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TRANSITION METAL COMPLEXES OF *o*-BENZOQUINONE, *o*-SEMIQUINONE, AND CATECHOLATE LIGANDS

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CONTENTS

A. INTRODUCTION

Quinone and quinoid molecules occupy a special position in the areas of organic and biochemistry [1]. The coordination chemistry of these potential ligands with transition metals has been relatively slow in development. Scattered accounts of complexes prepared with *o*-benzoquinone, catecholate and hydroxyquinone ligands appeared prior to 1975. In most cases characterization was confined to elemental analyses. As ligands, the quinones were not given nearly the attention received, for example, by the acetylacetonates [2], aromatic and aliphatic diimines [3], or chelating sulfur donor ligands [3,4]. Prior to 1975 there was but one structural report in the literature on a chelated quinone complex [5]. This general class of com-

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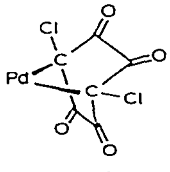
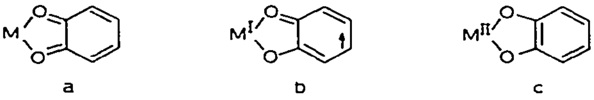
pounds shows a marked tendency to form solvates which are often nonstoichiometric after a few hours at room temperature. This obviously complicates interpretation of analytical data and structural work carried out over the past few years has shown that many of these early compounds had been mischaracterized or have unexpected structural features. To illustrate this, a relatively simple Pd(II) complex of the chloranilate ion was shown structurally to have the ring bonded through carbon atoms (I) [6].



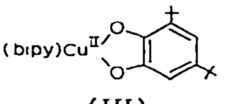
(I)

The primary focus of our review will be complexes containing *o*-quinone ligands. We will not deal with complexes of *p*-quinones [7] or hydroxyquinones. From the point of view of a coordination chemist benzoquinones exhibit two fundamental properties in common with transition metal ions. They show redox behavior at easily accessible (and chemically useful) potentials and they are able to fix substrate molecules by donor–acceptor complexation [8]. The electronic structure of the metal–quinone chelate ring can be viewed in terms of three isoelectronic forms related by the distribution of formal charge over ligand and metal (II). Copper complexes of



(II)

3,5-di-t-butylcatechol show a ligand dependence which illustrates this behavior. With nitrogen donor ligands a Cu(II)-catecholate complex is obtained (III) [9], but with phosphorus donors EPR spectra indicate semiquinone coordination to Cu(I) (IV) [10]. A fourth possibility is a fully



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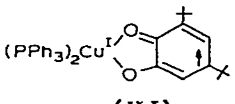


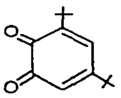
(IV)

delocalized chelate ring of the type found for the oxidized 1,2-dithiolene complexes [4a]. To our knowledge there is no evidence which shows significant delocalization within the metal–quinone chelate ring for any complex.

The various bonding descriptions shown above can be induced either chemically or electrochemically by the addition or removal of charge from ligand localized electronic levels by interaction with some external species (i.e. chemical agent, electrode surface). The tris(semiquinone)chromium(III) complexes show a seven membered redox series corresponding to stepwise oxidation to a cationic tris(*o*-benzoquinone)chromium(III) species or reduction to a tris(catecholato)chromium(III) trianion (V) [11].

$$\mathrm{Cr(BQ)_3^{3+}} \xleftarrow{-3e^-} \underset{\text{(V)}}{\mathrm{Cr(SQ)_3}} \xrightarrow{3e^-} \mathrm{Cr(Cat)_3^{3-}}$$

Nomenclature has proven to be a problem in reference to ligands of complexes where charge of metal has not been resolved. In our publications we have used the term "quinone" [12] to refer generally to ligands where charge assignment has not been established and more specific terms (*o*-benzoquinone(BQ), *o*-semiquinone(SQ), catecholate(Cat)) for well defined systems. Most of the work in this area has been carried out with three ligands in their various electronic forms: 3,5-di-t-butylbenzoquinone (VI), 9,10-phenanthrenequinone (VII), and tetrachloro-1,2-benzoquinone (VIII).



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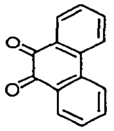

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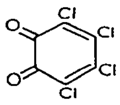
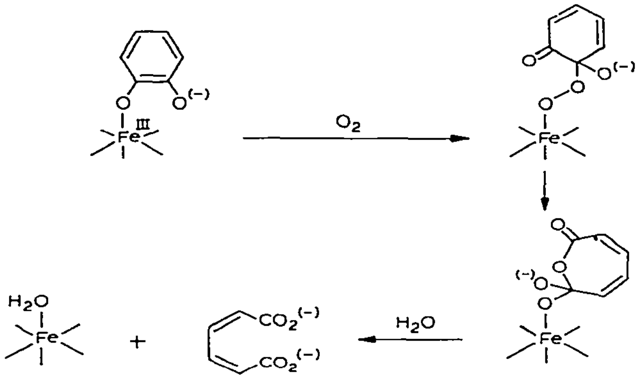


(VIII)

Much of the recent interest in catecholate ligands has been related to their affinity for ferric iron. Biologically, a specific iron sequestering agent (siderophore) known as enterochelin, found in enteric bacteria uses three catecholate groups to encapsulate the ferric ion [13]. Raymond and co-workers [13,14] have estimated a formation constant of 10^{52} for this complex! The coordination chemistry of tris(catecholato)iron(III) complexes has been thoroughly studied in this context by Raymond and recently extended to the development of chelating agents to be used in the treatment of Cooley's anemia [15]. An iron–catechol complex seems to occur in the biological oxidation of aromatic natural products, including lignin, catalyzed by dioxygenase enzymes [16]. Apart from the biological interest in the function of the pyrocatechase enzymes it is important to understand their mechanism of action to design catalysts which are capable of solubilizing aromatic polymers by oxidation to aliphatic carboxylic acids. Wood et al. have presented a mechanism which involves a peroxide intermediate coordinated to a ferric iron center (IX) [17]. Other work with synthetic copper catalysts has successfully led to the oxidation of *o*-benzoquinones, catechols and phenols. Dioxygen in one of these systems seems to serve to regenerate the Cu(II) catalyst by oxidation of a Cu(I) product [18].



(IX)

On a more fundamental level metal–quinone electron transfer reactions of the type that would relate the various electronic forms above (II) can provide specific information on the nature of ligand–radical species which are often the products of outer-sphere electron transfer processes and kinetic information on inner-sphere electron transfer. This is also tied to a more specific problem concerning metal–quinone electron transfer reactions which have been found to occur in mitochondria and in bacterial photosynthetic systems [19,20].

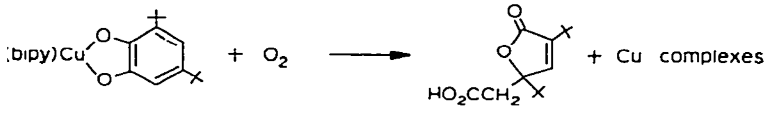
Our review will begin with a discussion of the synthetic procedures used in the preparation of catecholate, *o*-semiquinone, and *o*-benzoquinone complexes. The structural section which follows shows the unique geometric features of these complexes and points to the essential role which crystallography has played in their characterization. The semiquinone complexes are interesting examples of molecules containing paramagnetic ligands. Magnetic susceptibility measurements and EPR experiments have provided fundamental information on the electronic structure of these complexes and the results of these experiments are described in the third section. The final section of the review deals with inter- and intramolecular electron transfer reactions involving the quinone complexes, and their potential utility as electrocatalysts.

B. SYNTHETIC METHODS

Preparative procedures for catecholate and *o*-benzoquinone complexes date back to the turn of the century. Semiquinone complexes of transition metal ions are a more recent development. Implicit in this discussion is our ability to assign a formal charge to the quinone ligands of a given compound. In most cases this is relatively straightforward.

(i) Catecholate complexes

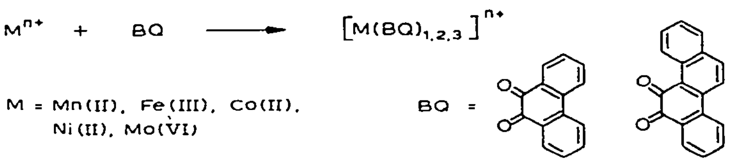
Very early syntheses of catecholate complexes were reinvestigated by Weinland and formed the basis for a comprehensive survey during the period from 1910 to 1930 [21]. Nearly all first row transition metals were included as well as many larger transition and post transition metals. Formulations for these compounds, based on chemical analyses, were in some cases unusual. From 1930 to 1960 there was relatively little activity on the coordination chemistry of catechols. More recently new research interests and improved methods of analysis have led to further examination of the early compounds as well as the development of new synthetic procedures. Holm and coworkers have thoroughly characterized bis(catecholato) complexes of Co(II), Ni(II), Cu(II) and Zn(II) as an extension of their work with 1,2-dithiolene and diimine ligands [22]. Several reports have appeared that deal with molybdenum [23] and vanadium [24] species including kinetic and mechanistic studies. Dolcetti and co-workers have prepared a series of catecholate-nitrosyl complexes with Rh(I) and Ir(I), and examined their activity as hydrogenation catalysts [25]. The biological relevance of catechol complexes has been recognized. Raymond has investigated the tris (catecholato)iron(III) and chromium(III) complexes as part of a larger study on biological chelating agents involved with iron transport [26]. Brown has been interested in the function of dioxygenase enzymes which catalyze the oxidation of catechols and has examined Cu(II) catecholate complexes (X) in this context [9,27]. The electrochemical properties of manganese catecholate systems have been studied by Sawyer and co-workers to better understand the role of manganese cofactors in biological electron transfer processes [28]. Synthetic methods used in these reports amount to addition of catecholate ion directly to the oxidized metal, often under anaerobic conditions.



(X)

(ii) o-Benzoquinone complexes

As diketones the unreduced *o*-benzoquinones are weak donor ligands and are easily displaced from a coordinated metal ion. Complexes have been prepared under anhydrous conditions with the earliest reports dating back to the turn of the century [29]. The most complete recent report discusses metal complexes prepared with 9,10-phenanthrenequinone and 1,2-chrysenequinone [30]. Crowley and Haendler used a relatively simple procedure to form mono, bis and tris quinone products (XI). The coordinated benzoquinones

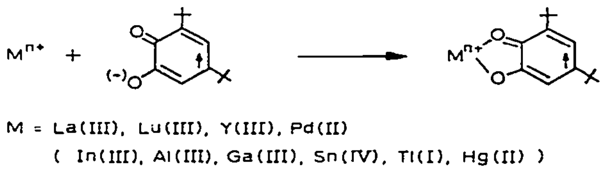


(XI)

show a characteristic decrease of approximately 50 cm^{-1} in the carbonyl stretching frequency upon coordination.

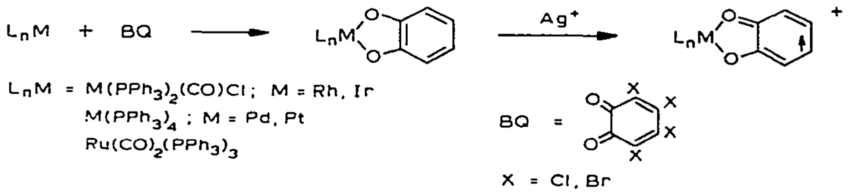
(iii) o-Semiquinone complexes

Synthetic routes to transition metal complexes of *o*-semiquinones have been developed mainly over the past fifteen years. A number of relatively simple compounds consisting of a single semiquinone bonded to a diamagnetic metal ion are known. Razuvaev and co-workers have prepared a large number of complexes of this general type by treating a metal halide directly with 3,5-di-t-butyl-semiquinone (XII) [31]. Balch has synthesized catecholate



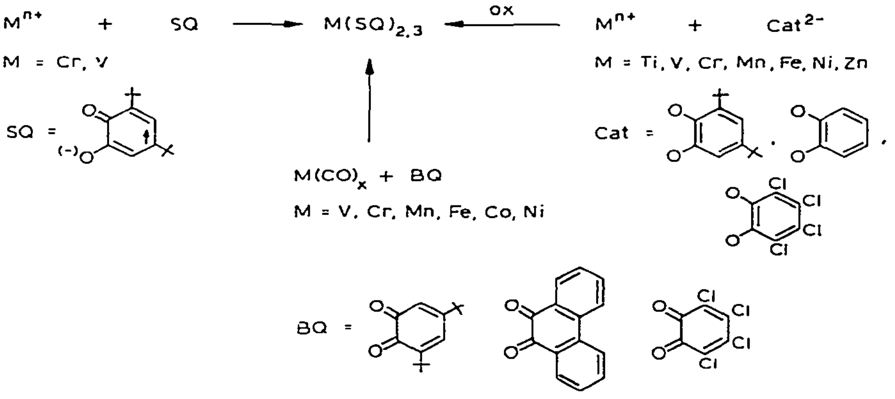
(XII)

adducts of platinum group metals by the oxidative addition of benzoquinone (XIII) [32]. The coordinated catechol can then be oxidized to the semi-



(XIII)

quinone with silver ion. Brown and Hemphill have also found that catecholate ligands coordinated to Co(III) are subject to chemical oxidation [33]. Both Brown and Hemphill [33] and Hendrickson and co-workers [34] have noted that *o*-benzoquinones undergo a one electron reduction upon addition to Co(II)–Schiff base complexes. Electron spin resonance has played an important role in the characterization of these compounds. There are inherent difficulties in the characterization of complexes containing two or more semiquinone ligands or complexes containing semiquinones coordinated to paramagnetic metal ions using magnetism or EPR methods. The neutral bis and tris semiquinone complexes of di- and trivalent metal ions are more complicated examples of semiquinone coordination. It is currently our view that first row transition metal complexes of this form do indeed contain semiquinone ligands. Related complexes prepared with second or third row metals contain catecholate ligands with higher oxidation states for the central metal ions. This appears from the comparison of $Cr(O_2C_6Cl_4)_3$ [35] with $Mo(O_2C_6Cl_4)_3$ [36] and $Fe(O_2C_6H_2(t\text{-}Bu)_2)_3$ [37] with $Os(O_2C_6H_2(t\text{-}Bu)_2)_3$ [38]. The Cr and Fe complexes are of form $M^{III}(SQ)_3$ while the Mo and Os analogs contain hexavalent metal ions, $M^{VI}(Cat)_3$. There are three general procedures which have been used in the synthesis of $M(SQ)_{2,3}$ complexes as shown in the scheme below. Products obtained from these

