone anion-radical and its derivatives [65,66] and later 3,6-di-*t*-butyl-*o*-semiquinone complexes of metals of the Periodic Table Groups I [67] and II [68] have been studied. The Coulombic interaction energy between the metal cation and the negative functional groups of anion-radicals (for example, oxygen atoms in semiquinones) is higher in the case of the non-symmetric position of the cation in relation to the oxygen atoms. So, a cation transferred from one position to another has an energetic barrier. Frequency and activation energy of the migration process depend on the nature of the cation solvent used and temperature. An EPR study of quinone complexes of alkali metals from $-60°C$ to $+60°C$ showed the presence of high frequencies only [67]. Studies of asymmetric complexes (Scheme 24) of group II metals showed [68] a superposition of EPR spectra of two forms, which are different thermodynamically and where a rapid exchange is absent.



SCHEME 24

In case of symmetric complexes of Group II metals, EPR spectra confirmed the following structures (Scheme 25):



SCHEME 25

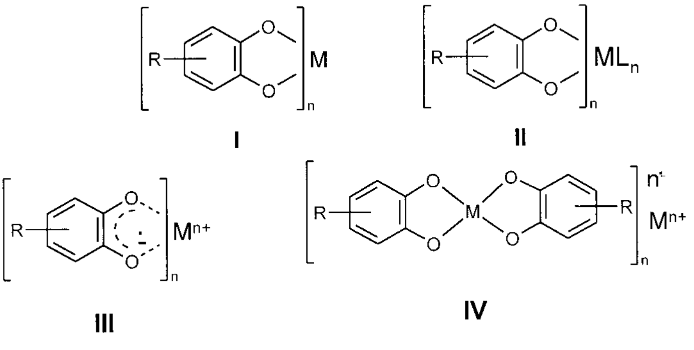
By using EPR data, the parameters of radical pairs (D/E) and the distance between radical centers (*I*) were calculated. When metal radii are increased (from Ba to Hg), *I* is also increased. Radical pairs of formed complexes are tetrahedral with *O* atoms at the top and metal ions in the center. Migration of the cation in the complex containing acetylacetonate groups takes place inside the tetrahedron formed by the oxygen atoms and the acetylacetonate ligands [68].

Thus, metal-quinone complexes have a series of peculiarities, which puts them into a special class of coordination compounds. As shown below, they can be synthesized by direct interaction between quinones and elemental metals (and also non-metals) or form their salts or complexes.

INTERACTION OF ELEMENTAL METALS AND NON-METALS WITH *o*-QUINONES

o-Quinones are extremely reactive ligands [9,69,71–83], especially those containing *t*-butyl substituents for metals. Complexes of *o*-benzoquinones, *o*-semiquinones, and catechols have been obtained by direct interaction between metal powders and the corresponding ligands [69]. Thermal decomposition of such copper complexes in solution leads to the formation of metallic copper and the initial *o*-quinone.

These compounds are radical species and play an important role in coordination chemistry [1,45,78,79]. In non-aqueous solvents (hexane, dimethoxyethane, toluene, THF, and chloroform) formation of complexes of types **I–IV** ($R = 3,5$- or $3,6,$-t-Bu_2) have been observed by EPR (Scheme 26) [69].

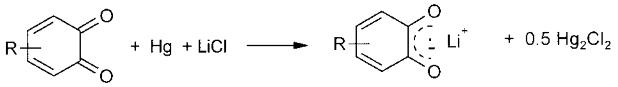


SCHEME 26

The formation of radical *o*-semiquinolates of type **I** has been detected for thallium [80], indium [74], Zinc [3,72,75], cadmium [72,75,81], magnesium [75], barium [75], aluminum [72], gallium [77], and tin [71]. The adducts II are characteristic of copper and silver ($L = PPh_3$, $m = 2$, $n = 1$) [70] and also of indium ($L =$ phen, $mn = 1$) [74]. Data on radical-anion salts of types **III** and **IV** have been presented in reviews [70,84] and other publications [71,81]. Metal complexes of catechols also can be obtained from tetrahalo-*o*-quinones, for example $Sn(X_4C_6O_2)_2$ ($X = Cl$, Br) [74].

In case of oxidation of mercury by *o*-quinones, no stable Hg-quinone complexes have been observed by direct oxidation of metallic Hg, with or without LiCl addition [85,86]. In the presence of LiCl, *o*-quinones are reduced (Scheme 27) by Hg to form

Hg_2Cl_2 and Li-semiquinone:



SCHEME 27

A detailed reaction mechanism of this reaction at different LiCl-quinone ratios was reported [85]. Among the few Hg-quinone complexes are those containing 3,5-DBCat with HgR and R {R = Et or Ge(*i*-Pr)$_3$} groups bound to different oxygen atoms have been prepared by treating HgR_2 with 3,5-DBBQ [87,88]. Also, the complex (3,6-DBSQ)Hg($B_{10}C_2H_{11}$) was obtained by photolysis of di-(carboran-9-yl)-mercury in the presence of 3,6-DBSQ [89].

