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Magnetic and spectral properties of paramagnetic metal-ion polyoxolene radical complexes

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Abstract

The magnetic properties of complexes containing paramagnetic metal ions bound to polyoxolene radicals are reviewed. First we report simple 1:1 complexes which provide useful criteria for the magnetic exchange involving radicals and metal ions. The second section is devoted to the magnetic properties and EPR spectra of metal–polyoxolene complexes of varying complexities. The complexes are collected according to the metal ion. Finally we report the optical properties of the complexes, particular attention being devoted to the interplay of optical and magnetic properties.

Introduction**

In the last years we have investigated the magnetic properties of metal complexes with ligands like dioxolenes, which can exist in several oxidation states, including radical states. The types of ligands, which we indicate generally as polyoxolenes, are shown in Fig. 1. They contain vicinal C–O groups, and can accept different numbers of electrons. Recently we have taken into consideration also a tridentate ligand Cat–N–SQ, also sketched in Fig. 1, where also a nitrogen donor atom is present.

The chemistry of polyoxolenes in general is very rich, associated with their redox properties, and their coordination chemistry has also been actively investigated in connection with the possibility of using metal ions to stabilize different oxidation states.

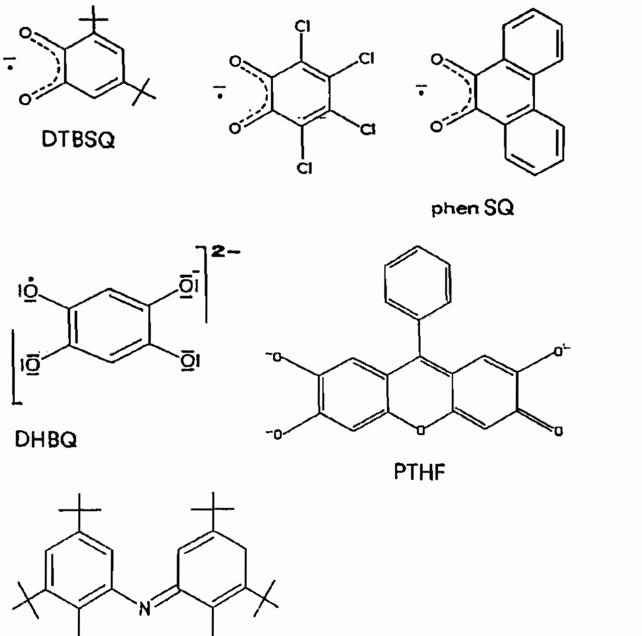

Fig. 1. Polyoxolene radical species involved in complex formation.

Good reviews are available on the chemistry of these molecules [1–3], but no one has been so far specifically dedicated to their magnetic properties. Given the large interest to molecular based magnetic materials, [4–7], metal–polyoxolenes are potential candidates to obtain

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**List of abbrevations: bpy, 2,2′-bipyridine; Cat, catecholate; Cat–N–BQ, Schiff base derivative of 3,5-di-tert-butyl -1,2-quinone and 3,5-di-tert-butyl catecholate with ammonia; Cat–N–SQ, Schiff base derivative of 3,5-di-tert-butyl-1,2-semiquinone and 3,5-di-tert-butyl catecholate with ammonia; CTH, dl-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; dmbpy, 2,9-dimethyl-1,10-phenanthroline; DTBCat, 3,5-di-tert-butylcatecholate; DTBSQ, 3,5-di-tert-butylbenzosemiquinonate; en, ethylenediamine; naphtSQ, 1,2-naphthoquinonate; H_2DHBQ, 2,5-dihydroxy-1,4-benzoquinone; n_3, 2,4,4-trimethyl-1,5,9-triazacyclo dodec-1-ene; NHpy, di-2-pyridylamine; phen, 1,10-phenanthroline; phenSQ, 9,10-phenanthrenesemiquinonate; PTHF, 9-phenyl-2,3,7-trihydroxy-6-fluorone; salen, Schiff base of salicylaldehyde and ethylenediamine; saloph, *N,N′*-(1,2-phenylene)bis(salicylidineaminate); salpren, Schiff base of salicylaldehyde and propylenediamine; SQ, semiquinonate; TCCat, 3,4,5,6-tetrachlorocatecholate; TCQ, 3,4,5,6-tetrachloroquinone; TCSQ, 3,4,5,6-tetrachlorosemiquinonate.

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bulk ferromagnets [6–7] and this is indeed the main aim of our investigation in this area.

We wish here to briefly review the magnetic properties of metal–polyoxolene complexes, showing how it is possible to give rise to strong ferro- and antiferromagnetic couplings between metal ions and radicals. Further we will report also the EPR and UV–Vis spectral properties, showing how these spectral investigations can be used to obtain first hand information on the electronic structure of the complexes.

The organization of the paper will be the following. First we will consider simple systems in which one metal ion interacts with one radical. This will provide us with useful criteria for the magnetic exchange involving radicals. The second section will be devolved to the magnetic properties and EPR spectra of general metal–polyoxolene complexes collected according to the metal ion, while the third will deal with the optical properties of these systems, particular attention being devoted to the interplay of optical and magnetic properties.

Magnetic interactions between metal ions and semiquinones

The number of complexes in which one metal ion interacts with one radical are not very numerous. This is unfortunate because they provide in principle direct information on the mechanism of exchange, and a basic knowledge which can be exploited in the interpretation of the magnetic properties of more complex systems. The available examples are summarized in Table 1.

There are two classes of complexes, namely pseudooctahedral complexes formed by salen and CTH ligands [8–13] and five coordinate formed by n_3 ligands [14]. A square planar copper(II) derivative is also reported [15]. An individual case is provided by the $Ni(n_3)(TCSQ)(TCQ)$ complex, which is characterized by peculiar properties [16].