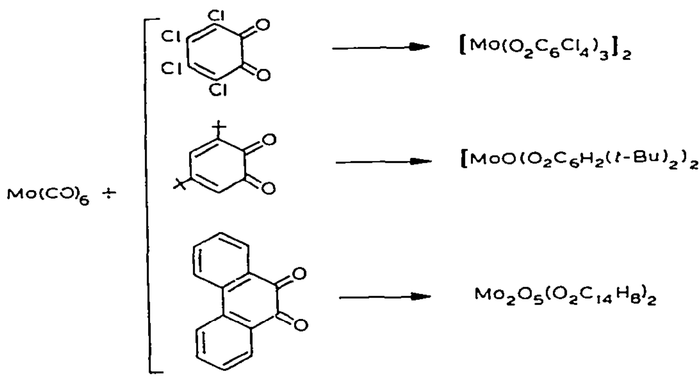


(XIV)

reactions are generally tris(semiquinone) species will all metals except Mn, Ni, Co and Zn which form oligomeric bis complexes. Wilshire and Sawyer, however, have reported a bis vanadium complex, $V(O_2C_6H_2(t\text{-}Bu)_2)_2$, which has been formulated as a V(IV) species [24d]. This complex is quite interesting since it appears to bind small molecules, O_2, NO, CO. Initial products obtained with the catecholate procedure above are anionic and require an oxidizing agent. The 3,5-di-t-butylcatechol ligand has been most widely used in this procedure with tetrachlorocatechol and catechol used to a lesser extent [39]. Razuvaev and co-workers have used 3,5-di-t-butylsemiquinone to prepare neutral Cr and V complexes directly [40]. The third procedure starting with a metal carbonyl and the unreduced form of the ligand was first used by Holm and co-workers [22] and later Calderazzo [41]. We have employed this method in our investigations and found it to be the most convenient in terms of product isolation and purification [42]. This is not to imply that characterization has been routine. Both the semiquinone and catecholate complexes have a marked tendency to form solvates and this leads to ambiguous or erroneous analytical data even for highly crystalline samples. The tris(tetrachlorosemiquinone) complexes of V, Cr and Fe illustrate this point. When prepared in benzene or toluene they are obtained as crystalline tetrasolvates, $M(O_2C_6Cl_4)_3 \cdot 4C_6H_6$. The solvent is not tightly bound in the crystal lattice and is slowly displaced over the course of days at room temperature. Tris(9,10-phenanthrenesemiquinone)iron is another example [37]. It is obtained from the reaction mixture as crystalline "$Fe(phen)_4$" which has been shown to actually be $Fe(9,10\text{-}phenSQ)_3 \cdot phen$. Crystallographic molecular structure determinations have proven to be a necessary method of characterization for many of the compounds of this series. The bis complexes of Co, Ni and Zn appear from their solubility properties to be oligomeric or polymeric. Only the Mn, Ni and Co complexes of 3,5-di-t-butyl-semiquinone have been characterized in detail [43]. Structural work has shown them to be tetrameric, $[M(O_2C_6H_2(t\text{-}Bu)_2)_2]_4$, with octahedral, divalent metal ions. We have further found that the oligomeric structure can be broken up with nitrogen base ligands. Monomeric $Co(O_2C_6H_2(t\text{-}Bu)_2)_2(bipy)$ can be prepared by treating the tetramer with 2,2′-bipyridine [44], and monomeric $M(9,10\text{-}phenSQ)_2py_2$ ($M = Co,Ni$) complexes can be obtained from the bis(phenanthrenesemiquinone) complexes with pyridine [45].

As an additional point of interest, we have found that the metal carbonyl reactions carried out with phenanthrenequinone require irradiation, while related reactions with the other two quinones occur thermally. In fact, the oxidative addition of phenanthrenequinone to $Ir(PPh_3)_2(CO)Cl$ [46] and even SO_2 [47] have been reported to be photochemical.

The scope of the metal carbonyl reaction has so far been limited mainly to metals of the first transition series. Only molybdenum of the larger metals has been investigated in detail and the results of these studies have produced



(XV)

quite different results (XV). In all cases Mo(VI) species are obtained and only with tetrachloro-1,2-benzoquinone is a tris complex obtained directly [36]. Crystallographic characterization has further shown that the complex is dimeric. Products obtained with the two other quinones are oxomolybdenum(VI) species. The dimeric product of the 3,5-di-t-butylbenzoquinone reaction is $[MoO(O_2C_6H_2(t\text{-}Bu)_2)_2]_2$ which has also been prepared by treating Mo(VI) directly with the catechol [23c,48]. With 9,10-phenanthrenequinone the reaction occurs photochemically yielding $Mo_2O_5(O_2C_{14}H_8)_2$ with semiquinone ligands [49]. This complex has been used as a precursor for $Mo(O_2C_{14}H_8)_3$, although the details of this synthesis remain something of a mystery [50]. All products obtained by these procedures are air stable and the unusual sensitivity of the Mo complexes to the nature of the quinone is not understood.

C. STRUCTURAL STUDIES

Structural investigations have proven essential to the characterization of quinone complexes. Metal–oxygen bond lengths are often characteristic of a particular oxidation state for metal; quinone carbon–oxygen lengths are sensitive to the charge of the ligand. Apart from providing indirect information on the charge distribution within the complex, crystallographic studies have revealed a unique tendency for donor–acceptor complexation with a variety of unsaturated molecules. Nearly all the work in this area has appeared since 1975. Only one detailed report on a transition metal quinone complex appeared in the literature prior to this year. A review of the publications which have appeared since, shows that it is possible to classify ligands in most complexes as either catecholate, semiquinone, or benzoquinone. In many cases there is supplemental spectroscopic or magnetic evidence to corroborate this assignment. Indeed, in two cases we have found evidence to suggest mixed valency for quinone ligands within a single complex molecule. In no case have we found evidence for the type of chelate ring delocalization associated with the sulfur analogs of the quinones, the 1,2-benzenedithiolate ligands [3,4a].

(i) Catecholate complexes

The first detailed crystallographic report on a transition metal quinone complex appeared in 1972 [5]. Atovmyan et al. reported the structural features of a molybdenum catecholate complex first reported by Weinland as the "$MoO_3(Cat)^{2-}$" ion. The result of the structural study showed that it was actually $Mo_2O_5(Cat)_2^{2-}$ and has a coordination geometry which we have since found in two other related oxomolybdenum(VI) quinone complexes. A

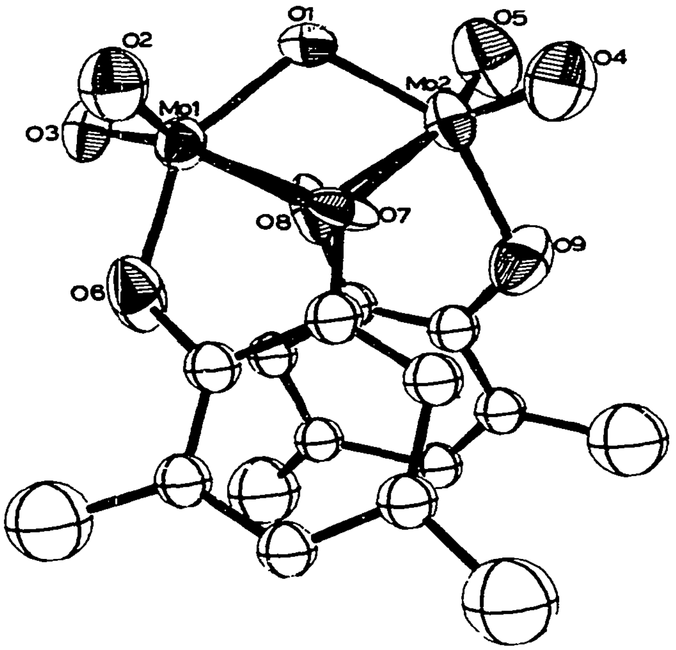


Fig. 1. View of the $Mo_2O_5(3,5\text{-DBCat})_2^{2-}$ anion. Methyl carbon atoms of the tert-butyl groups have been omitted.

view of the 3,5-di-t-butylcatecholate analog, $Mo_2O_5(3,5\text{-DBCat})_2^{2-}$, prepared by treating $[MoO(3,5\text{-DBCat})_2]_2$ with strong base, is shown in Fig. 1 [51]. Bond lengths for catecholate ligands of this and other complexes of this section are given in Table 1. We have also observed this geometry for neutral $Mo_2O_5(\text{phenSQ})_2$, a semiquinone complex with two fewer electrons than the two catecholate complexes [49]. The pentaoxodimolybdenum fragments in all three complexes show only minor variations in structure.

Atovmyan has also reported structural work on a second Weinland complex, $MoO_2(\text{Cat})_2^{2-}$. The complex has a *cis*-dioxomolybdenum structure characteristic of Mo(VI) [52]. A feature which may be significant in terms of the ability of catecholate ligands to destabilize oxo ligands coordinated to Mo(VI) is the unusually long Mo–O length of 1.77(2) Å to the oxo oxygen atoms. A value which is approximately 0.1 Å shorter would be more consistent with other *cis*-dioxomolybdenum(VI) species. We have prepared and characterized structurally the neutral complex related to this anion by loss of one oxo ligand, $MoO(3,5\text{-DBCat})_2$ [48]. The molecule is monomeric in coordinating solvents but is dimeric in solid state. A view of the dimer is shown in Fig. 2. Adjacent oxomolybdenum(VI) centers are bridged by catecholate oxygens in the same manner found for the $Mo_2O_5(\text{Cat})_2^{2-}$

TABLE 1
Chelate ring bond lengths (Å) for catecholate complexes characterized crystallographically

Complex	M–O	C–O	C–C	Ref.
$Cr(Cat)_3^{3-}$	1.986(3)	1.349(5)	1.411(4)	56
$Fe(Cat)_3^{3-}$	2.015(6)	1.349(3)	1.409(6)	56
Co(3,5-DBCat) (3,5-DBSQ)(bipy)	1.868(6)	1.358(10)	1.376(12)	44
$MoO_2(Cat)_2^{2-}$	2.05,2.17	[a]	[a]	52
$Mo_2O_5(Cat)_2^{2-}$	2.07,2.37	1.36	1.39	5
$Mo_2O_5(3,5\text{-DBCat})_2^{2-}$	2.157(5), 2.392(5)	1.37(2)	1.37(2)	53
$Mo_2O_5(3,5\text{-DBCat})_4$	1.965(3), 2.325(3)	1.360(6)	1.396(6)	48
$Mo_2(o\text{-}Cl_4Cat)_6$	1.919(6)	1.34(1)	1.39(1)	36
$Mo(9,10\text{-phenCat})_2(9,10\text{-phenSQ})$	1.952(5)	1.346(9)	1.348(10)	50
$Pd(PPh_3)_2(o\text{-}Cl_4Cat)$	2.033(5)	1.344(10)	1.366(11)	59a
$Ir(PPh_3)(NO)(o\text{-}Br_4Cat)$	1.956(14)	1.337(25)	1.358(28)	59b
$Rh(\eta^5\text{-}C_5Me_5)(Cat)$	2.011(11)	1.387(18)	1.403(21)	59c
$Os(Cat)_3$	1.962(5)	1.32(1)	[a]	55
$Os(3,5\text{-DBCat})_3$	1.958(6)	1.33(1)	[a]	55
$Hf(Cat)_4^{4-}$	2.207(3)	1.344(4)	1.414(5)	57
$Ce(Cat)_4^{4-}$	2.360(4)	1.353(6)	1.402(7)	57
$Th(Cat)_4^{4-}$	2.420(3)	1.345(5)	1.415(6)	57
$U(Cat)_4^{4-}$	2.376(4)	1.349(6)	1.407(7)	57

[a] Value not reported.

complexes. The Mo–O length to the oxo ligand is 1.668(3) Å. Molybdenum(VI) generally prefers a greater number of oxo ligands, yet this complex is quite inert to hydrolysis. Only in the presence of strong base and O_2 is it converted to $Mo_2O_5(3,5\text{-DBCat})_2^{2-}$ [53].

The unusual stability of oxygen deficient molybdenum(VI) catecholate complexes is further illustrated by the tris(tetrachlorocatecholato)-molybdenum(VI) dimer $[Mo(O_2C_6Cl_4)_3]_2$ shown in Fig. 3, with its inner coordination geometry shown in Fig. 4 [36]. Two catecholate ligands in this molecule are chelated to each of the octahedral molybdenum atoms. Two additional catecholate ligands bridge the two metals creating an open ten-membered ring. We have also prepared and investigated the structural features of the related 9,10-phenanthrenequinone complex but with quite different results. The $Mo(O_2C_{14}H_8)_3$ molecule is nominally monomeric with three quinone ligands chelated to the metal [50]. In this case the MoO_6 polyhedron is trigonal prismatic (Fig. 5), more similar to the trigonal prismatic 1,2-dithiolene molybdenum complexes [54]. One ligand is bent 60°

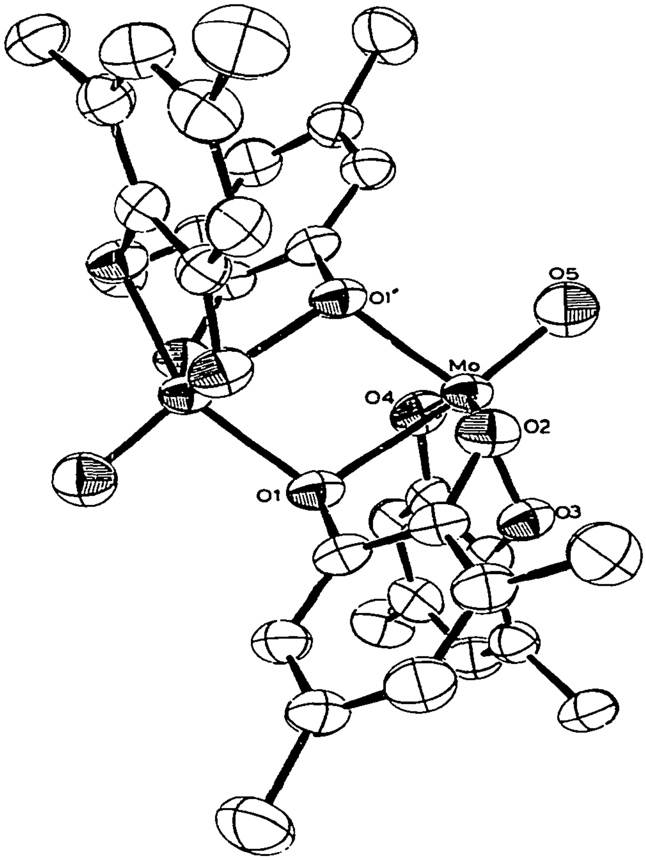


Fig. 2. View of the $[MoO(3,5\text{-}DBCat)_2]_2$ complex molecule.