The data of Ozarovski *et al.* [75] and Adams [77] are of great interest for the study of the properties and structures of type **I** complexes. Magnesium, barium, zinc, and cadmium complexes of 3,5-di-*tert*-butyl-1,2-*o*-benzoquinone (*L*) and their adducts with pyridine, 2,2′-bipyridyl, and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (L′), having the compositions ML_2 and ML_2nL' ($n = 1$, 2), were isolated and characterized in the first of these studies. Complex I and their adducts with L′ have been obtained by the reaction of the above elemental metals and ligands in toluene; detailed EPR spectroscopic studies confirmed their biradical nature and established the conformations of the biradical ligands. Two studies on the triradical gallium complex of 3,5-di-*tert*-butyl-1,2-*o*-benzoquinone **I** ($n = 3$) by Adams *et al.* and Ozarowski *et al.* [77] appeared almost simultaneously and presented similar conclusions. This compound was obtained by heating gallium and the ligand in boiling toluene (under an argon atmosphere) and was characterized by *X*-ray diffraction. The complex has the form of a three-blade propeller with the gallium atom in the center: the length of the C–C bond between the chelating oxygen atoms is 1.439(12) Å, which indicates the semiquinone nature of the ligands. It is striking that the above value differs little from the same bond (1.433 Å) in the chromium analogue, the structure of which had been characterized previously [83]. The gallium complex **I** ($n = 3$) exhibits ferromagnetic properties; its magnetic moment is 2.95 B.M. at 320 K and 3.58 B.M. at 9 K; it then again decreases and is 3.26 B.M. at 2 K.

Iminosemiquinone complexes of copper were prepared by treating metallic Cu with 2,4,6,8-tetra-*t*-butylphenoxazin-1-one (PhenoxBQ). Reactions carried out with PPh_3 gave $Cu^I(PPh_3)_2$(PhenoxSQ). Reactions carried out in the absence of coligand or in the presence of a nitrogen-donor coligand gave Cu^{II}(PhenoxSQ)$_2$ [90a]. Such copper complexes serve as models for Cu-biopterin complexes found in some metalloenzymes; similarly, PhenoxSQ complexes of iron resemble partially reduced iron-biopterin species.

Very reactive *Rieke* cadmium metal was allowed to react under vacuum with benzoquinone in THF. This resulted in the formation of several different paramagnetic species, $[Cd(C_6H_4O_2^{\bullet-})(THF)_3]^+,C_6H_4O_2^{\bullet-}$ or $\{[Cd(C_6H_4O_2^{\bullet-})(THF)_3]^+,C_6H_4O_2^{\bullet-}\}$ [90b]. The tetrahedral coordination sphere for each consists of three THF molecules and an anion radical that is asymmetrically or symmetrically coordinated to the metal dication. The original apparatus for the generation of the benzoqauinone anion radical *via* electron transfer from cadmium metal was reported [90b].

Activation of elemental metals by *mechanical methods* in the presence of solid organic acceptor molecules [69]. forms metal-polyradical complexes [82,91–94]. The radical-pair species have some unusual properties [92,93]. Compared with triplet radical pairs generated photochemically with the same donor–acceptor composition, these mechanically produced species appear to be much more stable [91]. Reaction of metals of the (IIB–VB) Groups (*M*) with di-*t*-butyl-*o*-benzoquinones (Q) provide examples of the synthesis of polyradical complexes (Scheme 28),

$$M^{n+} + nQ^{-\bullet} \rightarrow MQ^{\bullet}_{n}$$

SCHEME 28

where *n* indicates the valence state of the metal and $Q^{-\bullet}$ the semiquinone radical anion 3,5- or 3,6,-di-*t*-butyl-*o*-semiquinone or phenoxazine [91]. Such reactions occur when a toluene solution of the quinone is in contact with an amalgam of the metal (Zn, Cd, Al, Ga, In, Sn) [82,94]. For mechanochemical synthesis the mixed powder of metal and quinone is stirred in an agate or porcelain mortar at room temperature. Both synthetic techniques lead to the same di- and triradical species.

Non-metals also form complexes with quinones. Thus, elemental phosphorus reacts with $Cl_4C_6O_2$-*o*, providing a convenient one-pot synthesis (Scheme 29) of the phosphorane [10,95]:

$$0.25P_4 + 2Cl_4C_6O_{2-o} + 0.5Br_2 \rightarrow BrP(O_2C_6Cl_4)_2$$

SCHEME 29

Similarly, Te is oxidized (Scheme 30) by the same quinone [96]:

$$Te + 2Cl_4C_6O_{2-o} \rightarrow Te(O_2C_6Cl_4)_2$$

SCHEME 30

Tellurium-quinone complexes can also be obtained from Ph_2Te_2 [97]. The products in the reactions above are presented in Table I.