The magnetic properties of metal–semiquinone complexes can be understood on the basis of a very simple model. In fact the spins are coupled by direct exchange interactions, whose sign and intensity can be reasonably predicted on the basis of the overlap of the magnetic orbitals, i.e. those containing the unpaired electrons. The magnetic orbitals on the metal ions are to a good approximation the d orbitals, while for the radicals they are π^* orbitals of the type depicted in Fig. 2. If the magnetic orbitals of the two centers have a non-zero overlap, S, an antiferromagnetic coupling ($J>0$ for the spin Hamiltonian $\mathcal{H}=JS_1S_2$) is expected, proportional to S^2, while if they are orthogonal to each other, then a ferromagnetic coupling ($J<0$) is expected [17–20]. The extent of the ferromagnetic coupling depends on the overlap density of the two interacting orbitals. In general, even if the total overlap S is zero there are regions where the two orbital have a non-zero overlap, and these regions determine the extent of the ferromagnetic coupling.

TABLE 1. Magnetic properties of metal–polyoxolene radical complexes

Compound	μ_{eff} (μ_B)[a]	S	J[b]	Reference
$Cr(CTH)(DTBSQ)PF_6$	2.9	1	>0	8
$Mn(salen)(DTBSQ)$	4.21	3/2	>0	9
$Mn(CTH)(DTBSQ)ClO_4$	5.05	2	>0	10
$Fe(salen)(DTBSQ)$	4.86	2	>0	9
$Fe(salen)(phenSQ)$	4.89	2	>0	9
$Fe(salen)(naphtSQ)$	4.87	2	>0	9
$Fe(salpren)(DTBSQ)$	4.94	2	>0	11
$Fe(salpren)(phenSQ)$	4.79	2	>0	11
$Fe(saloph)(DTBSQ)$	4.57	2	>0	11
$Fe(saloph)(phenSQ)$	4.58	2	>0	11
$Ni(CTH)(DTBSQ)PF_6$	4.27	3/2	<0	12
$Ni(CTH)(TCSQ)ClO_4$	4.38	3/2	<0	13
$Ni(n_3)(DTBSQ)ClO_4$	1.89	1/2	>0	14
$Cu(NHpy_2)(DTBSQ)ClO_4$	2.69	1	<0	15
$Cu(n_3)(DTBSQ)ClO_4$	2.80	1	<0	14
$Ni(n_3)(TCSQ)(TCQ)$	2.97	1	<0	16

[a] Effective magnetic moment, $\mu_{eff}=(8\chi T)^{1/2}$ at room temperature. [b] The spin Hamiltonian is in the $\mathcal{H}=JS_1S_2$ form.

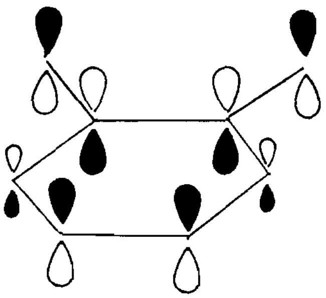

Fig. 2. Magnetic orbital of a semiquinone ligand.

The magnetic properties of the pseudo-octahedral complexes are particularly easy to interpret, because of the separation of the σ and π orbitals of the metal ions in this coordination. In fact the π^* orbitals of the semiquinones act as π orbitals to the metal ions, in such a way that they can couple antiferromagnetically to metal ions with unpaired electrons in the $t_{2g}(\pi^*)$ orbitals and ferromagnetically to metal ions with unpaired electrons in the $e_g(\sigma^*)$ orbitals. Very strong antiferromagnetic coupling is observed with $d^3(Cr^{III})$, $d^4(Mn^{III})$ and $d^5(Fe^{III}, Mn^{II})$ ions, which have three electrons in the t_{2g} orbitals [8–11]. The ground antiferromagnetic state is the only one which is thermally populated at room temperature, so that only an upper limit to the exchange coupling constant can be provided by the measurement of the magnetic susceptibility. In all these cases J is larger than 500 cm^{-1}, indicating that the interaction between the unpaired electrons is strong as expected on the basis of overlap considerations. However, whenever X-ray crystal structures are available, they show that the bond distances and angles within the ligand are intermediate between those observed for quinone and catecholate [1, 2], supporting that there is *not* a strong covalent bond between metal and radical. This is an important result, which must always be remembered when trying to interpret the properties of metal–polyoxolene complexes: the interaction is best described by an exchange interaction, rather than by a full covalent approach. On the other hand it is well known that the bonds connecting metal ions and oxygen donors are generally rather weak, and the radicals with their unpaired electrons act only as bond probes.

Quite remarkable are the strong ferromagnetic couplings observed with nickel(II) and copper(II) [12–15]. In fact parallel alignment of the spins must be expected on the basis of the orthogonality of the magnetic orbitals on the metal and on the radical, but the intensity of the interaction is surprisingly high. In particular in the nickel(II) semiquinonato complexes Ni(CTH)(DTBSQ)$^+$, whose structure is shown in Fig. 3, the ground $S=3/2$ state is the only one which is populated at room temperature, providing a lower limit for $|J|>500$ cm^{-1}. In the Cu(NHpy$_2$)(DTBSQ)ClO$_4$ complex the ground state is a triplet with $J=-220$ cm^{-1} [15]. It is also remarkable that $|J_{Ni}|>|J_{Cu}|$ in agreement with the fact that in nickel(II) there are two ferromagnetic pathways, involving the x^2–y^2 and z^2 orbitals, while in copper(II) there is only one with x^2–y^2.