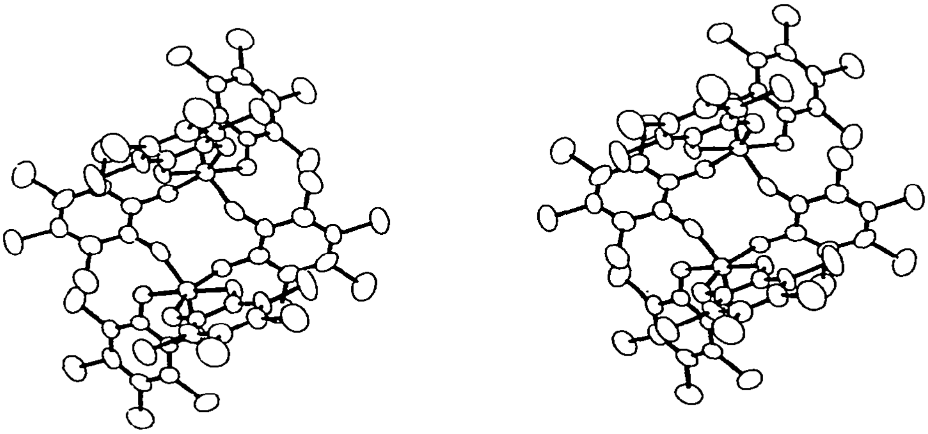


Fig. 3. Stereoview of the $Mo_2(o\text{-}Cl_4Cat)_6$ complex molecule.

from its MoO_2 plane so that the plane of the aromatic region of the ligand is parallel with an adjacent ligand. Within the unit cell two molecules pair together, as shown in Fig. 6, bent ligands being paired with ligands which chelate normally. Upon close inspection the structural features of the bent ligand are found to more closely resemble a semiquinone than a catecholate. The metal in this complex is therefore Mo(V) and intermolecular pairing occurs between catecholate and semiquinone ligands. With the d^1 Mo(V) ion paramagnetism could be expected, but weak antiferromagnetic coupling between semiquinone and metal results in a magnetic moment which is less than 1.0 μ_B at room temperature.

The ability of catecholate ligands to stabilize high oxidation state metal ions is also found in the case of osmium. Compounds described as tris(catecholato)osmium(VI) complexes have been prepared by Nielson and Griffith [38] and characterized structurally by Hursthouse et al. [55]. Unlike the molybdenum analogs they have simple tris chelated octahedral geometries. These complexes are found to be inert toward hydrolysis by dilute acid or base and are stable in pyridine. The results of the structural work, however, suggest that they may be compounds containing electronically different ligands similar to $Mo(O_2C_{14}H_8)_3$.

Raymond and coworkers have provided structural information on a number of catecholate complexes. Included in their investigations have been the tris(catecholato)iron(III) and chromium(III) trianions [56] and dodecahedral, eight coordinate tetrakis(catecholato)hafnium(IV), uranium(IV), thorium(IV) and cerium(IV) tetraanions [57]. Buckingham's group has also reported structural work on $Fe(Cat)_3^{3-}$ and on the $[[Fe(Cat)_2]_2(CH_3CO_2)]^{3-}$ anion [58]. In our own program we have studied two square planar catecholate complexes of d^8 metals, Pd(II) in $Pd(PPh_3)_2(O_2C_6Cl_4)$ [59a] and Ir(I) in

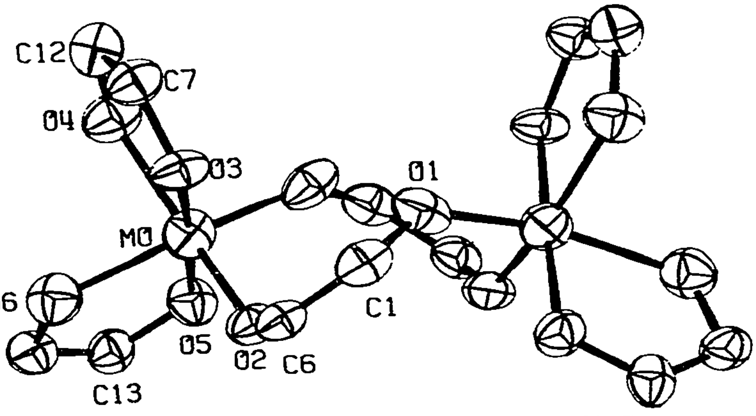


Fig. 4. View of the inner coordination sphere of $Mo_2(o\text{-}Cl_4Cat)_6$.

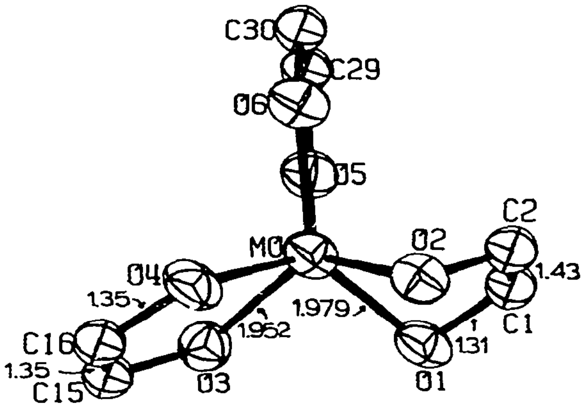


Fig. 5. The inner coordination sphere of Mo(9,10-phenCat)$_2$·(9,10-phenSQ).

Ir(NO)(PPh$_3$)(O$_2$C$_6$Br$_4$) [59b]. Drawings of the two complex molecules are shown in Figs. 7 and 8. In the latter case the Ir–O length *trans* to the nitrosyl ligand was found to be unusually short (1.905(14) Å), 0.1 Å shorter than the

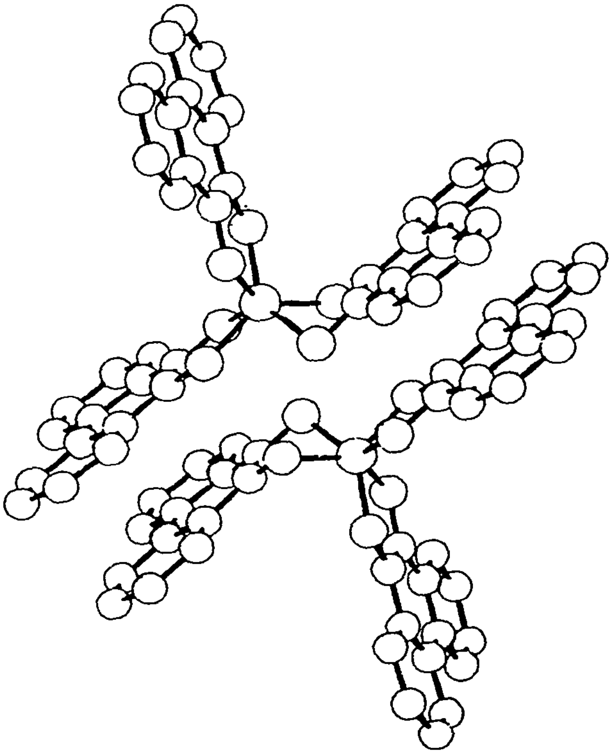


Fig. 6. Pairing of Mo(9,10-phenCat)$_2$(9,10-phenSQ) molecules in the crystal structure.

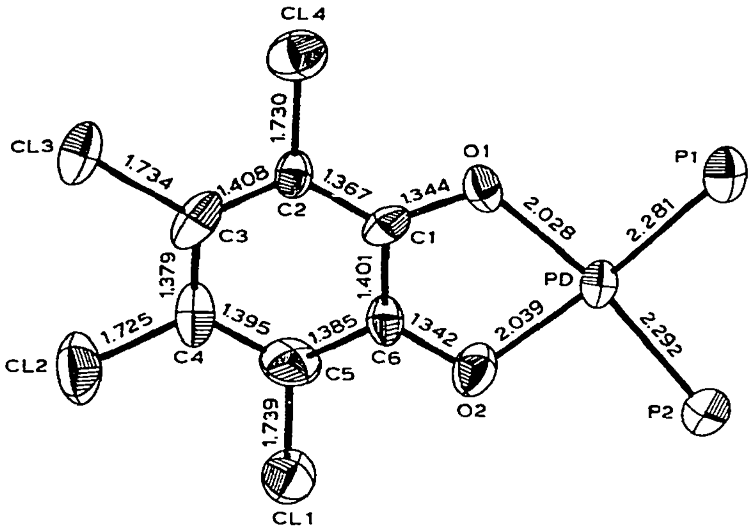


Fig. 7. View of the $Pd(PPh_3)_2(o\text{-}Cl_4Cat)$ molecule.

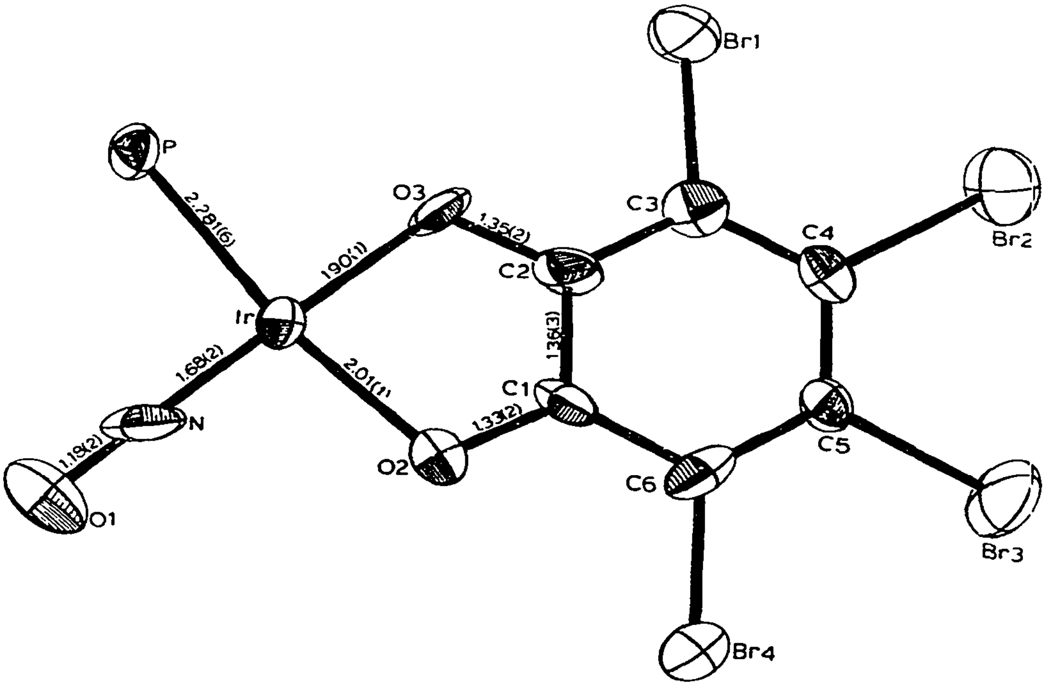


Fig. 8. View of the $Ir(NO)(PPh_3)(o\text{-}Br_4Cat)$ molecule.

bond length *trans* to the phosphorus atom. We rationalize this as resulting from the bonding effect of having a strong pi acceptor *trans* to a strong pi donor. The view that catecholate oxygen atoms serve as strong pi donors is also consistent with their destabilizing effect on terminal oxo ligands bonded to Mo(VI) [48].

Within Table 1 one finds that the carbon–oxygen lengths for chelated catecholate ligands remain reasonably constant with a value of 1.35(1) Å. Values found for bridging ligands are slightly longer, 1.37(1) Å.

(ii) *o-Benzoquinone complexes*

There is only one structural report in the literature describing a complex containing an unreduced *o*-benzoquinone ligand. We have treated MoO_2Cl_2 with excess 9,10-phenanthrenequinone in dichloromethane and obtained crystalline $MoO_2Cl_2(O_2C_{14}H_8)$ [60]. Chloro ligands are bonded *trans* to one another in this molecule (Fig. 9) with the quinone chelated at sites *trans* to the oxo ligands. Molybdenum–oxygen lengths to the quinone are quite long, 2.306(3) Å. Other structural features within the quinone chelate ring include carbon–oxygen lengths which are both 1.234(4) Å, slightly longer than values found for the free quinone, and a carbon–carbon bond length of 1.530(5) Å between carbonyl carbon atoms.

(iii) *Semiquinone complexes*

A structural investigation carried out in our laboratory on $Cr(O_2C_6Cl_4)_3$ at about the same time the structure of $[Mo(O_2C_6Cl_4)_3]_2$ was determined produced quite a different result [35]. The chromium complex was found to be monomeric with a simple tris chelated octahedral coordination geometry. A major difference in ligand structure was found for the quinone carbon–oxygen bond lengths. As noted in the previous section these values for the molybdenum structure were consistent with values reported for other catecholate ligands. In the chromium structure these values were found to be shorter, averaging to 1.28(1) Å as shown in Table 2. Further characterization of the tris quinone complexes prepared with vanadium, chromium and iron, with the quinone ligands tetrachloro-1,2-benzoquinone, 3,5-di-t-butyl-1,2-benzoquinone and 9,10-phenanthrenequinone indicated that the ligands are actually semiquinones and the metals trivalent ions, $M^{III}(SQ)_3$. Further structural work on members of the series $M(O_2C_6Cl_4)_3 \cdot 4C_6H_6$, where M = V, Cr, Fe, has shown that they are isostructural. The detailed results of our structural work on Fe(9,10-phenSQ)$_3$ have been published and are consistent with the semiquinone formulation [37]. The chromium analog Cr(9,10-phenSQ)$_3$ has also been characterized structurally in our laboratory

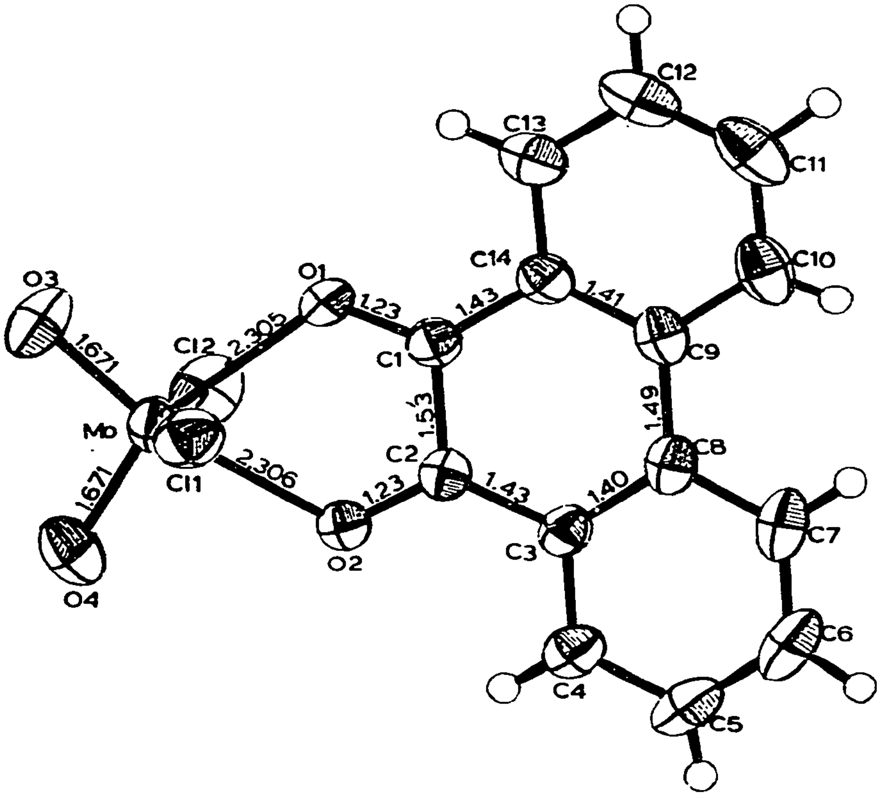


Fig. 9. View of the MoO_2Cl_2(9,10-phenDQ) molecule.