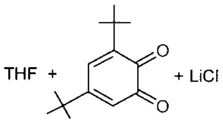
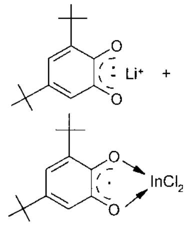
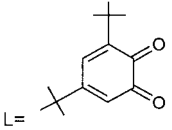
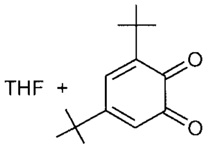
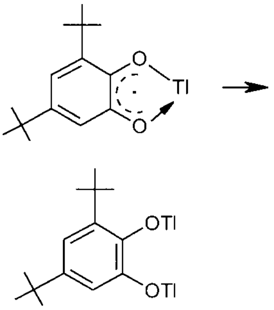
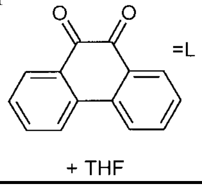
Synthesis from Metal Salts and Complexes

A series of organotin(IV) *o*-quinone complexes was prepared and characterized by Tuck *et al.* [99]. The primary process in the reaction of hexaphenylditin with 3,5-di-*t*-butyl-1,2-benzoquinone, 9,10-phenanthrenequinone, 1,2-naphthoquinone, and tetrahalogeno-*o*-quinone was shown to involve attack by the quinone at a phenyl ligand. The intermediate thus formed decomposes to yield $Ph_3Sn(SQ^{\bullet})$, where $(SQ^{\bullet-})$ is the corresponding semiquinolate. Rearrangement of these species in solution give biradicals, while intramolecular electron transfer leads to the formation and precipitation of $Ph_3Sn(Cat)$, where Cat^{2-} is the corresponding substituted catecholate. The proposed reaction sequence is presented in Schemes 31–34 [99]:

$$\begin{array}{c} Q + Sn_2Ph_6 \rightarrow SQ^{\bullet}(Ph^{\bullet})Ph_2SnSnPh_3 \\ \downarrow \\ (SO^{\bullet})SnPh_3 + {}^{\bullet}SnPh_3 \end{array}$$

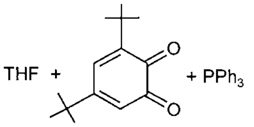
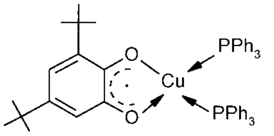
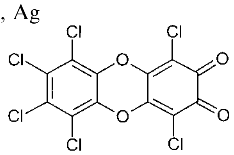
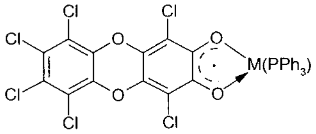
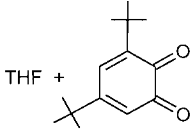
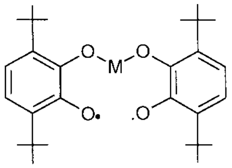
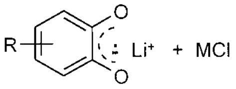
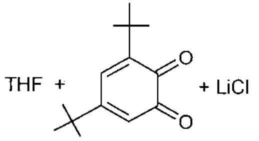
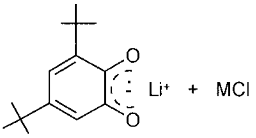
SCHEMES 31 AND 32

TABLE I Synthetic methods for obtaining metal-quinone complexes

Initial system	*Product*	*Conditions or observations*	*Reference*
a) Synthesis from elemental metals and non-metals			
$M = $ Ni, Pd, Pt; 1,2-Benzoquinone (BQ)	$M(BQ)_2$		1
In 	 In presence of phen or Et_2O: In$L^{\bullet}$phen or In$L$$Et_2O$		73, 86
Sn, Tetrahalogeno-*o*-benzoquinones $X_4C_6O_2$, toluene, N_2 ($X = $ Cl, Br) In the presence of I_2 and phen	$Sn^{IV}(X_4C_6O_2)$ $Sn_2(X_4C_6O_2)^{\bullet}$Phen		74
$M = $ Mg, Ba, Zn, Cd  in toluene, in the presence of $L' = $ pyridine, 2,2′-bipyridyl and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine	ML_2 $ML_2^{\bullet}nL'$ $(n = 1, 2)$		75
Tl 			80
Tl 	TlL		80

(*Table Continued*)

TABLE I (Continued)