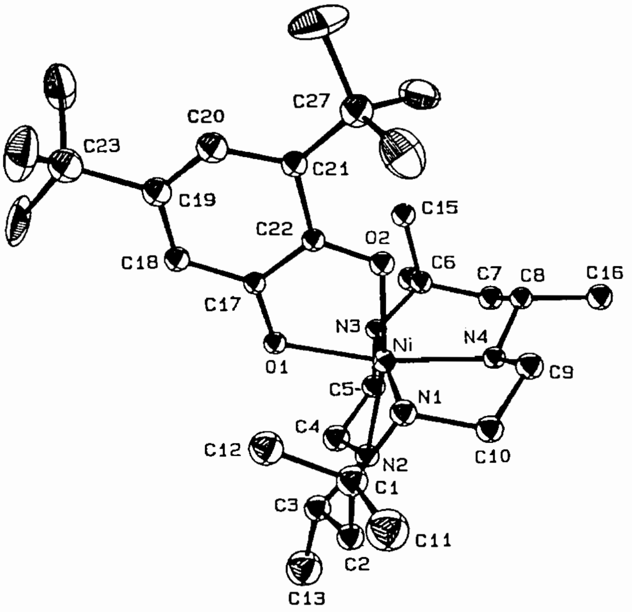

Fig. 3. Structure of [Ni(CTH)(DTBSQ)]$^+$; after ref. 12.

The effect of the coordination environment on the exchange interaction is dramatically shown by the comparison of the magnetic properties of Ni(CTH)(SQ)ClO$_4$ and Ni(n$_3$)(DTBSQ)ClO$_4$. While the former has a ground $S=3/2$ [12, 13] the latter has a ground $S=1/2$ state state [14]. In fact nickel(II) has presumably a distorted trigonal bipyramidal coordination in Ni(n$_3$)SQ and in this geometry the orthogonality of the metal and radical magnetic orbitals is no longer preserved. On the other hand the analogous copper(II) derivative, Cu(n$_3$)(DTBSQ)ClO$_4$, is ferromagnetically coupled, $J=-105$ cm^{-1}, indicating that the coordination around the d^9 ion must be close to a square pyramid [14].

Although no crystal structure is available for the two n$_3$ derivatives, EPR spectra provide support to the structural speculations based on the magnetic properties. In fact Ni(n$_3$)SQ has a broad signal at $g=2.5$, which can be decomposed into the contributions of the two individual metal ions as

$$g=\frac{4}{3}g_{Ni}-\frac{1}{3}g_{SQ}$$

which suggests $g_{Ni}\approx 2.4$. Such large g values have generally been reported only for trigonal bipyramidal nickel(II) complexes [21].

The complex Cu(n$_3$)(DTBSQ)ClO$_4$ is EPR silent in a normal (X and Q band) experiment. However, the use of a high frequency spectrometer operating at an exciting frequency of 8.17 cm^{-1} allowed us to record a triplet spectrum, which yielded $g_{\parallel}\approx 2.2$, $g_{\perp}\approx 2.0$, in agreement with tetragonal copper(II) coordination [22]. The zero field splitting is fairly large, $D=1.09$ cm^{-1}, $E/D=-0.24$.

A typical spectrum for a spin quartet largely split in zero field is observed for Ni(CTH)(DTBSQ)Y (Y = ClO$_4$, PF$_6$, BPh$_4$) [12]. Only the transitions within the $M_s=\pm 1/2$ levels are observed, with $g_1=5.8$, $g_2=2.4$, $g_3=1.7$. These effective g values correspond to $g=2.22$, $D=2.54$ cm^{-1} and $E/D=0.3$. In this case the large zero field splitting may be due both to single ion effects and to exchange determined contribution. In Cu(n$_3$)(DTBSQ) ClO$_4$ on the other hand it is only the exchange interaction which determines the large zero field splitting.

Finally we would like to mention a compound, 'Ni(n$_3$)(TCCat)TCQ', which is much more puzzling to describe [16–23]. The compound is obtained by reaction of Ni(n$_3$)TCCat with TCQ. The X-ray crystal structure shows that the two dioxolene molecules are very different from each other, as shown in Fig. 4 [16]. The bidentate dioxolene has structural parameters which are typical of semiquinones, with C–O distances of 127 pm and C–C distances for the two carbon atoms bound to the oxygen atoms of 147 pm. The monodentate dioxolene

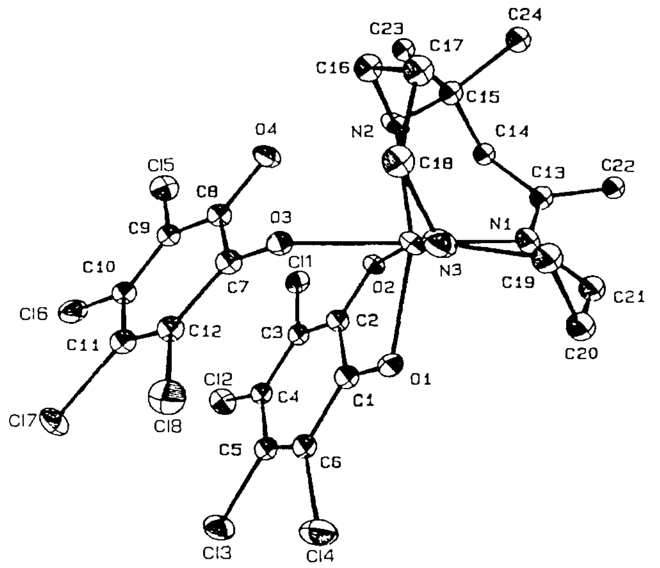

Fig. 4. Structure of 'Ni(n$_3$)(TCCat)(TCQ)'; after ref. 16.