TABLE 2
Chelate ring bond lengths (Å) for semiquinone complexes characterized crystallographically

Complex	M–O	C–O	C–C	Ref.
Cr(*o*-Cl_4SQ$)_3$	1.949(5)	1.280(8)	1.42(1)	35
Cr(3,5-DBSQ$)_3$	1.933(5)	1.285(8)	1.433(9)	39c
Fe(9,10-phenSQ$)_3$	2.027(3)	1.283(5)	1.435(6)	37
Co_4(3,5-DBSQ$)_8$	2.050(4)	1.285(7)	1.448(9)	43
Co(3,5-DBCat)(3,5-DBSQ)-(bipy)	1.897(6)	1.297(9)	1.446(11)	44
Ni(9,10-phenSQ$)_2$(py$)_2$	2.058(7)	1.272(11)	1.442(14)	45
Mo_2O_5(9,10-phenSQ$)_2$	2.141(4), 2.495(4)	1.312(7)	1.426(9)	49
Mo(9,10-phenCat$)_2$(9,10-phenSQ)	1.978(5)	1.312(8)	1.427(10)	50

with similar results. Raymond and co-workers have reported the structure of tris(3,5-di-t-butyl-semiquinone)chromium(III) [39]. Its features are similar to the *o*-chloranil and 9,10-phenanthrenequinone analogs but with a *cis* isomeric structure for the unsymmetrically substituted ligands. As shown in Figs. 10 and 11 the complexes of this series all have regular chelated octahedral structures. Table 2 shows that the ligand carbon–oxygen lengths are essentially constant with a value of 1.29(1) Å.

Bis(semiquinone) complexes of cobalt(II) and nickel(II) appear to be more complicated than the octahedral tris complexes of the earlier transition metals. Only the 3,5-di-t-butylsemiquinone complexes have been characterized structurally. Our work on $Co(O_2C_6H_2(t\text{-}Bu)_2)_2$ and the Ni and Mn analogs have shown that they are tetrameric and, as shown in Fig. 12, the ligands bridge adjacent metal ions [43]. A view of the inner coordination geometry shown in Fig. 13 reveals that the tetramer actually consists of simple chelated ligands, ligands which bridge two metals, and ligands which bridge three metals through a single oxygen. The metal ions all have octahedral coordination geometries. In this structure and in the two

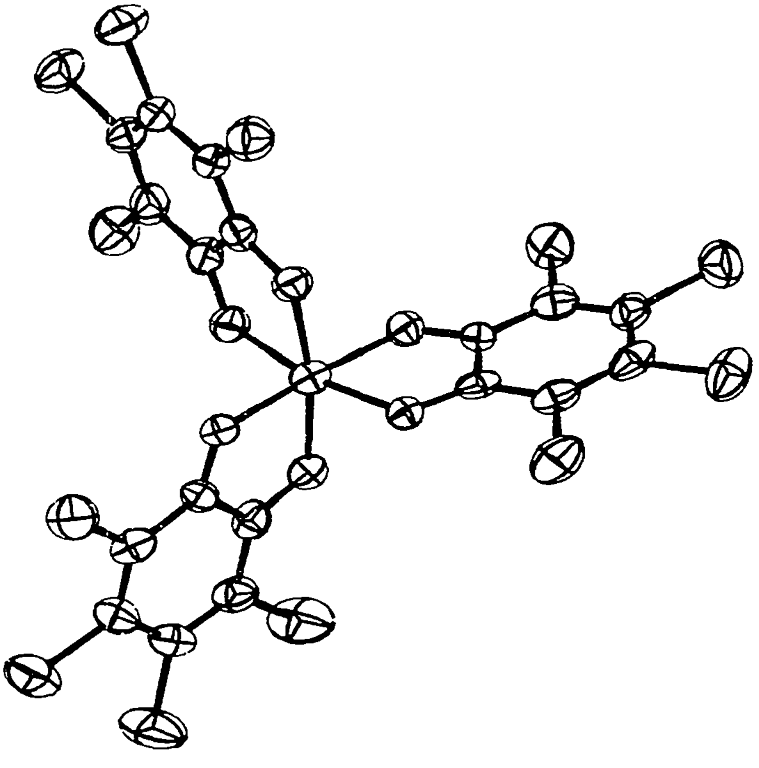


Fig. 10. View of the $Cr(o\text{-}Cl_4SQ)_3$ complex molecule.

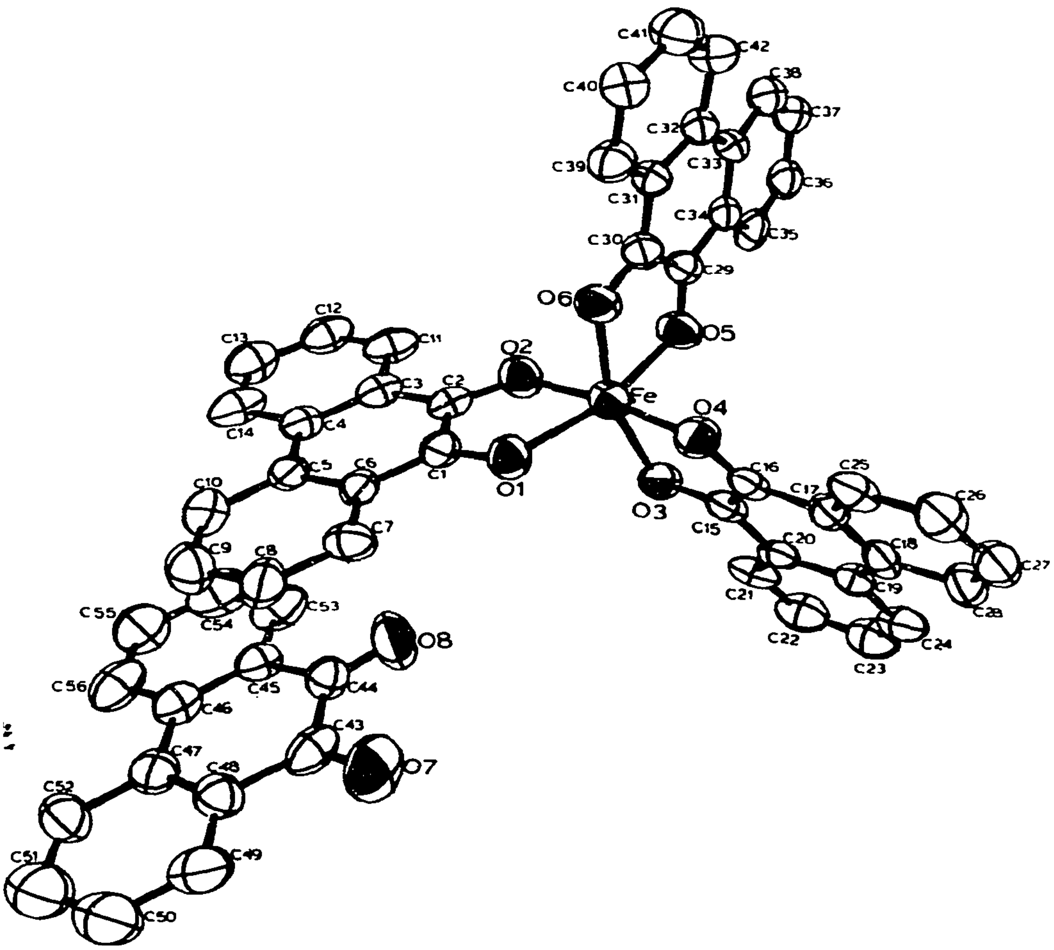


Fig. 11. View of the Fe(9,10-phenSQ)$_3$ complex molecule and the additional 9,10-phenanthrenequinone molecule of crystallization.

molybdenum structures which contain bridging 3,5-di-t-butyl-catecholate ligands the bridging oxygen atoms are all bonded to the carbon atom at the 1 ring position. We have been unable to obtain suitable crystals of the related 9,10-phenanthrenequinone or *o*-chloranil complexes to determine whether this oligomeric structure prevails in other nickel and cobalt complexes of the series. The bis(pyridine) adducts of the 9,10-phenanthrenequinone nickel and cobalt complexes have, however, been obtained in crystalline form as their pyridine solvates [45]. A view of Ni(9,10-phenSQ)$_2$(py)$_2$ is shown in Fig. 14. It has a monomeric *cis* octahedral structure. Nickel–oxygen and nickel–nitrogen lengths are consistent with Ni(II) and the carbon–oxygen lengths of the ligands are similar to other values found for semiquinone

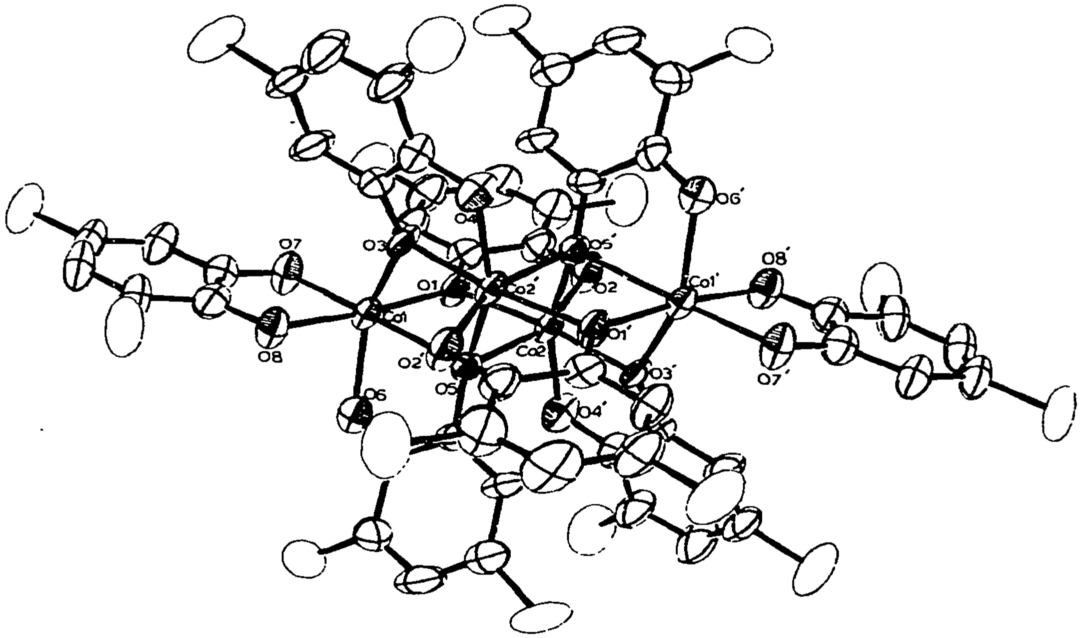


Fig. 12. Structure of the $Co_4(3,5\text{-DBSQ})_8$ tetramer.

ligands. The cobalt analog appears to be isostructural with the nickel complex. In contrast to this result, the bipyridine adduct of $[Co(O_2C_6H_2(t\text{-}Bu)_2)_2]_4$, $Co(O_2C_6H_2(t\text{-}Bu)_2)_2$ (bipy), has structural features which suggest a Co(III) metal center (Fig. 15) [44]. Cobalt–oxygen lengths in the structure are 1.883(6) Å compared with an average value of 2.05(2) Å found for the parent tetramer and a Ni–O value of 2.058(7) Å for $Ni(9,10\text{-phenSQ})_2(py)_2$. Additionally, the structural features of the quinone ligands are consistent with mixed valence catecholate–semiquinone coordination. The catecholate ligand has C–O lengths of 1.36(1) Å, while the semiquinone has values of 1.29(1) Å. As in the case of $Mo(9,10\text{-phenCat})_2(9,10\text{-phenSQ})$ and perhaps $Os(O_2C_6H_2(t\text{-}Bu)_2)_3$ the complex contains distinctly different quinone ligands.

As mentioned earlier, we have prepared and characterized structurally $Mo_2O_5(9,10\text{-phenSQ})_2$ [49]. This was the first structural report on a semiquinone complex and it is of interest to compare the features of this molecule with the related catecholate anion, $Mo_2O_5(Cat)_2^{2-}$. Despite the presence of two nominally paramagnetic ligands the complex is diamagnetic at room temperature and at low temperature (4.2 K). The mechanism of spin–spin coupling in the neutral molecule very likely involves direct interaction of the pi systems of the two ligands. The side-on view of the molecule

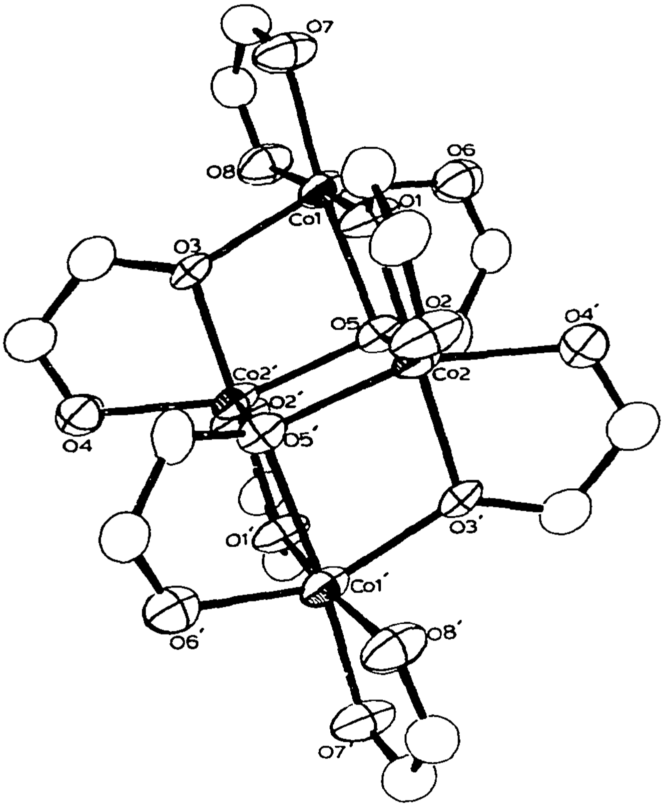


Fig. 13. The inner coordination geometry of $Co_4(3,5\text{-}DBSQ)_8$.

shown in Fig. 16 shows the nature of overlap between ligands and the end-on view of Fig. 17 shows the close separation of ligand planes. The shortest interatomic separations for atoms of the two ligands range from 2.65 to 2.83 Å and the dihedral angle between ligand planes is 19.3(3)°. Atomic coordinates are not available for $Mo_2O_5(Cat)_2^{2-}$ but are for the 3,5-di-t-butylcatecholato complex $Mo_2O_5(3,5\text{-}DBCat)_2^{2-}$ shown in Figs. 1 and 18. Molybdenum–oxygen lengths for the oxo and catecholate ligands are quite comparable to $Mo_2O_5(9,10\text{-}phenSQ)_2$. Even the disposition of the quinone ligand is similar with contacts between carbon and oxygen atoms of the carbonyl regions of the two ligands as short as 2.67 Å. The significant difference is found in the dihedral angle between ligand planes which in this structure is found to be 50.0(4)°. One might argue that this is the effect of a steric interaction between adjacent t-butyl groups. While this cannot be ignored, it is also likely that the interaction between catecholate ligands is repulsive.