Initial system	*Product*	*Conditions or observations*	*Reference*
Cu 			81
Cu, Ag 			81
Amalgam of Zn or Cd (*M*) 			82
$M = Ag, Cu, Hg$ 1) 3,5-di-*t*-butyl-1,2-benzoquinone 2) 3,6-di-*t*-butyl-1,2-benzoquinone + dimethoxyethane 3) phenanthrenequinone + dimethoxyethane 4) *o*-chlororanil			81, 86
$M = Cu, Hg$ 			86
$M = Zn, Cd, Al, Ga, In, Sn$; 3,5- or 3,6-di-*t*-butyl-*o*-semiquinone or phenoxazine	$MQ^{\cdot}_n$		91
Te RO_2: $R = Cl_4C_6$, Br_4C_6, 3,5-t-$Bu_2H_2C_6$	$Te(O_2R)_2$		96
Sb Tetrahalogeno-*o*-benzoquinones $X_4C_6O_2$, Et_2O ($X = Cl, Br$)	$Sb^V(X_4C_6O_2)_{2.5}\cdot Et_2O$ $X = Cl$, $n = 1.5$; $X = Br$, $n = 1$		119

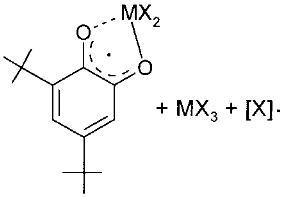
(*Table Continued*)

TABLE I (Continued)

Initial system	*Product*	*Conditions or observations*	*Reference*
b) Synthesis from metal carbonyls			
$Co_2(CO)_B$, 3,6-di-*t*-butyl-1,2-benzoquinone (3,6-DBBQ), 2,2′-*bis*(pyridine) (oxy, thio, seleno, telluro) ether Py_2X, toluene	$Co(Py_2X)(3,6\text{-}DBQ)_2$ ($X = O$, S, Se,Te)	$Co(Py_2O)(3,6\text{-}DBSQ)(3,6\text{-}DBCat)$ was obtained by recrystallization from acetone. $Co(Py_2O)(3,6\text{-}DBSQ)_2$ was obtained by recrystallization from toluene. 3,6-DBSQ is a semiquinolate form of 3,6-DBQ, 3.6-DBCat is a catecholate form.	40
$Ni(CO)_4$, 3,6-di-*t*-butyl-1,2-benzoquinone (3,6-DBBQ), CH_2Cl_2, hexane	$Ni(3,6\text{-}DBSQ)_2$	In case of 3,5-DBSQ use, the strongly paramagnetic complex (at rt) $[Ni(3,5\text{-}DBSQ)_2]_4$ is formed [120a].	42
$Ru_3(CO)_{12}$, toluene, 3,6-di-*t*-butyl-1,2-benzoquinone (3,6-DBBQ) or 2,4,6,8-tetra-*t*-butylphenoxazin-1-one (L)	$Ru(CO)_2L_2$		55
$Re(CO)_5Br$ or $Re_2(CO)_{10}$, 3,5-di-*t*-butylcatechol (3,5-DBCat), 3,5-di-*t*-butyl-1,2-benzoquinone (3,5-DBBQ), NH_3, EtOH	$Re(CO)_3(C_{14}H_{21}NO)(C_{28}H_{39}NO_2)$	Reaction takes place under photoytic conditions at 0°C under N_2. The product is a complex of divalent rhenium with three carbonyl ligands, one anionic monodentate 3,5-di-*t*-butyl-2-iminophenolate ligand, and one anionic chelating 1-hydroxy-2,4,6,8-tetra-*t*-butylphenoxazinyl ligand.	56
$Mo(CO)_6$, DBBQ	In oxygen-free atmosphere: $Mo(DBCat)_3$. In the presence of traces of O_2: $[MoO(DBCat)_2]_2$.		120b, 121
$M_2(CO)_{10}$ ($M = Mn$,Re), benzoquinone (BQ)	$M(SQ)(CO)_4$		122
c) Synthesis from metal salts			
$RuCl_3{\cdot}3H_2O$, 3,5-di-*t*-butylcatechol, KOH, CH_3OH	$Ru(DBQ)_3$	Its osmium analogue was prepared from OsO_4 and 3,5-di-*t*-butylcatechol [126,127].	50
3,5-DBBQ, Hg_2Cl_2, LiCl	Li(DBSQ)		85
In_2I_4, 3,5-di-*t*-butyl-1,2-benzoquinone (TBQ), toluene, 4-picoline (ratio $In_2I_4 : 2TBQ$)	$(TBSQ)InI(pic)_2{\cdot}C_7H_8$	When ratio $In_2I_4 : 4TBQ$ is used (without 4-picoline), $(TBSQ)InI_2$ is isolated.	100

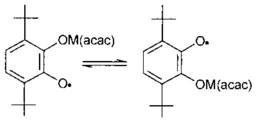
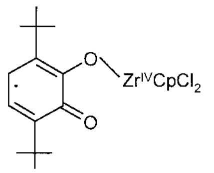
(*Table Continued*)

TABLE I (Continued)