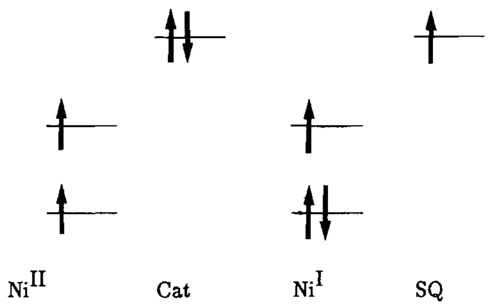

Fig. 5. Scheme of double exchange effects in $\mathrm{Ni^{I}SQ} \leftrightarrows \mathrm{Ni^{II}Cat}$ electron transfer.

on the other hand has the typical bond distances of quinones, with C–O distances of 123 pm, only slightly longer than observed for the free quinone (121 pm). If the two dioxolenes are described as TCSQ and TCQ, respectively, then the metal ion must be described as nickel(I). Since the compound has $\mu_{\rm eff} = 2.97\ \mu_{\rm B}$, practically independent of temperature, it must be concluded that nickel(I) and TCSQ are strongly coupled in a ferromagnetic way. In this respect the interaction of the d^9 Ni$^{\rm I}$ ion with the semiquinonate would be similar to that observed for copper(II) [14, 15]. This is the description corresponding to a localized view. However, if some delocalization between $\mathrm{Ni^{I}SQ}$ and $\mathrm{Ni^{II}Cat}$ is taken into account, spin polarization (double exchange) should stabilize the triplet spin state over the singlet, as shown in Fig. 5. In fact the internal transfer of one electron in $\mathrm{Ni^{I}SQ}$ to give $\mathrm{Ni^{II}Cat}$ must be performed by a down-spin, because the two electrons on nickel(II) must be kept parallel to each other according to the Hund's rule. Therefore the excited triplet stabilizes the ground triplet state. Even if the ground state appears to be localized, according to the structure determination, the presence of a strong absorption at 12 700 cm^{-1} indicates that the internal charge transfer state is very close in energy.

Metal–polyoxolene radical complexes

Vanadium

Two neutral vanadium tris(dioxolene) complexes, namely V(DTBSQ)$_3$ and V(TCSQ)$_3$, have been reported [24–26]. V(DTBSQ)$_3$ is rather unstable in the solid, and no magnetic data are available for either compound. However, isomorphism with the analogous chromium(III) and iron(III) derivatives to be described below and IR spectra suggested that they can be formulated as V$^{\rm III}$(SQ)$_3$ complexes.

The solution EPR spectra show that these materials have one unpaired electron which is mainly localized on one semiquinonate ligand. These data have been interpreted within a MO formalism which suggests that the unpaired electron is in an a_2 orbital centered on the ligand. However, if this description is correct, it requires that the charge distribution in the complex is close to V$^{\rm V}$(Cat)$_2$SQ. Therefore the EPR spectra support such a description, but with strong localization. Similar conclusions were reached on the basis of electrochemical measurements [26].

In the presence of traces of oxygen, the V(DTBSQ)$_3$ complexes yield stable dinuclear species which must be formulated as [VO(DTBCat)(DTBSQ)]$_2$, as supported by X-ray data [24].

A doublet ground state vanadium semiquinonato derivative was recently synthesized as a product of the reaction of VCl$_3$ with DTBCat and NH$_3$ under aerial conditions [10]. X-ray data showed that this compound must be formulated as V(IV)(Cat–N–SQ)$_2$ in analogy with the manganese analogue to be described below. The spin multiplicity of the electronic ground state of this compound is interpreted as a result of the strong antiferromagnetic coupling of the two semiquinonato ligands with the d^1 metal ion.

Chromium

Several Cr(SQ)$_3$ complexes have been reported as products of reactions involving DTBQ, phenQ and TCQ [27–31]. The crystal structure data agree with the presence of three equivalent semiquinones. All the complexes have a ground $S = 0$ state, in agreement with a strong antiferromagnetic coupling.

Cr(dioxolene)$_3{}^+$ complexes have been characterized in solution together with Cr(dioxolene)$_2$(bpy)$^+$ species [32, 33]. They both have one unpaired electron mainly located on the metal ion. The most striking feature of these compounds is the large ^{53}Cr hyperfine splitting of *c.* 25 G which is observed in the EPR spectra. In fact the hyperfine splittings usually reported for chromium(III) complexes are very close to 15±2 G. It is certainly tempting to try to rationalize these data within a spin Hamiltonian formalism. If we assume that the ground state is described by an antiferromagnetic coupling between the chromium(III) and the semiquinone spins, then the chromium hyperfine in the complex is expected to be 5/3 the splitting usually observed in complexes with diamagnetic ligands [34, 35]. Conversely the hyperfine splitting of the radical should be −1/3 that usually observed in free semiquinones. Also the low g values observed in these compounds can be justified by the same model. In fact the g values of the complex must be given by

$$g = 5/3\, g_{Cr} - 2/3\, g_{SQ}$$

where g_{Cr} and g_{SQ} are the g values of the isolated chromium(III) and semiquinone, respectively. By setting $g_{SQ} = 2.00$, the observed $g = 1.97$ would be justified by $g_{Cr} = 1.98$, which corresponds to the normal range of g_{Cr} values.

This explanation is valid also for the monoanionic species $Cr(dioxolene)_3^-$, which can be described as $Cr^{III}(SQ)_2(Cat)^-$, and for $Cr(dioxolene)_2(bpy)^+$, which can be described as $Cr(SQ)_2(bpy)^+$.

$Cr(dioxolene)_2(bpy)$ have two unpaired electrons, and do not give any EPR spectra [33]. They should be described as $[Cr^{III}(SQ)(Cat)(bpy)]$, while $[Cr(dioxolene)_2(bpy)]^-$ have three unpaired electrons, suggesting a $[Cr(Cat)_2(bpy)]^-$ description. The fact that they do not show EPR spectra can be justified on the basis of large zero field splitting of the ground multiplet.