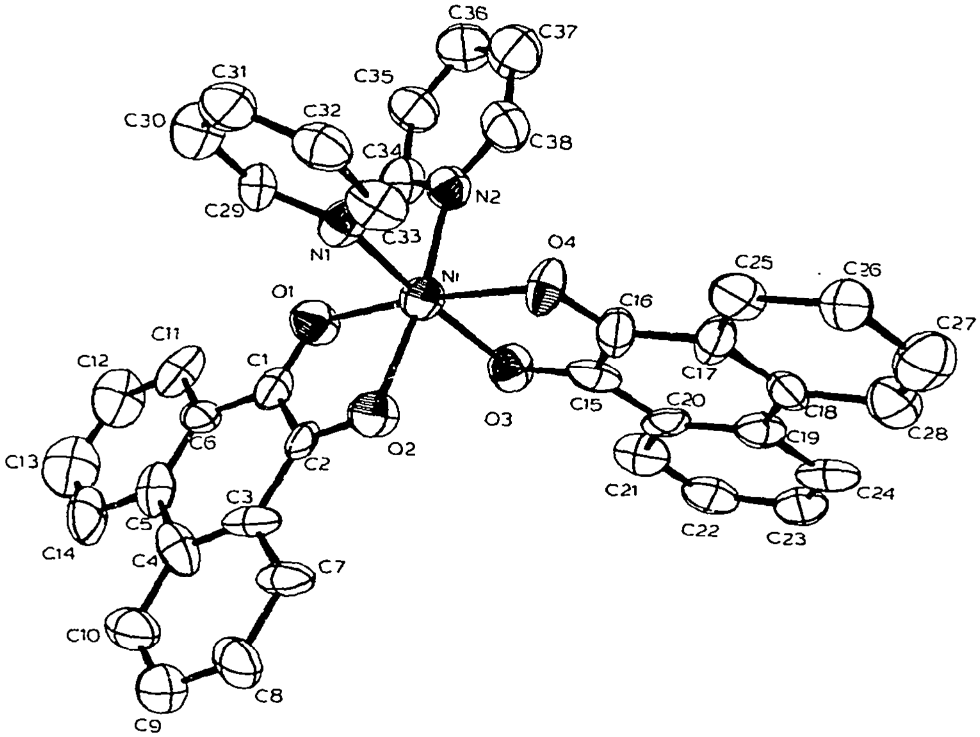


Fig. 14. View of the $Ni(py)_2(9,10\text{-phenSQ})_2$ molecule.

Review of the carbon–oxygen lengths of semiquinone ligands given in Table 2 shows little variation from the average value of 1.29(1) Å. This is midway between the 1.35(1) Å value of chelated catecholates and 1.23 Å value found for the 9,10-phenanthrenequinone complex. It is slightly longer than the 1.25 Å values found for the chloranilate bridged Ni(II) and Cu(II) complexes $Ni_2(tren)_2(O_4C_6Cl_2)^{2+}$ and $Cu_2(Me_5dien)_2(O_4C_6Cl_2)^{2+}$ [61]. The dihydroxynaphthoquinone bridge in $Cu_2(dien)_2(O_4C_{10}H_4)^{2+}$ has C–O lengths of 1.28 Å which compare well with the semiquinone values [62]. In a few instances it is possible to compare semiquinone coordination directly with catecholate analogs. The semiquinone complexes $Fe(9,10\text{-phenSQ})_3$ and $Cr(o\text{-}Cl_4SQ)_3$ can be compared with $Fe(Cat)_3^{3-}$ and $Cr(Cat)_3^{3-}$ and the semiquinone and catecholate ligands of Co(3,5-DBSQ)(3,5-DBCat)(bipy) can be included in this comparison. Aside from the difference in C–O lengths, a slight lengthening of the C–C length within the chelate ring is to be expected for semiquinones (1.44 Å) compared with catecholates (1.40 Å). Also, the O–M–O bite of the semiquinones seems to be consistently 2° smaller than that of catecholates. There seems to be no significant difference in metal–oxygen lengths for the two types of ligands.

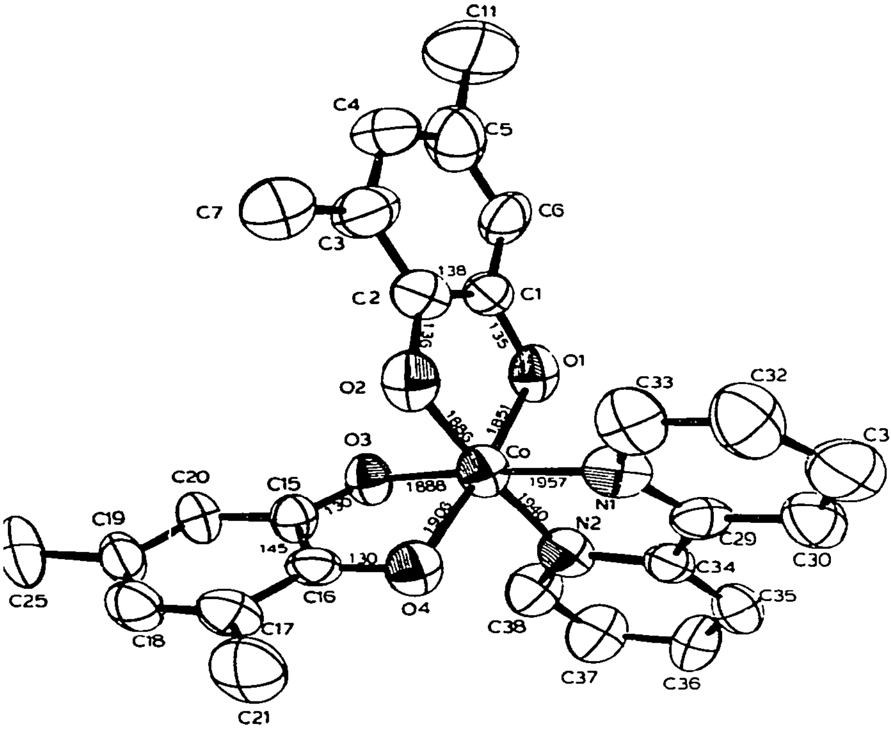


Fig. 15. Structure of the Co(3,5-DBCat)(3,5-DBSQ)(bipy) molecule.

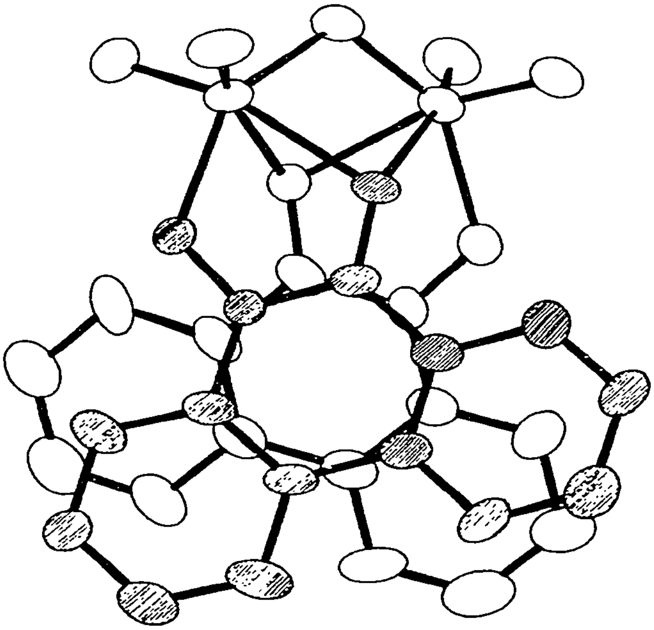
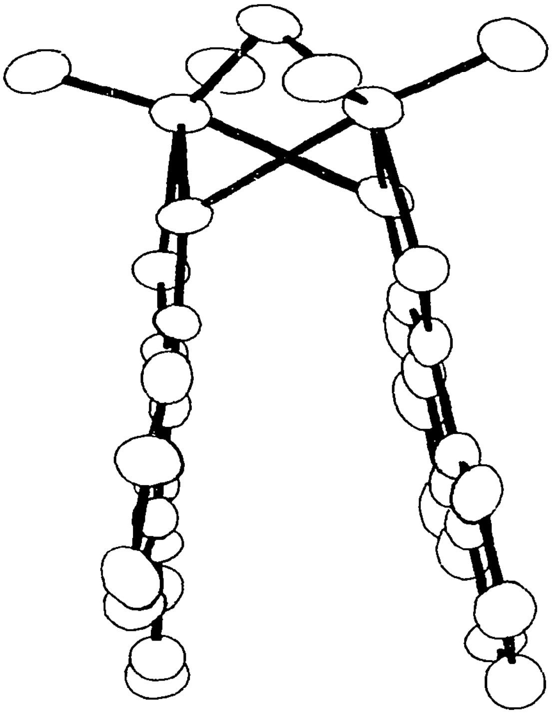


Fig. 16. Side view of the Mo_2O_5(9,10-phenSQ)$_2$ molecule.



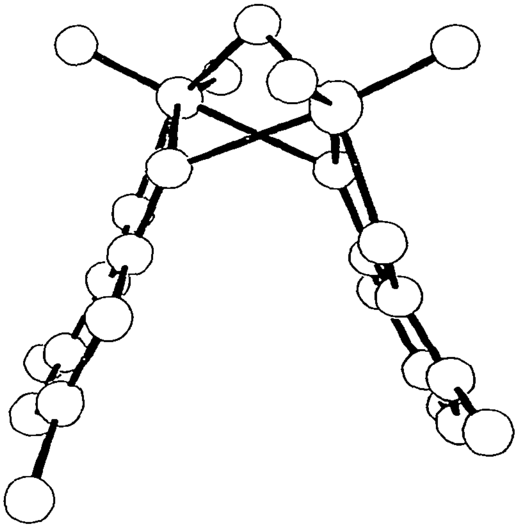
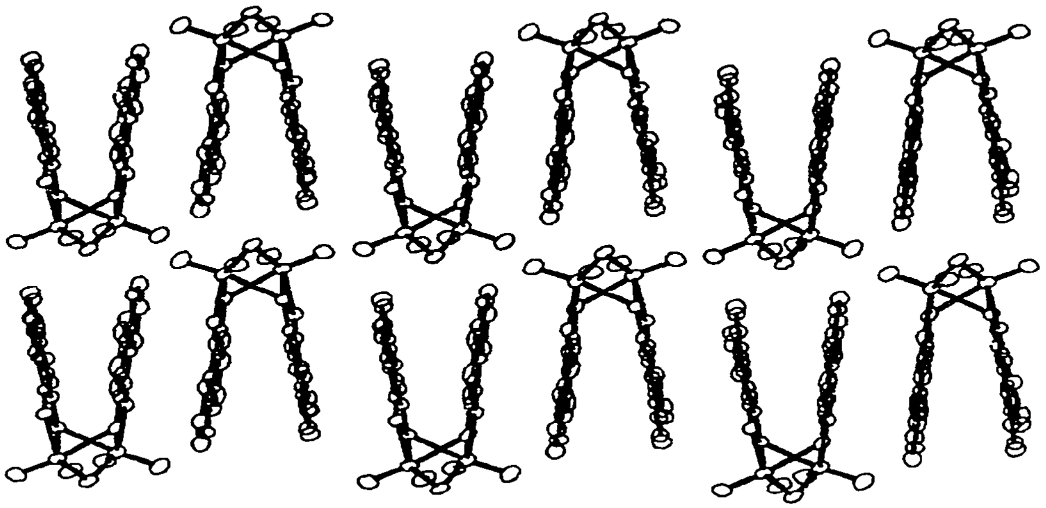


Fig. 17. End view of the $Mo_2O_5(9,10\text{-phenSQ})_2$ molecule.

Fig. 18. End view of the $Mo_2O_5(3,5\text{-DBCat})_2^{2-}$ anion.

(iv) Intermolecular interactions in the crystal structures of quinone complexes

A problem which complicated the characterization of many compounds discussed earlier in this report relates to the tendency of quinones and quinone complexes to form charge transfer complexes with unsaturated molecules. Indeed, crystallization of these materials has often become a matter of finding the right solvent or counter molecule to give a stable crystal lattice. Weak interactions between planar molecules generally result in interplanar separations which exceed 3.5 Å. Strong coupling of the type found between benzoquinones and hydroquinone results in separations which are sometimes less than 3.2 Å. In the case of the benzene solvate $Mo_2(o\text{-}Cl_4Cat)_6 \cdot 3C_6H_6$ benzene molecules are located 3.5 Å above ligand planes and crystals of the complex slowly lose solvent at room temperature [36]. The catecholate–semiquinone interaction between molecules of $Mo(9,10\text{-phenCat})_2(9,10\text{-phenSQ})$ shown in Fig. 6 is much stronger with a separation of 3.24 Å between ligand planes [50]. Complexes prepared with



ig. 19. Crystal structure of $Mo_2O_5(9,10\text{-phenSQ})_2$.

9,10-phenanthrenequinone are generally found to have stacked structures. The pairing of $Mo_2O_5(9,10\text{-phenSQ})_2$ molecules in the crystal structure is shown in Fig. 19 [49]. The form of $Fe(9,10\text{-phenSQ})_3$ obtained from the reaction mixture was found to have an additional quinone [37]. In this case there are four membered stacks consisting of two quinone molecules and two ligands (Fig. 20) as well as direct pairing of ligands associated with adjacent molecules. Ligand–ligand separations were found to be 3.35 Å. A particularly interesting mixed solvate structure was found for $Cr(o\text{-}Cl_4SQ)_3$. Recrystallization from benzene produces a tetrabenzene solvate $Cr(o\text{-}Cl_4SQ)_3 \cdot 4C_6H_6$ and further recrystallization of this material from carbon disulfide produces the mixed solvate $Cr(o\text{-}Cl_4SQ)_3 \cdot CS_2 \cdot \frac{1}{2}C_6H_6$ shown in Fig. 21 [35]. The unit cell consists of a five membered stack including two

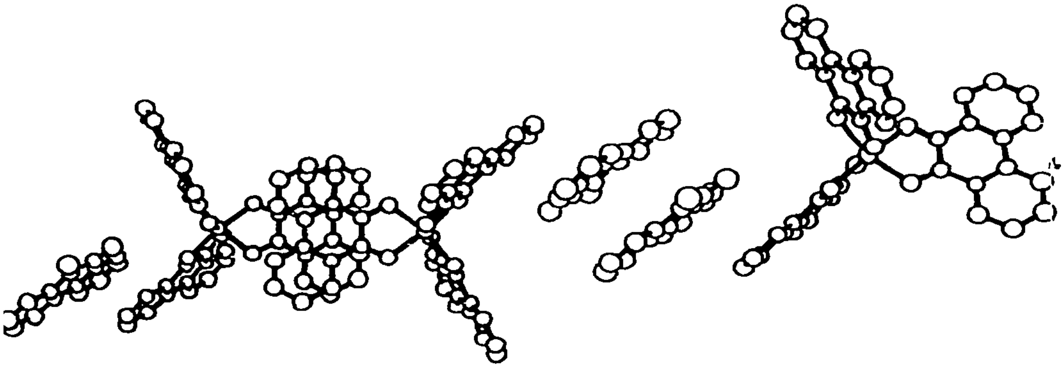


Fig. 20. Crystal structure of $Fe(9,10\text{-phenSQ})_3 \cdot 9,10\text{-phenQ}$.