Initial system	*Product*	*Conditions or observations*	*Reference*
InX_3 (X = Cl,Br,I), THF, $Na^+TBSQ^{\cdot -}$ (TBSQ = 3,5-di-*t*-butyl-*o*-benzosemiquinolate anion)	Solutions of the diradicals InX$(TBSQ)_2$	Addition of pyridine or γ-picoline (L) produces In(TBCat)XL_n {3,5-di-*t*-butylcatecholate-indium(III) halide adducts}.	101
5−EtaqoH$_2^+$Cl$^-$ (5-EtaqoH = 5-1,2-benzoquinone), methanol : water, K_2CO_3 or KOH	K(5-Etaqo)(5-EtaqoH)$\cdot 2H_2O$		105
$TiCl_3$, VCl_3, $GeCl_4$, $SnCl_2$ in EtOH, 3,5-di-*t*-butylcatechol	M(Cat-N-SQ)$_2$	The products can be formulated as M^{II}(Cat-N-SQ)$_2$, M^{III}(Cat-N-BQ)(Cat-N-SQ) or M^{IV}(Cat-N-SQ)$_2$, where Cat-N-SQ is the dianion of the radical ligand 3,-di-*t*-butyl-1,2-semiquinolato 1(2-hydroxy-3,5-di-*t*-butyl-phenyl)imine and Cat-N-BQ is the corresponding quinone monoanion.	106
M_2Cl_6 (M = In, La, Lu, Y, Sn), 3,5-di-*t*-butyl-1,2-benzoquinone			123–125
d) Synthesis from metal complexes			
[$Re^VO(PPh_3)_2Cl_3$], H_2Cat/air/Et_2NH	[$Re^{VII}O_2(Cat)_2$]$^-$	Using $H_2Cat/N_2/Net_3$, the anion [$Re^VO(Cat)_2$]$^-$ is formed.	1
$CoCp_2$, Ni(3,6-DBSQ)$_2$, CH_2Cl_2, hexane	($CoCp_2$)[Ni(3,6-DBCat)$_2$]		42
Ph_2Te_2, $X_4C_6O_2$-*o* (X = Cl,Br), toluene	[($X_4C_6O_2$)TeC_6H_5]$_2$O	[($X_4C_6O_2$)TeC_6H_5]$_2$O$\cdot$2-THF is formed by recrystallization of [($X_4C_6O_2$)TeC_6H_5]$_2$O from THF.	97
Sn_2Ph_6, 3,5-di-*t*-butyl-1,2-benzoquinone (TBQ) or 9,10-phenanthrenequinone (PQ), *n*-hexane or CH_2Cl_2	$Ph_3Sn(TBSQ^\bullet)$ or $Ph_3Sn(PSQ^\bullet)$		99

(*Table Continued*)

TABLE I (Continued)

Initial system	*Product*	*Conditions or observations*	*Reference*
M_2(DBA)$_3$ (M = Pd, Pt; DBA = dibenzylideneacetone), 3,5-di-*t*-butyl-1,2-benzquinone, CH_2Cl_2	Pd(DBSQ)$_2$ Pd$_2$[Pd(DBSQ)$_2$]$_2$ Pt(DBSQ)$_2$		104
M(acac)$_2$ (M is metal of II Group of the Periodic Table), 3,6-di-*t*-butyl-*o*-quinone, toluene or EtOH			128
Cp_2ZrCl_2, 3,6-DBBQ		hν	129

followed by

$$2^{\bullet}SnPh_3 \rightarrow Sn_2Ph_6$$

SCHEME 33

or

$$Q + {}^{\bullet}SnPh_3 \rightarrow Ph_3Sn(SQ^{\cdot})$$

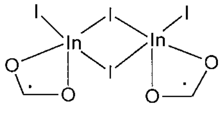
SCHEME 34

The comparable sequence for Ph_4Sn, which was also used as a precursor of tin-quinone complexes and gives related products, is shown in Scheme 35:

$$Q + Ph_4Sn \rightarrow SQ^{\bullet}(Ph^{\bullet})SnPh_3 \rightarrow Ph_3Sn(SQ^{\bullet}) + Ph^{\bullet}$$

SCHEME 35

Similarly, the reaction of In_2I_4 (having the structure $In^+[InI_4]^-$ in the solid state) with substituted *o*-benzoquinones proceeds *via* attack of the quinone on the solvated In^+ cation which is present in solutions of In_2I_4 in toluene [100]. The final products have compositions (SQ)InI_2 or (SQ)InI_2(pic)$_2$ (pic is 4-picoline), depending on the particular *o*-quinone and on the reaction conditions. It is proposed [100] that (SQ)InI_2 complexes with phenantrene-9,10-quinone, tetrabromo-*o*-benzoquinone, and 1,2-naphthoquinone as ligands exist in the form of halide bridged dimmers (Scheme 36):