The dinuclear compound $Cr_2(CTH)_2(DHBQ)(ClO_4)_3$ is characterized by a $S = 5/2$ ground state [36]. This compound has been formulated as containing a trinegative radical $DHBQ^{3-}$ bridging the chromium(III) cations. Support to this hypothesis comes from electronic spectra. Magnetic data indicate that the sextet ground state originates from the antiferromagnetic coupling of the two $S = 3/2$ metal ions with the radical within the $Cr^{III}(DHBQ)Cr^{III}$ moiety. The observed coupling constant J is 273(18) cm^{-1}. The EPR spectra provide evidence of a large rhombic zero field splitting, with a signal at $g \approx 4.3$, as generally observed for $S = 5/2$ spins. The smaller value of J observed here compared to the complexes with dioxolenes indicates that the higher delocalization of DHBQ determines a less effective overlap with the metal orbitals.

Manganese

The complex $Mn^{IV}(DTBCat)_2(py)_2$ in the solid state has the charge distribution indicated in the formula [37]. However the electronic spectra in toluene led the authors to suggest an equilibrium yielding $Mn^{II}(DTBSQ)_2(py)_2$, but no magnetic data are available. No EPR was observed.

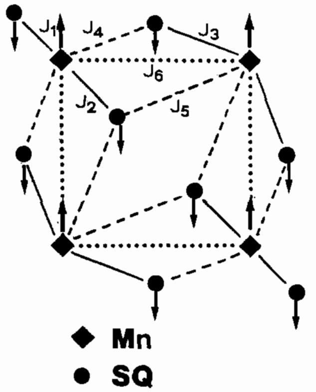

Fig. 6. Suggested preferred spin alignment in $Mn_4(DTBSQ)_8$.

The complex $Mn(Cat\text{–}N\text{–}SQ)_2$ has been formulated as bis-semiquinonato derivative on the basis of its structural parameters [38]. This compound is characterized by a doublet ground state, resulting from the strong antiferromagnetic coupling of the two radical ligand with the d^3 Mn^{IV} metal ion. The solution EPR spectra support this hypothesis. A rhombic spectrum with $g_{\parallel} = 1.977$, $g_{\perp} = 2.04$, $A_{\parallel} = 153$ G and $A_{\perp} = 84.2$ G is observed.

The tetranuclear $Mn_4(DTBSQ)_8$ complex [37] has a structure similar to that of the cobalt and nickel analogues [39], and presumably can be described as a manganese(II) complex. The temperature dependence of μ_{eff} has never been reported in detail, but $\mu_{eff} = 10.2$ μ_B at room temperature and 11.3 μ_B at 10 K. The scheme of the interaction relevant to the magnetic properties is shown in Fig. 6. In the absence of detailed data it is impossible to draw any conclusion. However the high moment observed at low temperature is in favor of a parallel alignment of the manganese spins. This can be achieved by a network of antiferromagnetic couplings between metal ions and with radicals, as shown in Fig. 6. For complete spin alignment μ_{eff} should be 12.96 μ_B.

Iron

Several $Fe(SQ)_3$ complexes have been reported [28]. All of them can be described as indicated in the formula, according to the crystal structure data and to the Mössbauer spectra. All the complexes have a ground $S = 1$ state in agreement with a strong antiferromagnetic coupling. The largest coupling constant is observed for DTBSQ, whose magnetic data indicate that the individual molecules are relatively well isolated in the solid state. For both TCSQ and phenSQ ligands there is ample evidence of strong intermolecular interactions.

Several $Fe(dioxolene)_2L$ complexes have been reported [40], where L = bpy, phen, dmbpy, en, which are formulated as $Fe^{III}(SQ)(Cat)L$, taking advantage of Mössbauer spectra. The derivatives with phenSQ and with DTBSQ show a strong ferromagnetic coupling between Fe^{III} and semiquinones. However the latter show larger intermolecular coupling, contrary to the usual results, suggesting that the complex may be oligonuclear.

A similar situation is found in the Fe(Cat–N–SQ)(Cat–N–BQ) derivative [41]. Again structural data and Mössbauer spectra support the assignment of this derivative as containing an iron(III) semiquinonato moiety thus justifying the observed quintet ground state.

$Fe_4(DTBSQ)_4(DTBCat)_4$ has the tetranuclear structure shown in Fig. 7 [42]. The DTBSQ and DTBCat ligands can be easily recognized from the X-ray data. The scheme of the relevant magnetic exchange interaction is shown in Fig. 7. The effective magnetic moment decreases steadily on decreasing temperature from 5.94 μ_B at 321 K to 0.72 μ_B at 5.0 K. Recently the introduction of a fast and efficient procedure for calculating the energy levels of high nuclearity spin clusters [43] made it possible to attempt a quantitative rationalization of the magnetic properties of $Fe_4(DTBSQ)_4(DTBCat)_4$. A reasonable agreement with the experimental data was obtained by using values of the coupling constants obtained by the comparison with simpler compounds.

The temperature dependence of the effective magnetic moment was satisfactorily reproduced for $Fe_2(CTH)_2(DHBQ)(ClO_4)_3$, which contains, as the chromium(III) analogue, a $DHBQ^{3-}$ radical bridging the metal ions [36]. This compound has a ground $S=9/2$ state, as expected for antiferromagnetic coupling between the two $S=5/2$ metal ions and the radical. However while in the iron(III)–semiquinonato derivatives there is no evidence of thermally excited states, indicating $J>500$ cm^{-1}, in the $Fe^{III}DHBQFe^{III}$ moiety the exchange coupling constant was found to be 372(28) cm^{-1}. The origin of this difference may be the same as indicated for the chromium(III) complexes, namely the higher spin delocalization in the polyoxolene compared to semiquinones. The EPR spectra show only one signal at $g \approx 6.3$. An extension of the theory worked out for $S=5/2$ spins showed that a large rhombic ($E/D=1/3$) zero field splitting gives a symmetric pattern of energy levels for spins $S=9/2$. In analogy to the $S=5/2$ case the central Kramers doublet gives rise to an isotropic EPR spectrum , with $g=6.3$. A further extension of the model showed that similar behavior must be expected for spin $S=(4n+1)/2$, where n is an integer. The expected isotropic g values for various S are shown in Table 2.