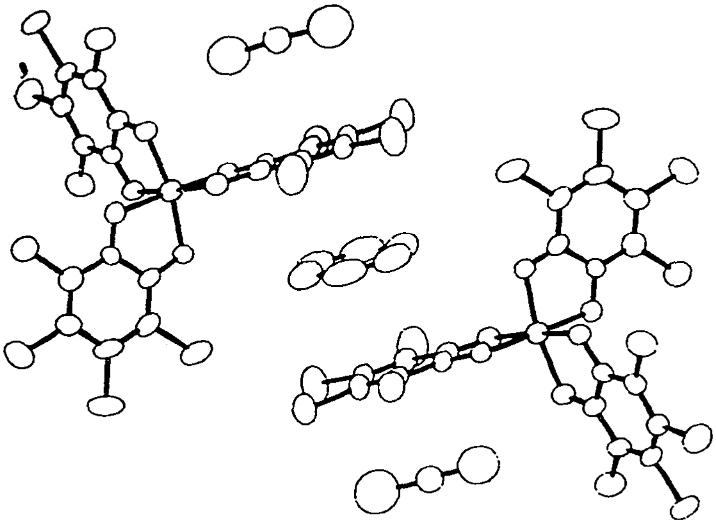


Fig. 21. Crystal structure of $Cr(o\text{-}Cl_4SQ)_3 \cdot CS_2 \cdot \frac{1}{2}C_6H_6$.

CS_2 molecules, two semiquinone ligands and a benzene molecule located about a crystallographic inversion center. Interplanar benzene–ligand separations are 3.28 Å, relatively short for the chlorine substituted ligand. The closest contact of the CS_2 molecule to the complex occurs between a sulfur atom and one of the chelated oxygens with a value of 3.35 Å. Apart from its interesting solvate structure the CS_2 interaction illustrates a potential mechanism for complex–substrate outer sphere electron transfer.

D. MAGNETIC PROPERTIES OF SEMIQUINONE COMPLEXES

Electron paramagnetic resonance and variable temperature magnetic susceptibility experiments have proven to be important methods of characterization for complexes containing paramagnetic semiquinone ligands. Systems containing a single unpaired spin have been studied using EPR. Hyperfine coupling with the metal and ligand substituents have greatly aided spectral interpretation. Complexes containing a number of paramagnetic centers, generally including the metal ion, have been found to exhibit temperature dependent magnetic moments. This is thought to result from antiferromagnetic coupling of unpaired electrons at the metal with the semiquinone ligands.

(i) Spin–spin coupling in semiquinone complexes

Antiferromagnetic coupling between a paramagnetic metal center and one or more paramagnetic ligands is uncommon. Magnetic measurements carried out in the laboratory of Professor D.N. Hendrickson of the University of Illinois on the neutral tris(quinone) complexes prepared with Fe and Cr provided initial clues that the ligands in these molecules were in the semiquinone form. Iron complexes prepared by treating $Fe(CO)_5$ with 3,5-di-t-butylbenzoquinone, tetrachloro-1,2-benzoquinone or 9,10-phenanthrenequinone have been shown to have tris chelated octahedral coordination geometries. The structural features of $Fe(9,10\text{-}phenSQ)_3$ and the Mossbauer parameters for all three complexes (Table 3) point to ferric iron [37]. Plots of magnetic moment versus temperature are shown in Fig. 22. At room temperature values of 3.96, 3.34 and 2.95 μ_B were found for $Fe(o\text{-}Cl_4SQ)_3$, $Fe(9,10\text{-}phenSQ)_3$ and $Fe(3,5\text{-}DBSQ)_3$, respectively. As temperature is decreased values for the first two compounds decrease. The magnetic moment

TABLE 3
Iron-57 Mossbauer data (90 K) for tris(*o*-semiquinone)iron(III) complexes

Compound	$\delta_I(\mathrm{mm\ d^{-1}})^{a,b}$	$\Delta E_a(\mathrm{mm\ s^{-1}})^{b}$	$\nabla(\mathrm{mm\ s^{-1}})^{b,c}$	
$Fe(3,5\text{-}DBSQ)_3$	+ 0.559(2)	0.752(2)	0.140(2)	0.133(2)
$Fe(o\text{-}Cl_4SQ)_3 \cdot 4\phi$	+ 0.536(7)	0.940(7)	0.201(8)	0.211(8)
$Fe(phenSQ)_3 \cdot PhenQ$	+ 0.530(4)	0.924(4)	0.245(4)	0.270(5)

[a] Relative to Fe metal. [b] Error in last significant figure in parentheses. [c] Halfwidth at half-maximum listed in order of increasing velocity of the peak.

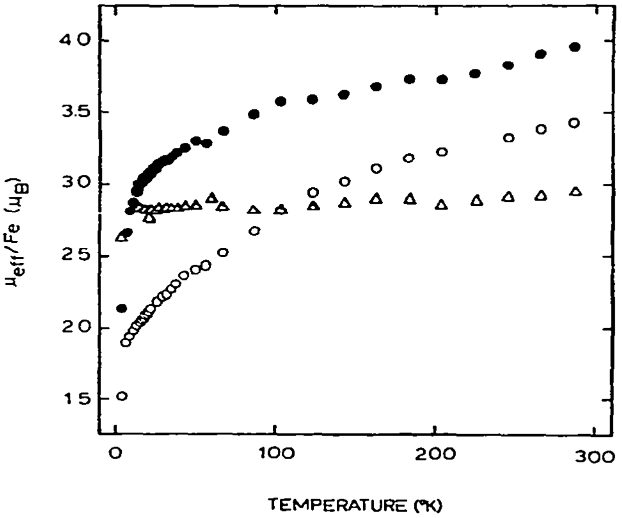


Fig. 22. Magnetism of the $Fe(SQ)_3$ complexes: ●, $Fe(9,10\text{-}phenSQ)_3$; ○, $Fe(o\text{-}Cl_4SQ)_3$; △, $Fe(3,5\text{-}DBSQ)_3$.

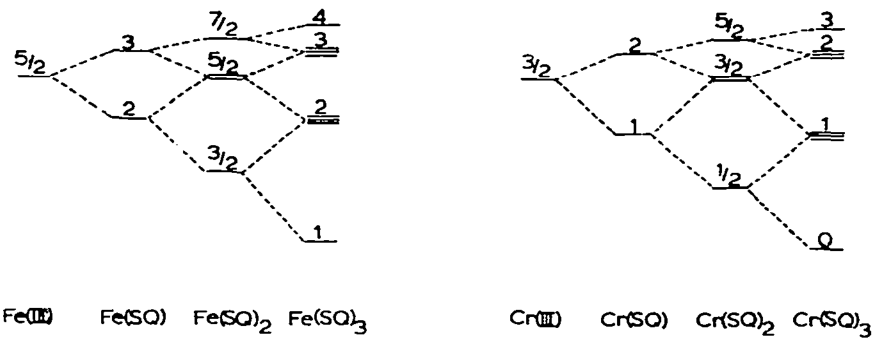


Fig. 23. Spin states arising from coupling of Fe(III) and Cr(III) ions to $S = \frac{1}{2}$ semiquinone ligands.

for Fe(3,5-DBSQ)$_3$ remains essentially constant to 4.2 K. If one views these compounds in terms of an $S = \frac{5}{2}$ metal ion interacting with three $S = \frac{1}{2}$ ligands as shown in Fig. 23 an $S = 1$ ground state would be expected. The moment of Fe(3,5-DBSQ)$_3$ is in accord with this formulation, while the room temperature moments of Fe(o-Cl$_4$SQ)$_3$ and Fe(9,10-phenSQ)$_3$ show a contribution from higher spin states. At 4.2 K values of 2.14 and 1.52 μ_B were found for Fe(o-Cl$_4$SQ)$_3$ and Fe(9,10-phenSQ)$_3$. These are obviously below the $S = 1$ value and are thought to result from an intermolecular spin coupling mechanism. This is not unreasonable because the crystal structures

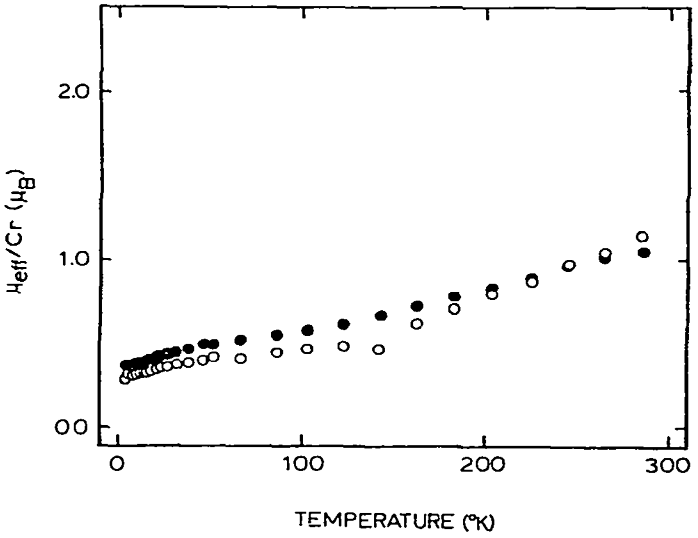


Fig. 24. Magnetism of the Cr(SQ)$_3$ complexes: ●, Cr(o-Cl$_4$SQ)$_3$; ○, Cr(9,10-phenSQ)$_3$.

of complexes containing planar quinone ligands (i.e., Fe(9,10-phenSQ)$_3$) show strong intermolecular interactions, while bulky t-butyl substituents tend to keep molecules separated in the crystal lattice. It is perhaps significant that the least electrophilic ligand of this series shows the strongest coupling with the metal center. Similar behavior has been found for the analogous chromium complexes. In this case an $S=\frac{3}{2}$ Cr(III) metal ion coupled to three semiquinones would be diamagnetic in the strongly coupled extreme. Cr(3,5-DBSQ)$_3$ is found to be diamagnetic at all temperatures while Cr(*o*-Cl$_4$SQ)$_3$ and Cr(9,10-phenSQ)$_3$ show weak paramagnetism at room temperature (Fig. 24) [37].

We have similarly investigated the bis(semiquinone) complexes of Co and Ni. Interpretation of the magnetic data in terms of a simple spin coupling mechanism is complicated in these cases by their oligomeric structures. Ni(3,5-DBSQ)$_2$ and Co(3,5-DBSQ)$_2$ are isostructural and exist as tetramers in solid with the structure shown in Fig. 12. The related 9,10-phenanthrenesemiquinone complexes have not been crystallized. Magnetic data on the nickel and cobalt complexes are shown in Fig. 25. Room temperature moments of all four complexes are above values expected for an isolated metal ion strongly coupled to two semiquinone ligands. As with the tris complexes a decrease in temperature produces a decrease in magnetic

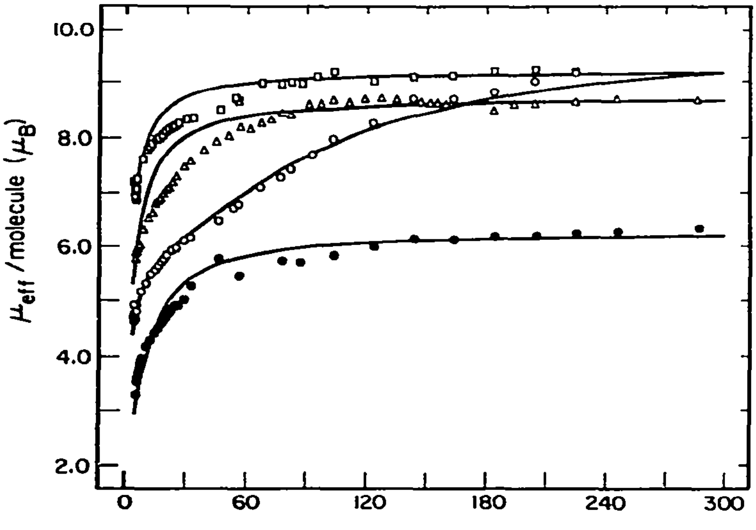
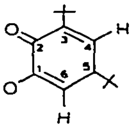


Fig. 25. Magnetism of the tetrameric bis(semiquinone) complexes of Co(II) and Ni(II): □, Co$_4$(9,10-phenSQ)$_8$; ○, Co$_4$(3,5-DBSQ)$_8$; △, Ni$_4$(3,5-DBSQ)$_8$; ●, Ni$_4$(9,10-phenSQ)$_8$. Solid lines show the values calculated with the theoretical model.

moment. Values obtained at 4.5 K remain well above the $S=0$(Ni) and $S=\frac{1}{2}$(Co) ground state moments. Despite the complexity of the 3,5-DBSQ molecules a simple model consisting of an octahedral metal ion coupled to two semiquinones can be used to fit the experimental magnetic data quite well [63]. Examination of the $[Co(3,5\text{-}DBSQ)_2]_4$ molecule (Fig. 13) reveals that each metal has two chelating semiquinone ligands. The success of this model suggests that coupling through oxygen bridges does not contribute significantly to the magnetic properties of the oligomer.

(ii) EPR spectra of semiquinone complexes

The tris(semiquinone)vanadium(III) complexes prepared with 3,5-DBSQ and *o*-Cl_4SQ have $S=\frac{1}{2}$ spin states resulting from strong coupling of two semiquinone ligands to the d^2 metal ion. The remaining spin is localized on one of the ligands. Vanadium hyperfine coupling of only 4.1 G is observed for V(*o*-$Cl_4SQ)_3$ and the *g* value is 2.0079 [64]. For comparison, $V(bipy)_3$ is reported to have a *g* of 1.9831 and hyperfine coupling of 84 G. Spectra obtained for the 3,5-DBSQ complexes are potentially more informative because they would show additional coupling to ligand substituents. 3,5-Di-t-butylsemiquinone in its free form shows coupling of 3.8 G to the ring proton at the 4 position (XVI) and additional coupling of 0.3 G to the t-butyl protons at the 5 position.



(XVI)

The EPR spectrum of $V(3,5\text{-}DBSQ)_3$ is quite complicated due to apparent equivalence of ring protons and t-butyl groups. It shows the same weak metal coupling observed for V(*o*-$Cl_4SQ)_3$. We have been quite interested in the $V(3,5\text{-}DBCat)_2$ complex reported by Wilshire and Sawyer [24d]. In our hands the reaction between $VO(acac)_2$ and 3,5-di-t-butylcatechol gives two EPR active products. In addition to $V(3,5\text{-}DBCat)_2$ which shows a *g* value of 1.98 and metal hyperfine coupling of 108 G, we have observed a second product which gives the spectrum shown in Fig. 26. The *g* value for this species is 2.004. Hyperfine coupling to the metal and ring proton at the 4 position are both 3.0 G and the hyperfine coupling to the t-butyl protons at the 5 position is 0.3 G. We have also found that by placing the EPR solution under an atmosphere of O_2 the spectrum intensity of this species drops markedly without broadening. The results of a recent structural investigation have shown that this compound is $[VO(3,5\text{-}DBSQ)(3,5\text{-}DBCat)]_2$ in solid state with a structure identical to $[MoO(3,5\text{-}DBCat)_2]_2$.