SCHEME 36

The reaction of indium(III) halides ($X = \mathrm{Cl}$, Br, 1) with 2 mol of $\mathrm{Na^+TBSQ^{\bullet -}}$ (TBSQ = 3,5-di-*t*-butyl-*o*-benzosemiquinolate anion) yields (Scheme 37) solutions of diradicals $\mathrm{In}X\mathrm{(TBSQ)_2}$ [101]:

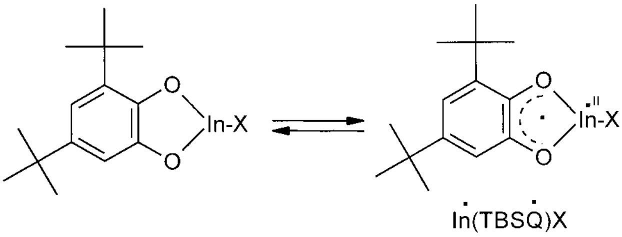
$$\mathrm{In}X_3 + 2\mathrm{NaTBSQ^\bullet} \rightarrow \mathrm{In(TBSQ^\bullet)_2}X + 2\mathrm{Na}X$$

SCHEME 37

Addition of pyridine or γ-picoline (L) to the complexe produces $\mathrm{In(TBC)X}L_\mathrm{n}$ {3,5-di-*t*-butylcatecholate-indium(III) halide adducts}. The product recrystallized from DMF with composition $[\mathrm{In(TBC)}L\mathrm{(pic)_2} \cdot 2\mathrm{DMF}$ belongs to the monoclinic crystal system with space group $P2_1/n$. The dimeric nature of this molecule is its most interesting feature, involving an $\mathrm{In_2O_2}$ four-member ring, with In–O distances of 2.216(6) and 2.146(5) Å. The detailed reaction mechanisms of formation of indium-quinone complexes [101], included two steps (Schemes 38–39), in particular, an initial loss of a neutral ligand in toluene solution of $\mathrm{In(TBC)}XL_n$ and further internal electron transfer which "allows the indium(III) catecholate species to function as an indium(III) semiquinone":

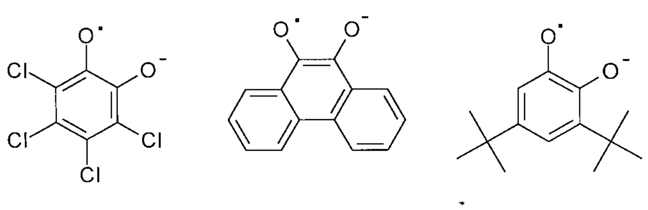
$$\mathrm{In(TBC)}XL_n \Longleftrightarrow \mathrm{In(TBC)}X + nL$$

SCHEME 38



SCHEME 39

A series of *o*-semiquinone (SQ) (Scheme 40) complexes of Fe(III) and Cr(III) of general formula $\mathrm{M(SQ)_3}$ have been described [102].

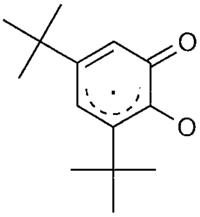


$o\text{-}\mathrm{Cl_4SQ^-}$ phenSQ$^-$ 3,5-DBSQ$^-$

SCHEME 40

The complexes were characterized by x-ray diffraction and magnetic measurements [57]. Fe Moessbauer spectroscopy data for $\mathrm{Fe(SQ)_3}$ complexes are consistent with the iron ion being high-spin iron(III) [102, 103a].

Reactions carried out with $M_2\mathrm{(DBA)_3}$ ($M = \mathrm{Pd}$, Pt;. DBA = dibenzylideneacetone) and 3,5-di-*t*-butyl-1,2-benzquinone gave as major products the $\mathrm{M(DBSQ)_2}$ complexes [103b]. In the case of palladium, an additional product $\mathrm{Pd_2[Pd(DBSQ)_2]_2}$ was detected, whose molecular structure consists of two planar *cis*-Pd(DBSQ)$_2$ units bridged by two Pd atoms. The Pd atoms are "sandwiched" between semiquinone rings of adjacent Pd(DBSQ)$_2$ units with three Pd–C lengths and an allyl structure for the semiquinone rings (Scheme 41):

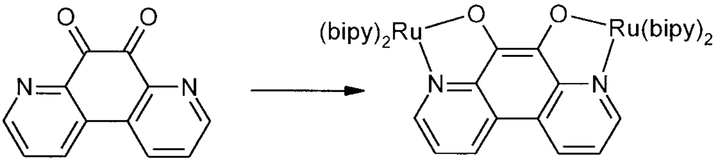


SCHEME 41

It was noted [103b] that magnetic exchange between radical semiquinone ligands results in the near diamagnetism of M(DBSQ)$_2$ (M = Pd, Pt).