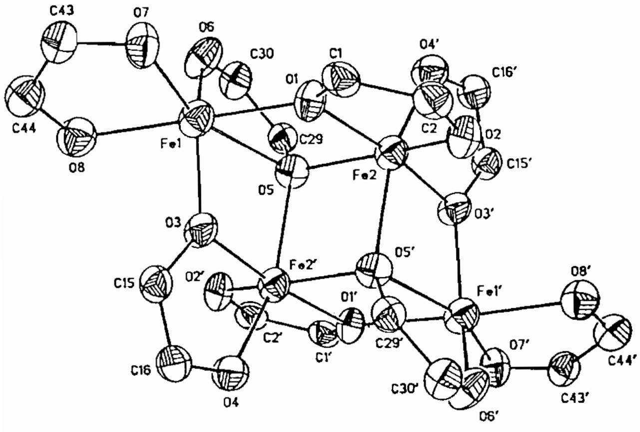

Fig. 7. Structure of $Fe_4(DTBSQ)_4(DTBCat)_4$; after ref. 42.

TABLE 2. Isotropic g values for $S=\frac{4n+1}{2}$ spins with large rhombic zero field splittings

S	5/2	9/2	13/2	17/2	21/2
g	4.3	6.3	8.3	10.2	12.0

Cobalt(II)

$Co_4(DTBSQ)_8$ has a structure similar to that of the nickel(II) analogue (Fig. 8) [39]. No attempt was made to interpret the magnetic properties, due to the complications inherent to the orbital degeneracy of the individual cobalt(II) ions.

Co(DTBCat)(DTBSQ)(bpy) can be described as a cobalt(III) compound, as confirmed by the X-ray crystal structure and the magnetic and EPR data in the solid state [43]. However it has a very peculiar behavior in solution: in fact the low temperature (200 K) EPR spectra and magnetic susceptibility indicate the presence of the same cobalt(III)–semiquinonato species seen in the solid, while at room temperature they suggest the presence of a cobalt(II)–bis(semiquinonato) species.

Nickel

$Ni(phenSQ)_2(py)_2$ has the dimeric association shown in Fig. 9 in the solid state [39]. The two semiquinones bound to nickel have their π^* orbitals, orthogonal to the e_g orbitals of nickel, while two semiquinones of two different molecules show evidence of strong stacking interaction, with interplanar distances of 3.33 A. The effective magnetic moment per dimer is 5.94 μ_B at room temperature, decreasing to 3.7 μ_B at 4.2 K. The decrease of the effective magnetic moment is rather gradual and accelerates drastically only below 30 K. The room temperature value is in excess of that expected for uncorrelated spins. In fact this would require $g_{Ni}=2.4$, much higher than usually observed for octahedral complexes. Several approximate models were used [39] to justify the observed magnetic behavior.

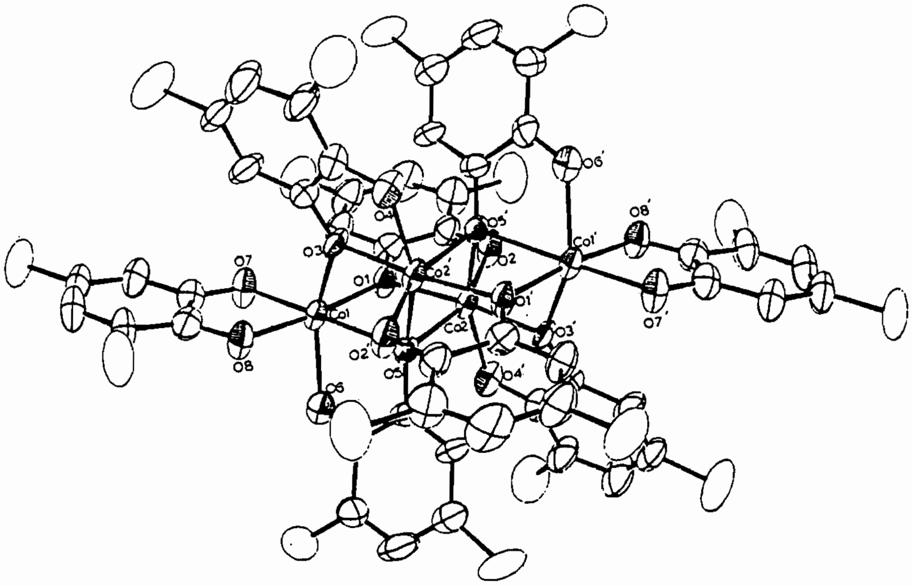

Fig. 8. Structure of $Co_4(DTBSQ)_8$; after ref. 39a.

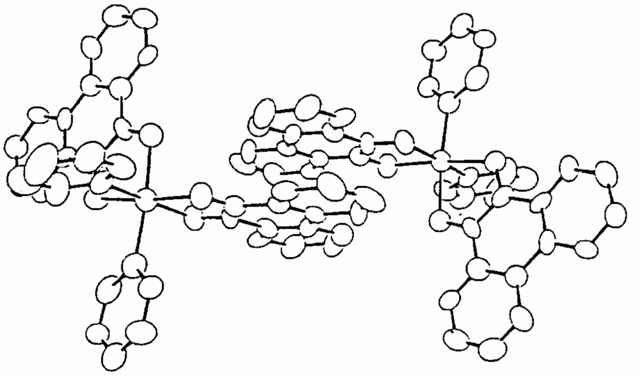

Fig. 9. Structure of $Ni(phenSQ)_2(py)_2$; after ref. 39b.