EPR investigations of transition metal semiquinone complexes date back to Eaton's work which appeared in 1964 [65]. As with 3,5-DBSQ, the spin density of most semiquinones is concentrated at locations within the molecule away from the bonds associated with the chelate ring. Consequently, hyperfine interactions with chelated metal ions which have a nuclear spin are relatively small. This is evident from the vanadium work and also the simple systems studied by Eaton. In this case solutions of semiquinone added to excess metal ion were investigated. Approximately ten years later Balch described the oxidation of catecholate complexes of platinum group metals which also had coordinated phosphine ligands [32]. Weak phosphorus coupling and *g* values close to 2.00 indicated oxidation of catecholate to semiquinone rather than oxidation of the metal ion. In neither of these investigations were stable semiquinone complexes isolated. Brown and co-workers in 1976 [66] described a preparative procedure for the oxidation of $[Co(trien)(3,5\text{-}DBCat)]^+$ which gave the stable Co(III)–semiquinone complex $[Co(trien)(3,5\text{-}DBSQ)]^{2+}$. More recent work by Brown and Hemphill [33], Hendrickson and co-workers [34] and Kabachnik and co-workers [67] has provided other examples of this type by the oxidation of Co(II) species with *o*-benzoquinones. In all cases weak ^{59}Co coupling of approximately 10 G is observed with *g* values close to 2.00.

Some particularly interesting work has been carried out on copper–quinone systems. Brown et al. have reported a series of Cu(II)–catecholate complexes containing chelating nitrogen donor ligands (XVII) [9]. While no EPR spectral data have yet appeared on these compounds, recent structure determinations carried out in our laboratory on (bipy)Cu(3,5-DBCat) have shown that it exists in both monomeric and dimeric forms. Razuvaev et al.

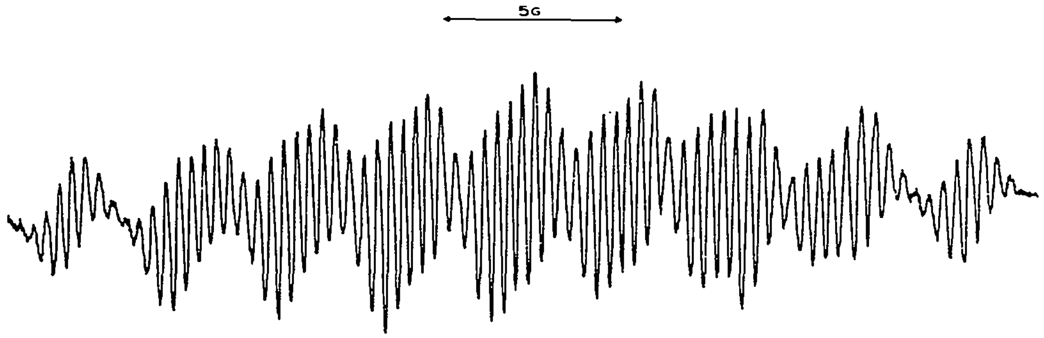
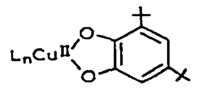
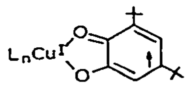


Fig. 26. EPR spectrum obtained for the $[VO(3,5\text{-}DBCat)(3,5\text{-}DBSQ)]_2$ dimer in toluene solution.



L_n = en, bipy ophen

(XVII)



L_n = PR_3, AsR_3, CO, 1, 5-COD, Ph_2C_2

(XVIII)

have investigated a similar series of complexes with phosphine, CO and unsaturated organic counter ligands (XVIII) [10]. Copper hyperfine values which are less than 11 G and g values close to 2.00 indicate Cu(I)–semiquinone coordination. These two classes of compounds illustrate in a clear way the tautomeric nature of the copper–quinone chelate ring.

Returning to the tris(semiquinone)chromium complexes, EPR has contributed substantially to our understanding of the species generated by either oxidation or reduction of the neutral complex. $Cr(3,5\text{-}DBSQ)_3$, $Cr(o\text{-}Cl_4\text{-}SQ)_3$ and $Cr(9,10\text{-}phenSQ)_3$ all undergo reversible one electron oxidations and reductions (XIX) forming $S=\frac{1}{2}$ cations and anions [11]. In all cases

$$Cr(SQ)_2(BQ)^+ \overset{e^-}{\rightleftharpoons} Cr(SQ)_3 \overset{e^-}{\rightleftharpoons} Cr(SQ)_2(Cat)^-$$

(XIX)

EPR spectra show coupling to the ^{53}Cr isotope ($I=\frac{3}{2}$, 9.5%), although the band widths of the -1 complexes are such that only the outer hyperfine lines are observed (Fig. 27). While semiquinone complexes with spin density localized on the ligand show uniquely weak metal hyperfine coupling, the ^{53}Cr coupling in both the $+1$ and -1 complexes is the strongest yet observed. This is quite different from the result of $V(o\text{-}Cl_4SQ)_3$ and this difference can be understood in terms of a tautomeric difference in charge distribution. Oxidation of the neutral $Cr(SQ)_3$ complexes seems to occur at

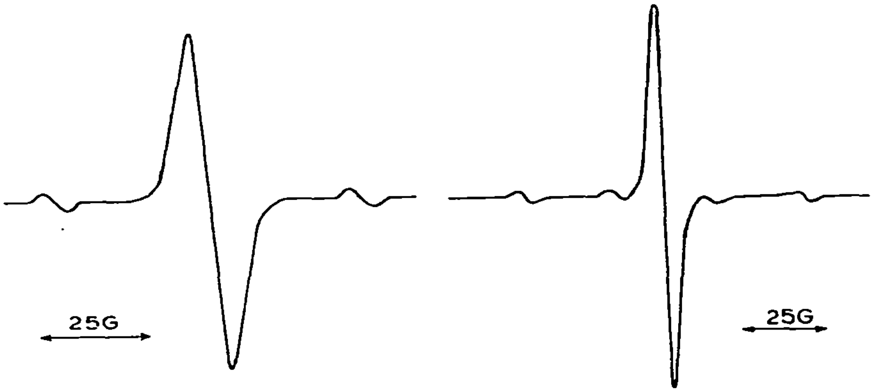


Fig. 27. EPR spectra on the $Cr(O_2C_6Cl_4)_3^{-1}$ (left) and $Cr(O_2C_6Cl_4)_3^{+1}$ (right) complexes.

TABLE 4
EPR data for the Cr(quinone)$_3^n$ complexes with $n = +1$ and -1

	$Cr(O_2C_6H_2(t\text{-}Bu)_2)_3^n$		$Cr(O_2C_{14}H_8)_3^n$		$Cr(O_2C_6Cl_4)_3^n$	
	$+1$ [a]	-1	$+1$	-1	$+1$	-1
$\langle g \rangle$	1.9709	1.9698	1.9686	1.9676	1.9689	1.9701
$A^{53}Cr$ [b]	27.3	24.5	28.2	27.9	27.2	22.2

[a] Line width at half height for the +1 complexes is approximately 3 G, for the −1 complexes 10 G. [b] $I(^{53}Cr) = \frac{3}{2}$, isotopic abundance 9.54%.

one ligand forming a $Cr(SQ)_2(BQ)^+$ species rather than at the metal which would produce a Cr(IV) complex. This serves to decouple one semiquinone ligand from the d^3 Cr(III) ion giving a complex with spin density concentrated at the metal center. Strong hyperfine coupling and g values which show an orbital contribution result (Table 4). Molecular orbital calculations carried out on isoelectronic tris(diimine) complexes of V and Cr provide an alternate view of bonding in these molecules [68]. There are four important levels shown in Fig. 28. The levels highest and lowest in energy are of e symmetry and correspond to pi bonding and antibonding combinations of metal d_{xy} and $d_{x^2-y^2}$ with an appropriate ligand set. There are two additional levels which are rather close in energy, an a_2 level which is a ligand pi combination and an a_1 level which is metal d_{z^2}. The neutral vanadium and cationic chromium complexes each place five electrons in this array. Differences in ground state which are reflected in the spectral features of the two complexes indicate a difference in order of the a_1 and a_2 levels. In the

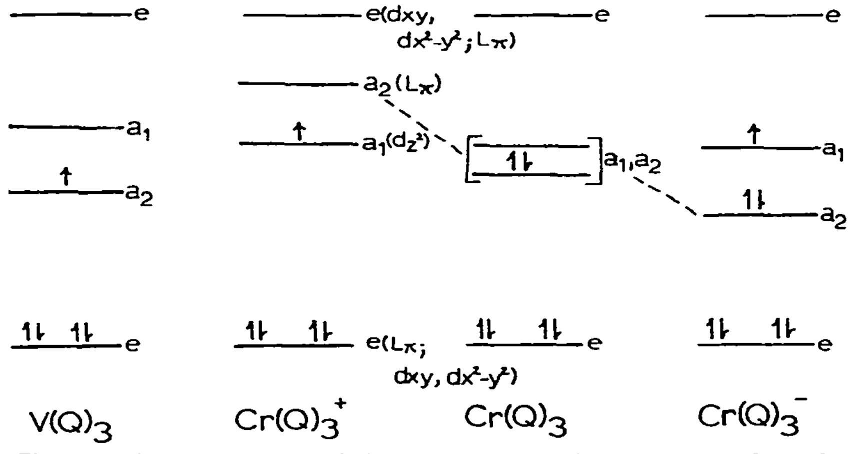


Fig. 28. Electronic levels of the tris(quinone) chromium complexes based on calculations carried out for $Cr(bipy)_3$.

vanadium case a ligand localized $^2A_2$ term results while for the chromium cations the unpaired spin resides in the metal level of a_1 symmetry. Additionally, spectral similarities, similar g values and hyperfine coupling constants, for the cationic and anionic chromium complexes suggest similar ground states. This could result from an inversion in order of the a_1 and a_2 levels upon reduction of the chromium cation giving in both cases an $^2A_1$ ground state. The neutral complex would have the a_1 and a_2 levels at quite similar energies accounting for the temperature dependent paramagnetism of $Cr(o\text{-}Cl_4SQ)_3$ and $Cr(9,10\text{-}phenSQ)_3$.

E. METAL–QUINONE ELECTRON TRANSFER REACTIONS

In earlier sections we considered tautomeric forms of the metal–quinone chelate ring related by transfer of charge between metal and ligand. The counter ligand dependence shown by the copper complexes illustrates this property but fails to provide specific information on metal–ligand electron transfer within the chelate ring. Chemical and electrochemical methods can be used to reduce the coordinated quinone ligand. Multiligand complexes can exhibit redox series consisting of two electrons per quinone ligand. In reduced form a quinone (catecholate) complex is capable of providing several electrons within a relatively short period of time to an oxidized substrate molecule by the concerted action of a number of ligands at a single site of substrate attachment. This requires facile interligand electron transfer within the complex molecule as well as a mechanism for substrate interaction. In this section aspects of inter- and intramolecular electron transfer will be reviewed and the results of experiments directed at small molecule addition will be described.

(i) Redox chemistry of tris(semiquinone)chromium(III) complexes

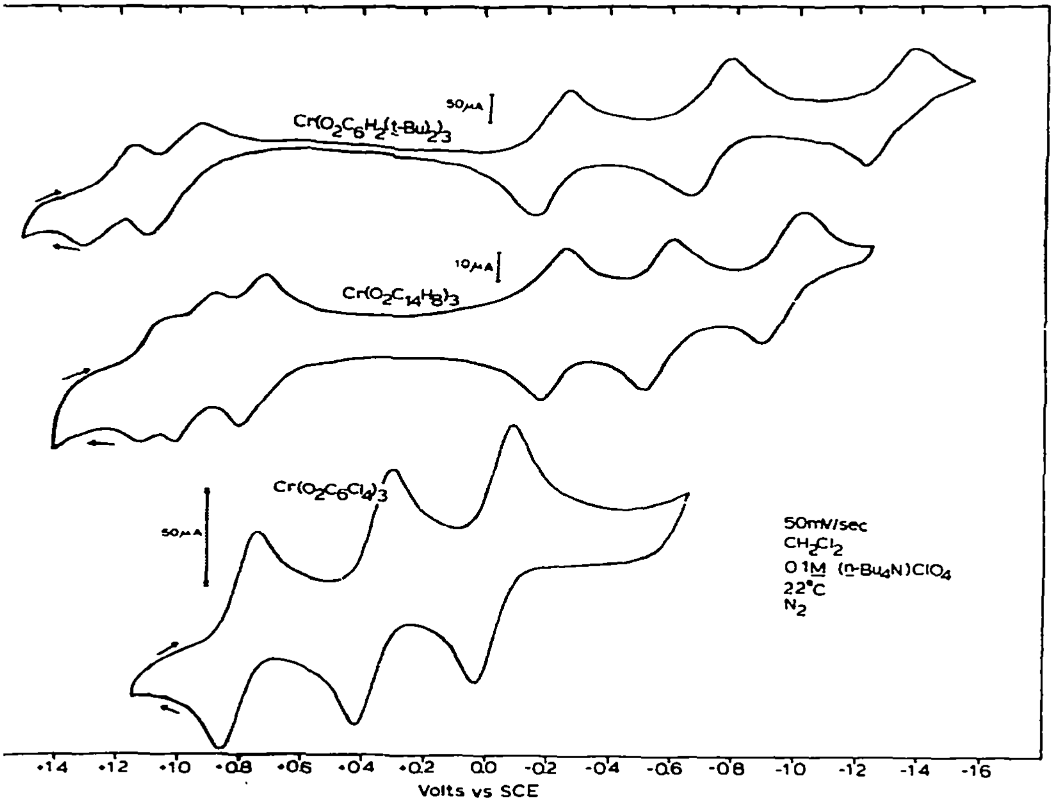
Tris(o-semiquinone)chromium(III) complexes can be prepared by treating $Cr(CO)_6$ directly with the o-benzoquinone form of the ligand. This neutral species can potentially undergo three reductions and three oxidations corresponding to stepwise oxidation or reduction of the quinone ligands (XX) [11]. If precautions are taken to avoid side reactions members of this series

$$\mathrm{Cr(BQ)_3^{3+}} \overset{e^-}{\rightleftharpoons} \mathrm{Cr(BQ)_2(SQ)^{2+}} \overset{e^-}{\rightleftharpoons} \mathrm{Cr(BQ)(SQ)_2^{+}} \overset{e^-}{\rightleftharpoons} \mathrm{Cr(SQ)_3^{0}}$$

$$\overset{e^-}{\rightleftharpoons} \mathrm{Cr(Cat)(SQ)_2^{-}} \overset{e^-}{\rightleftharpoons} \mathrm{Cr(Cat)_2(SQ)^{2-}} \overset{e^-}{\rightleftharpoons} \mathrm{Cr(Cat)_3^{3-}}$$