Similar molybdenum chain compounds [Mo$_2$(O$_2$CCF$_3$)$_4L$]$_n$ (L = 9,10-anthraquinone or 2,6-dimethylbenzoquinone) were prepared and characterized by x-ray structure analyses, ^{13}C-NMR spectrum, and cyclic voltammetry [104a,b]. When 2,6-di-*t*-butyl-*p*-benzoquinone (2,6-*t*-Bu-BQ) was used, a *bis*-*p*-quinone adduct [Mo$_2$(O$_2$CCF$_3$)$_4$ (2,6-*t*-Bu-BQ)$_2$] was isolated [104b].

State paramagnetic binuclear complexes {[Ru(bipy)$_2$]$_2$(μ-L)}$^{3+}$ with L being N,O; N′,O′-coordinating 4,7-phenantroline-5,6-semidione and P,O; P′,O′-coordinating 2,5-*bis*(diphenylphosphino)-*p*-benzosemiquinone were reported [104c]. An *o*-semiquinone phdo$^{\bullet-}$ complex is formed as follows (Scheme 42):



SCHEME 42

Spectroscopic and EPR data showed that these binuclear semiquinone complexes are situated at the borderline between anion radical complexes and metal-centered mixed-valent dimers.

Although most of metal-quinone compounds involve transition metals, alkali metal-quinone complexes have also been reported. Additionally to Li-3,5-di-*t*-butyl-1,2-benzoquinone, the potassium complex K(5-Etaqo) (5-EtaqoH)·2H$_2$O (5-EtaqoH = 5-ethylamino-4-methyl-1,2-benzoquinone), obtained from potassium carbonate as starting salt, was prepared [105a]. The potassium atom in this complex is coordinated to one neutral and one ionic ligand *via* the oxime nitrogens and the quinonoid carbonyl oxygen forming a five-membered chelate ring. The metal is therefore coordinated to seven donor atoms and is in a distorted pentagonal bipyramidal environment.

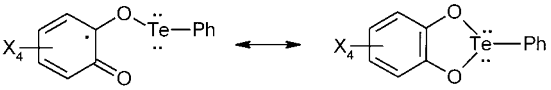
Additionally to complexes of a variety of metals and substituted *o*-benzoquinones [69], the unusual tellurium(IV) derivatives [(X_4C$_6$O$_2$)TeC$_6$H$_5$]$_2$O (X = Cl, Br) were obtained from tetrahalogeno-*o*-benzoquinones and diphenyl ditelluride [97] (see also the reaction in Scheme 30, with use of elemental tellurium). The reaction pathway includes three steps: the reduction of *o*-quinone to catecholate, the oxidation of tellurium from + 1 to + 4 with the retention of the Te-C_6H_5 linkage, and the cleavage of the Te–Te bond of $(C_6H_5)_2Te_2$ (Schemes 43–44) [97]:

$$Ph_2Te_2 \rightarrow PhTe^{\cdot}$$

$$PhTe^{\cdot} \rightarrow (SQ^{\cdot})TePh$$

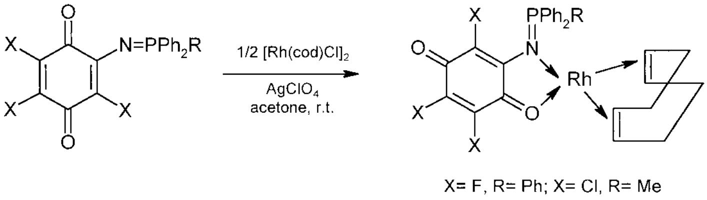
SCHEME 43 AND 44

The intramolecular electron transfer process (Scheme 45) is typical for Q/SQ/Cat ligand systems.



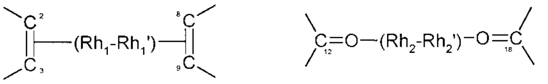
SCHEME 45

p-Quinones also produce complexes of various types with transition metals, acting as a bridge-type ligand. Thus, the reaction shown in Scheme 46 of substituted *p*-quinones with $[Rh(cod)Cl]_2$ and $AgClO_4$ in acetone at 25°C gives complexes in high yields (69–73%) [105b]:



SCHEME 46

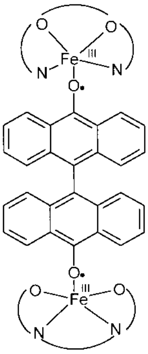
The reaction of rhodium(II) pivalate dimer, $Rh_2(O_2CCMe_3)_4$, with 1,4-benzoquinone (BQ) in hexane gave a chain complex, $[Rh_2(O_2CCMe_3)_4\ BQ]_n$, where the rhodium(II) pivalate dimers are connected by the *p*-quinone through its carbonyl oxygen or C=C double bond, working here as a bifunctional ligand, i.e. the chain structure consists of two kinds of dimer units (Scheme 47) [105c–e]:



SCHEME 47

Rhodium complexes with derivatives of *p*-quinone (1,4-napthoquinone and 2,3-dimethyl-1,4-benzoquinone) were also reported [105d].