All of them require antiferromagnetic coupling between nickel(II) and semiquinone, but this assumption seems now to have little justification, because strong ferromagnetic coupling has always been observed between octahedral nickel(II) and semiquinones (see preceding section). We have now performed [43] complete calculations in the dimers showing that the experimental data can be justified assuming strong ferromagnetic coupling between nickel(II) and semiquinones and moderate antiferromagnetic coupling between the stacked semiquinones.

Recently we have described a dinuclear nickel(II) derivative containing a bridging radical, namely $Ni_2(CTH)_2(PTHF)(ClO_4)_2$ [45]. The magnetic behaviour of this compound is consistent with an $S=5/2$ ground state, as a result of the ferromagnetic coupling between the two metal ions ($S=1$) and the bridging $PTHF^{2-}$ radical. The best fit parameters of the magnetic data gave $J=-61(3)$ cm^{-1} with $g_{Ni}=2.21$. The EPR of this derivative shows a broad feature centered at $g=4.53$ in agreement with the value expected for a $S=5/2$ in a rhombic environment, supporting the above formulation. The smaller value of the observed coupling constant, when compared to the values observed for the $Ni(CTH)(SQ)^+$ complexes [12, 13], can be due to a less effective overlap of the metal and radical orbitals or to a not perfect orthogonality.

Copper

$[Cu(DTBSQ)_2]_2$ has the structure shown in Fig. 10 [46]. The coordination around each copper(II) is best described as distorted five coordinate. In this geometry the coupling between copper(II) and semiquinonates is expected to be antiferromagnetic, and the experimental susceptibility agrees with this view [15].

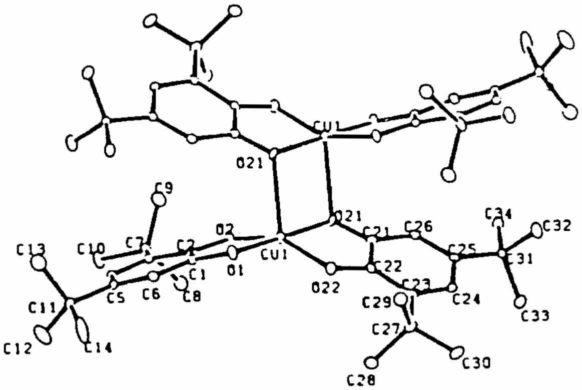

Fig. 10. Structure of $[Cu(DTBSQ)_2]_2$; after ref. 46.

Optical properties

The polyoxolene complexes of transition metal ions, formed either from catecholato or semiquinonato ligands, are characterized by rich electronic spectra whose interpretation is not always straightforward. Indeed they exhibit a pattern of bands due either to internal ligand transitions or to charge transfer transitions of different origin and intensities and, especially for the semiquinonato chromophores, their assignment is often difficult to perform. For this reason electronic spectroscopy has not been frequently used for the characterization of these compounds; however some recent studies [8, 10, 13, 47–49] on simple 1:1 metal–dioxolene chromophores have shown how this technique can be useful for elucidating the nature of the metal–dioxolene adduct, i.e. catecholato or semiquinonato, and for predicting the ferro- or antiferromagnetic nature of the coupling in the metal–semiquinonato moiety, the redox behaviour and the chemical reactivity (as an example towards dioxygen). In addition the strong coupling between the metal ion and the semiquinonato ligands determines a dramatic enhancement of the intensities of transitions which are spin forbidden on the isolated metal ion, thus providing information on the magnetic coupling involving excited states. In the following we will provide some simple examples which can be considered as useful models for more complex spectra and shed light on the magnetic properties of metal–polyoxolene complexes.

The catecholato complexes are characterized by two intense π–π internal ligand transitions in the UV region, as unambiguously shown by the electronic and CD spectra of the optically active Zn(SS–CTH)(Cat) complex [13]. All the intense bands observed in the visible region of the spectra of the catecholato complexes of the 3d metal ions must be assigned as charge transfer transitions. Indeed by comparing the spectra of the metal–catecholato complex formed by different catecholato ligands, all the bands falling in the near IR and visible regions may be reasonably assigned as ligand-to-metal charge transfer (LMCT) transitions, whose intensities depend on the metal ion. For example the iron(III)–catecholato adducts exhibit two intense bands in the visible region ($\epsilon = 2000$–4000) [47, 48], whereas the spectrum of the cobalt(III) analogues are characterized by two weak absorptions ($\epsilon = 100$–200) [49]. This different behaviour can be explained by taking into account the different nature of the metal acceptor orbitals, i.e. t_{2g} (π^*) and $e_g(\sigma^*)$ for iron(III) and cobalt(III), respectively. Since the catecholato HOMOs involved are two π^* orbitals, the transitions characterizing the cobalt(III) chromophore must be weaker because the overlap between the metal and π^* orbital of the radical is smaller than in the iron complex where the metal orbitals are π^*.