(XX)

can be generated either electrochemically or chemically. Figure 29 shows cyclic voltammograms recorded at a relatively slow scan rate for Cr(3,5-DBSQ)$_3$, Cr(9,10-phenSQ)$_3$ and Cr(*o*-Cl$_4$SQ)$_3$. The three redox couples which occur at negative potentials for Cr(3,5-DBSQ)$_3$ and Cr(9,10-phenSQ)$_3$ and the three shown for Cr(*o*-Cl$_4$SQ)$_3$ correspond to reductions of the neutral complexes to species with charges of -1, -2 and -3. Structural data are available for the neutral and -3 complexes. The features of these complex molecules together with EPR spectra recorded on the $+1$ and -1 complexes seem to indicate that the metal remains in its trivalent form through the redox series. In the case of Cr(*o*-Cl$_4$SQ)$_3$ the reduction series occurs at potentials which are roughly one volt more positive than the series of the other two complexes prepared with less electrophilic ligands. The trianionic complexes can be synthesized directly by treating Cr^{3+} with three equivalents of catecholate ion. They are powerful reducing agents and undergo oxidation to the neutral species upon prolonged exposure to air. Stoichiometric oxidation experiments carried out by titrating the anionic species with silver ion can be used to cleanly prepare the complexes of



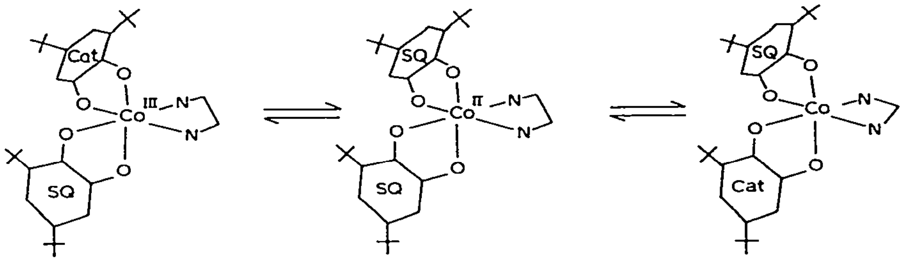
ig. 29. Redox series of the Cr(SQ)$_3$ complexes.

intermediate charge. Silver ion can also be used to oxidize the neutral complex. One equivalent has been used to generate the EPR active 1+ complexes. Further Ag^+ results in loss of the EPR signal presumably related to the formation of the 2+ complex. Attempts have been made to investigate the cationic series of $Cr(3,5\text{-}DBSQ)_3$ and $Cr(9,10\text{-}phenSQ)_3$; the corresponding series of $Cr(o\text{-}Cl_4SQ)_3$ would occur at quite positive potentials, likely exceeding 2.0 V. In both cases the 0/+1 couple is observed and at more positive potentials other couples are observed which correspond to species with higher positive charge. Only in the case of $Cr(9,10\text{-}phenSQ)_3$ do we see all three oxidation steps. The 3+ complex would contain three ligands which are essentially diketones. Even with the kinetic stability of the Cr^{3+} ion under the conditions of the electrochemical experiment (polar solvent, excess electrolyte) ligand dissociation occurs.

This electrochemical activity is not general to other quinone complexes. In the case of the iron complexes, while $Fe(BQ)_3^{3+}$, $Fe(SQ)_3$ and $Fe(Cat)_3^{3-}$ species have all been isolated and characterized, their redox chemistry generally consists of two or three reversible couples. The chromium series is unique among the first row metal ions. Further, the ligand dependence of the series suggests that the range of potentials can be "tuned" by choice of quinone.

(ii) Intramolecular electron transfer reactions of quinone complexes

Intramolecular interligand exchange of an electron between coordinated catecholates and semiquinones is known to occur for mixed ligand complexes of P, Si, Al and B. EPR studies indicate that the rate of transfer is of the order of 10^9 sec^{-1}. A second type of electron transfer reaction involving the formal transfer of an electron between ligand and metal ion has been observed for a cobalt complex. The 2,2′-bipyridine adduct of $[Co(3,5\text{-}DBSQ)_2]_4$ has been found to be a Co(III) catecholate semiquinone complex in solid state at room temperature [44]. In solution over the temperature range from −60°C to +60°C an equilibrium exists between Co(III) and Co(II) forms with the Co(II) species formed at higher temperatures. In solid



at room temperature the magnetic moment of the complex is found to be 1.92 μ_B. At −60°C in toluene solution the value is 2.5 μ_B and as temperature is increased the magnetic moment increases. This behavior is shown in Fig. 30. At 60°C a maximum value of 4.3 μ_B is obtained which is close to the 4.6 μ_B moment found per cobalt ion of the parent tetramer.

In solid and in solution at temperatures up to −40°C the complex shows a simple first derivative EPR signal (Fig. 31). In solution, as temperature is increased and the paramagnetism of the complex increases, the intensity of the EPR signal decreases. At −25°C indications of ^{59}Co hyperfine begin to appear with a coupling constant of 10.7 G. The *g* value is 2.00 and these parameters compare well with values found for the simple Co(III)–semiquinone complexes discussed in the previous section. As temperature is further increased resolution of hyperfine improves but signal intensity continues to decrease. At approximately 65°C only baseline is observed. Upon recooling the solution the original spectrum returned and similar results can be observed reversibly by heating or cooling the solution. Identical results have been obtained in diethyl ether and toluene solutions over the concentration range 10^{-2} M to 10^{-5} M.

At temperatures where the EPR signal of $Co(O_2C_6H_2(t\text{-}Bu)_2)_2(bipy)$ decreases in intensity and eventually disappears, an NMR signal can be

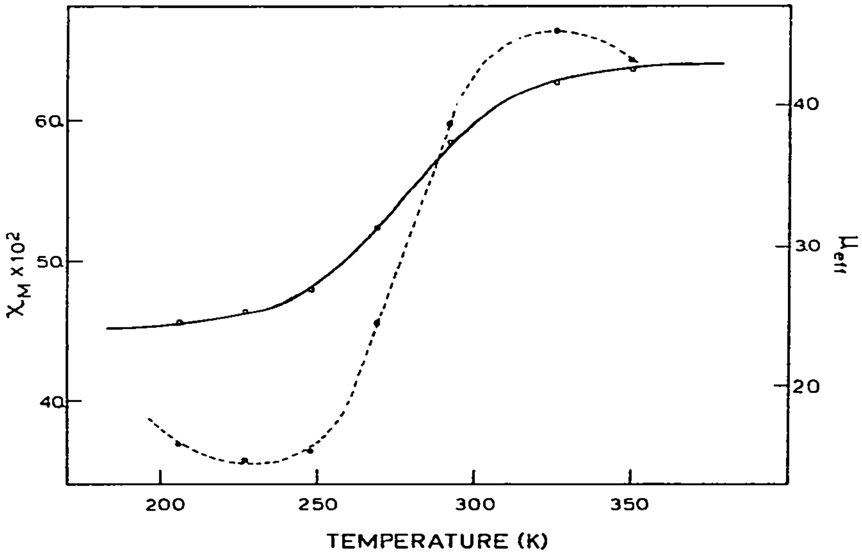


Fig. 30. Solution magnetism of $Co(O_2C_6H_2(t\text{-}Bu)_2)_2(bipy)$ obtained by the Evans method in toluene.

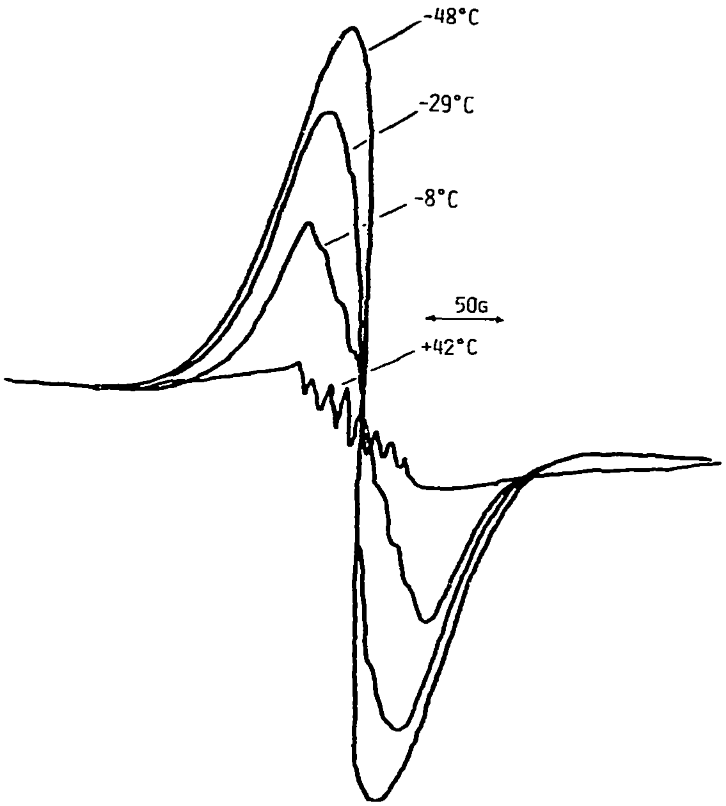


Fig. 31. EPR spectrum of $Co(O_2C_6H_2(t\text{-}Bu)_2)_2(bipy)$ in toluene solution.

detected. As shown in Fig. 32 the spectrum consists of two resonances at 10.1 and 2.8 ppm which integrate at a 9 : 1 ratio with other less intense resonances. At 70°C three additional resonances at 29.4, 43.9 and 86 ppm are observed. The more intense resonances appear to be t-butyl protons of the quinone ligands; the less intense resonances are assigned as ring protons of either the bipyridyl or quinone ligands. If the *cis* structure found in solid (Fig. 15) remained rigid in solution four t-butyl resonances would be expected. While trivalent Co(III) complexes are stereochemically rigid in solution, divalent cobalt complexes are known to undergo nondissociative optical inversion at room temperature. (4,7-Dimethyl-1,10-phenanthroline)-bis(acetylacetonato)-cobalt(II) shows equivalence of acac methyl groups due to such a process [69]. A similar mechanism could be responsible for the equivalence of two sets of t-butyl groups at temperatures above 20°C providing additional evidence for the existence of a Co(II) species formed by intramolecular electron transfer. Electronic spectra recorded on a solution of

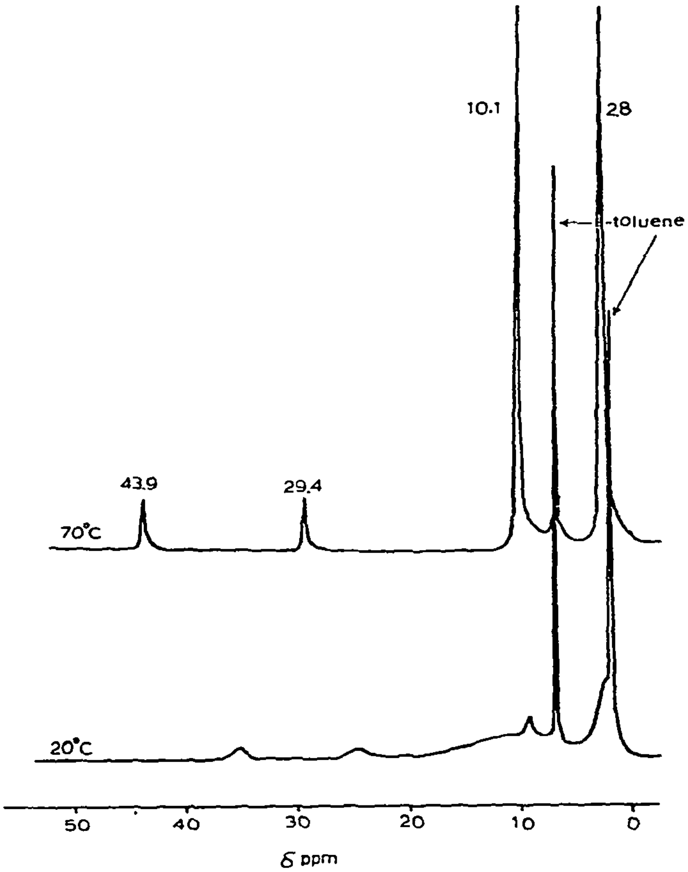


Fig. 32. NMR spectrum of $Co(O_2C_6H_2(t\text{-}Bu)_2)_2(bipy)$ in d_8-toluene solution.

the complex over the temperature range 0° to 60°C have shown that there are two distinctly different species associated with the equilibrium.

The magnetic and spectral properties in solution are most conveniently and consistently interpreted in terms of an equilibrium between Co(III) and Co(II) forms of the complex. None of the experiments provide direct information on the rate of electron transfer within the molecule. The EPR spectrum of $P(3,5\text{-}DBCat)_2(3,5\text{-}DBSQ)$ shows coupling to a single ring proton at −100°C but coupling to three equivalent rings at −40°C [70]. A rate of 1.2×10^9 sec^{-1} has been calculated for the intramolecular interligand electron transfer at 20°C. Certain features of the $Co(O_2C_6H_2(t\text{-}Bu)_2)_2(bipy)$ spectrum are likely related to a thermal delocalization of spin over the two quinone ligands. Improved resolution of the hyperfine lines will enable estimation of the interligand electron transfer rate for this molecule.

(iii) Small molecule interactions with quinone complexes

The redox properties of quinone complexes demonstrate their capability for providing numbers of electrons for the reduction of a substrate molecule. They also exhibit rapid interligand electron transfer showing that within the complex a number of ligands can act in concert on a bound substrate providing charge in a short time period. The outer-sphere interaction of the CS_2 molecule found in the crystal structure of $Cr(o\text{-}Cl_4SQ)_3 \cdot CS_2 \cdot \frac{1}{2}C_6H_6$ and shown in Fig. 21, illustrates a mode of substrate attachment which does not directly involve the metal center. Biological electron transfer reactions involving quinone and quinoid molecules occur commonly by the initial formation of a similar π complex. In this final section of our review we would like to include the results of various studies which focus on the interaction of small molecules with quinone complexes.

The metal which has been the subject of most investigations in this context is vanadium. Shilov and co-workers have developed a process for the reduction of N_2 using a vanadium(II)–catecholate complex [71]. The active species is thought to be tetrameric, an observation which is quite interesting in light of the tetrameric structures found for the bis(semiquinone) complexes of Mn(II), Co(II) and Ni(II).

Sawyer has monitored the reversible formation of O_2, NO and CO adducts of $V(3,5\text{-}DBCat)_2$ spectroscopically [24d]. The oxygen adduct is diamagnetic and has been proposed to consist of a peroxo bridge between two vanadium complex molecules. The NO adduct has been characterized on the basis of its EPR spectrum as square pyramidal with an apical nitrosyl ligand. Less is known of the CO adduct and it is surprising that it forms at all. Both O_2 and NO are known to add oxidatively to nucleophilic metals but not CO. Sawyer and co-workers have also reported the reversible formation of an O_2 adduct of $Mn(3,5\text{-}DBCat)_3^{2-}$ [72]. The product, $[Mn(3,5\text{-}DBCat)_2(3,5\text{-}DBSQ)O_2]^{2-}$, contains a superoxo ligand formed by oxidation of one of the catecholate ligands. The formation constant for this product has been estimated to be 2.9 atm^{-1} at 25°C.

The chemistry contained in these reports points to a fascinating area of intermolecular electron transfer reactions promoted thermally or photolytically either involving direct attack at the metal or through π complexation with one of the quinone ligands.

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