The molecule Fe^{II}(salen) (salen = *N*,*N'*-ethylene*bis*(salicylideniminate) reacts with *p*-quinones (1,4-benzoquinone and its derivatives, 1,4-naphthoquinone, and biantrone) to give a compound $[Fe(salen)]_2Q$, where Q is the quinone moiety [105f]. The compound consists of high-spin ferric ions bridged by the dianion of a hydroquinone. It was suggested that the metal ions are oxidized to *M*(III) and the bridge Q is the dianion of the hydroquinone. The ^{57}Fe Mössbauer data and magnetic measurements (μ_{eff} = 5.1–5.7 B.M. at 285.5 K) indicated that in all compounds there is only one type of iron site, most likely a high-spin Fe(III) ion. For the biantrone complex, the following structure was suggested (Scheme 48):



SCHEME 48

There is a cobalt *p*-quinone adduct with *N*,*N*′-ethylene*bis*(salicylideniminate). *o*-Quinone complexes with the same ligands have the composition 1 : 1 [Fe(salen)Q] (Q = 9,10-phenanthrenequinone and 1,2-naphthoquinone) complex $[Co(salen)(py)]_2Q$ [105g].

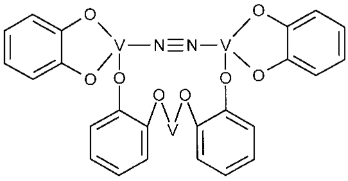
The resulting products in the reactions above are presented in Table I.

APPLICATIONS

Quinone functionalities appear as components in organic switches, and the coupled redox chemistry of quinones with transition metals may provide the basis for an organo-transition metal switch [40]. A system that may exhibit light-induced switching was studied by a quinone-tethered form of $Ru(bipy)_3^2+$ [108], but the charge-separated state that results from the Ru(II) → Q electron transfer is short-lived [40,108].

A triple catalytic system consisting of $Pd(OAc)_2$, hydroquinone, and a transition metal macrocycle (for example, iron phthalocyanine) was reported [109]. The catalysis occurred by the interaction of Pd(II) with the substrate and two electrons, which are transferred to the benzoquinone that is reduced to hydroquinone. The hydroquinone is then reorganized to benzoquinone by the O_2/metal macrocycle system. 1,4-oxidation of conjugated dienes, oxidation of terminal olefins to methyl ketones, and allylic oxidation were carried out in mild conditions using the developed system.

Vanadium(II)–catechol systems can be useful in fixation of atmospheric nitrogen, reducing it to ammonia [110–112]. A detail EPR study concluded that the active catalyst is a trinuclear V-Cat species (Scheme 49) [1,112,113]:



SCHEME 49

A simple and effective chemical method, based on their reaction with metallic zinc and zinc ions, was developed for quantitatively reducing quinones [114]. Comparison of this method with conventional electrochemical reduction [115–118] revealed the chemical method to be considerably superior. A reduction reaction of vitamin K_1 and other quinones in the presence of Zn^0 and Zn^{2+} eliminates the need to apply large negative potentials and may also be performed in the absence of an applied electrochemical potential. Some quinones used such as UQ-10, menadione and vitamin K of the menaquinone series (MKs 4–10) could all be reduced to their corresponding hydroquinones in these conditions.

Tc-catecholate complexes could have potential medicinal organ-imaging applications. Some of these complexes were synthesized with this purpose, in particular $[TcO(Cat)_2]^-$ [4] and $[TcO(Cl_4Cat)_2]^-$ [5]. If the last complex is treated with *N*,*N*-diphenylhydrazine, the dimeric anion $[Tc(NNPh_2)Cl_4Cat)_2]^-$, containing a Tc–Tc bond, is formed. Other Tc-quinone complexes can be obtained by β decay of $^{99}MoO_4^{2-}$ which further reacts with catechol producing $Tc^{VI}(DBCat)_3$ [47].

CONCLUSIONS

Direct evidence for the formation of radical *o*-quinone (and sometimes *p*-quinone) complexes was established in the studies quoted above. Various synthetic techniques starting from elemental metals, non-metals, metal salts, and complexes have been developed for obtaining these coordination compounds. The peculiarities of their structure and physical-chemical properties were investigated. The obtained products have practical applications, in particular for medical purposes. Quinone-based metal complexes have the potential applicability as co-catalysts on a wide range or reactions involving electron exchange between substrate and catalysts. Further studies on this field and on mechanisms of electron mobility between the metal center and the *o*-quinone ligands, are still necessary to understand the vast and complex redox chemistry of these compounds.

Acknowledgements

The authors are very grateful to *Universidad Autónoma de Nuevo León* (Monterrey, Mexico) for financial support (project PAICyT CA362-00), CONACyT-Mexico (MRMA partial scholarship 134716), and to Prof. Cortlandt Pierpont (University of Colorado) for useful comments.

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