It is possible to associate the intensities of the LMCT transitions in catecholato complexes with the magnetic coupling observed in the corresponding semiquinonato complexes. In fact the overlap of the magnetic orbitals has been previously shown as a necessary requirement for explaining the ferro- or antiferromagnetic coupling between two interacting magnetic centers, like a 3d metal ion and a semiquinonato ligand. It can be anticipated therefore that catecholato chromophores showing intense LMCT transitions (i.e. π^*–π^*) will originate antiferromagnetically coupled metal semiquinonato complexes by one-electron oxidation, whereas a ferromagnetic coupling must be expected for the chromophores characterized by weak LMCT transitions (π^*–σ^*). This prediction is based on the fact that the π^* HOMO orbital of the catecholato has the same symmetry properties of the SOMO of the semiquinonato ligand. A typical example of the validity of this simple model is provided by the spectra of the five coordinate Ni(n_3)(Cat) and Cu(n_3)(Cat) chromophores, which exhibit intense and weak, respectively, LMCT transitions in their electronic spectra [14]. In fact the Ni(n_3)(SQ)$^+$ complexes are characterized by a doublet ground state resulting from the antiferromagnetic coupling between the $S = 1$ metal ion and the $S = 1/2$ radical, whereas the Cu(n_3)(SQ)$^+$ derivative has a triplet ground state consequent to ferromagnetic interaction.

The spectra of the semiquinonates are more complicated than those of the catecholates mainly because for the former there are more internal ligand transitions present. The electronic and CD spectra of the Zn(SS–CTH)(SQ)$^+$ chromophores show that four different transitions characterize the coordinated semiquinonato ligand, two in the UV region, one in the near UV and one in the near IR region, respectively [13]. The latter two bands are diagnostic of the radical character of the coordinated ligand. They are of significantly different intensity, that occurring in the near IR region being weak, whereas the other is intense, and are both characterized by a vibronic progression.

The oxidation of the catecholato removes one electron from the HOMO and transitions involving the internal levels and the resulting SOMO are possible. At the same time the electronic redistribution induces a different order of the relative energies of the internal orbitals. The SOMO has π^* character, but the highest doubly occupied molecular orbital is localized in the dioxolene plane. The weak band in the IR is suggested to involve this orbital and the SOMO and is therefore n–π^* in character, whereas the band occurring in the near UV region is associated with a π^*–π^* allowed transition, again involving the SOMO as acceptor orbital. These two bands characterize all the known semiquinonato derivatives as evidenced by literature data [50] and provide an unambiguous tool for the assignment of the formal oxidation state of a coordinated dioxolene. An example of the use of these transitions for the correct assignment of the charge distribution in metal complexes is provided by Mn(CTH)(DTBSQ)ClO_4 and Mn(CTH)(TCCat)PF_6 [10]. They are characterized by the same effective magnetic moment and are ESR silent. Indeed the quintet ground state of the former is due to the presence of antiferromagnetically coupled manganese(II) and the semiquinonato ligand, whereas in the latter it originates from manganese(III), as shown by the electronic spectra.

The spectra of the semiquinonato chromophores are in general characterized by more intense charge transfer spectra, compared to the catecholato complexes. Indeed either MLCT or LMCT transitions are possible, depending on the relative energy of the SOMO and t_{2g} metal orbitals. However in the chromophores investigated with some detail, as ML(diox) (L = CTH or n_3) chromophores [8, 12–14], the experimental data are consistent with a MLCT character of the observed transitions.

A relevant feature of the spectra of metal semiquinonato complexes is the intensity enhancement of optical transitions consequent to magnetic exchange effects. Intensity enhancements of spin-forbidden transitions of a given metal ion due to exchange effects in a pair with another paramagnetic metal ion are well known [51], but the phenomenon has been found particularly dramatic in metal–semiquinonato adducts. In their electronic spectra bands attributable to forbidden d–d transitions appear with intensities of the same order of magnitude as those characterizing the spin allowed, transitions provided that their energy is not too different from that of an allowed charge transfer transition. As an example in the spectra of $Cr(CTH)(SQ)^{2+}$ very narrow bands are present at *c.* 14 000 cm^{-1} ($\epsilon = 3000-5000$) [8] (Fig. 11). The position and the shape of this band are in accord with ${}^4A_{2g}$–${}^2E_g$ transition of chromium(III), and also the insensitivity of its frequency to ligand-field variation agrees with this assignment. However the oscillator strength is orders of magnitude higher than expected, and observed, for spin-forbidden transitions. We justified this behavior with the effects associated to magnetic coupling. In fact the antiferromagnetic coupling between the ${}^4A_{2g}$ of the metal ion and the semiquinonato originates a triplet ground state with an excited quintet state, while the excited ${}^2E_g$ will originate a singlet and a triplet state. A transition between the two triplet terms becomes therefore allowed. The proximity of an allowed MLCT transition involving terms of the same multiplicity offers a mechanism for intensity enhancement [52]. The effect is in general very dramatic as compared to the couple of metal ions pairs because the energy associated to the charge transfer responsible of the intensity enhancements is much smaller in these chromophores. Indeed metal-to-ligand rather then metal-to-metal electron transfer processes are involved.

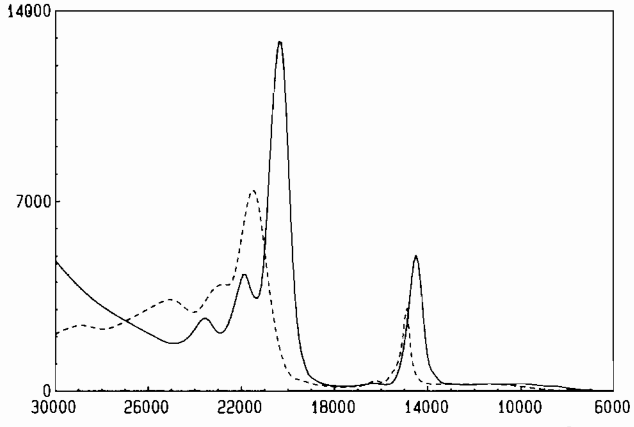

Fig. 11. Acetonitrile solution spectra of $[Cr(CTH)(SQ)]^{2+}$ complexes: SQ = TCSQ (——), DTBSQ (– – –); after ref. 8.

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