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Articles

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Tetraoxolene Radical Stabilization by the Interaction with Transition-Metal Ions

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Metal complexes of formula $M_2(CTH)_2(DHBQ)Y_2$ (M = Mn, Fe, Ni; CTH = *dl*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; Y = ClO_4, PF_6) have been obtained by reaction of the appropriate $M(CTH)^{2+}$ cation and 2,5-dihydroxy-1,4-benzoquinone (H_2DHBQ) in alkaline medium. On the basis of their spectral and magnetic properties, it is suggested that these complexes are dinuclear with the $DHBQ^{2-}$ ligand bridging the two dipositive metal ions. The coupling between the metal ions is weakly antiferromagnetic. When $Cr(CTH)^{2+}$ is used as reacting species, complexes of formula $Cr_2(CTH)_2(DHBQ)Y_3$ are obtained. A compound of the same stoichiometry is obtained by oxidizing the above diiron(II) derivative. On the basis of IR, electronic, EPR, and Mössbauer spectra, evidence is found that these compounds contain the radical species $DHBQ^{3-}$ bridging the tripositive metal ions. Electrochemical data support this formulation. Magnetic susceptibility measurements in the range 4–298 K are consistent with a $S = {}^5/_2$ and a $S = {}^9/_2$ ground state for the chromium(III) and iron(III) derivatives, respectively, as a result of a strong antiferromagnetic coupling between the metal ions and the bridging radical. The stabilization of the radical ligand in the latter derivatives is discussed on the basis of the electronic properties of the tetraoxolene moiety. The unusual EPR spectra are discussed and interpreted in terms of a general approach valid for high-spin values.

Introduction

Currently several different approaches are followed in order to synthesize molecular based ferromagnets.[1-3] One that is particularly appealing is the metal–radical approach,[3] in which transition-metal ions are connected through stable organic paramagnetic ligands in extended networks, eventually yielding ordered magnetic states below critical temperatures, which are now in the range of 20 K.

In order to increase the transition temperatures, it is necessary to design three-dimensional networks of metal ions and radicals, providing efficient exchange pathways between them. The nitroxides which we have used so far[3-8] have the defect that they are rather poor ligands toward transition-metal ions, so that they require the presence of appropriate coligands which enhance the Lewis acidity of the metal cations. The coligands are generally fluorinated diketones or carboxylates, which do not provide useful exchange pathways to the metal ions, thus limiting the magnetic dimensionality and decreasing the critical temperature of the transition to magnetic order.

Dioxolene molecules are much stronger ligands than the nitroxides, so they might in principle efficiently be used in the metal–radical approach to molecular based ferromagnets. In fact it is known that *o*-semiquinones can bind to metal ions yielding a large range of different couplings. In particular, when the binding geometry is appropriate both strong ferro- and antiferromagnetic coupling can be obtained.[9-15]

However simple *o*-semiquinones are rather reluctant to bridge between metal ions,[16] so they are difficult to be employed as building blocks of extended magnetic structures. Tetraoxolenes, on the other hand, which have four oxygen donor atoms, can act as bis-bidentate ligands toward two different metal ions. Recently we reported[17] dinuclear ruthenium complexes with tetrox, 1,4,5,8-tetraoxonaphthalene, $[Ru_2(bpy)_4(tetrox)]^{n+}$, n = 2–4, but no complex was found to contain a radical species.

Now we have taken into consideration 2,5-dihydroxy-1,4-benzoquinone, H_2DHBQ, which can undergo either a one-electron oxidation or two one-electron reduction processes, yielding species with charges ranging from −4 to −1 (Scheme I).[18] The species with charges −1 and −3, respectively, are radical anions. These molecules have already been studied as ligands to transition-metal ions but in the nonradical $DHBQ^{2-}$ form.[19-21] They were found to bridge two metal ions, and the resulting complexes were found to be only weakly antiferromagnetically coupled via superexchange interaction.

We decided therefore to determine the conditions under which the radical states of the $DHBQ^{n-}$ can be stabilized as bridging ligands in different dinuclear M–(DHBQ)–M moieties, where M is a 3d metal ion. Along the line of our previous work on metal–dioxolene systems,[13-15,22,23] we have then synthesized a series

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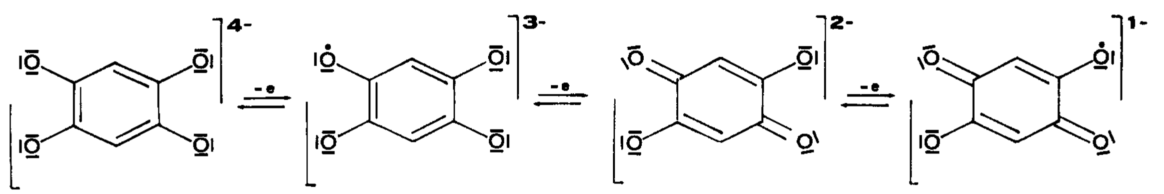
Scheme I



of dinuclear metal complexes of formula $M_2(CTH)_2(DHBQ)Y_n$ (M = Cr, Mn, Fe, Ni; CTH = *dl*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; Y = ClO_4, PF_6), where we have found that with both iron(III) and chromium(III) the trinegative radical state $DHBQ^{3-}$ can indeed be stabilized.

Experimental Section

Materials. The ligand 2,5-dihydroxy-1,4-benzoquinone (H_2DHBQ) (Aldrich) was used as received. The ligand CTH and the complex $Ni(CTH)(PF_6)_2$ (α isomer) were prepared according to literature methods.[24,25]

$M(CTH)Cl_2$ (M = Cr, Fe). A 5-mmol amount of the appropriate metal chloride was gently refluxed for 0.5 h in 30 mL of a 2/1 mixture of dimethylformamide/triethylorthoformate under a nitrogen atmosphere. The resulting solution was slowly added to 6 mmol of CTH in 40 mL of dimethylformamide and then gently warmed for 10 min. Deep blue (chromium) and light blue-green (iron) crystals separated on cooling. They were collected on a sintered glass funnel, washed with a deaerated mixture of 1/4 absolute ethanol/diethyl ether, and then dried in a stream of nitrogen. These compounds are extremely sensitive toward dioxygen and must be prepared immediately before use.

$Mn(CTH)Cl_2$. $(NEt_4)_2MnCl_4$ (3 mmol) was dissolved in 40 mL of acetonitrile, and the resulting solution was then mixed with a solution of CTH (4 mmol) in the same solvent (40 mL). After few minutes white crystals began to appear. They were filtered out, washed with acetonitrile, and then dried in the air.

$[M_2(CTH)_2(DHBQ)]Y_2\cdot nH_2O$ (M = Mn and Ni, Y = PF_6, n = 1; M = Fe, Y = ClO_4, n = 2). H_2DHBQ (1 mmol) was added to a suspension of the appropriate M–CTH derivative (2 mmol) in deaerated methanol (40 mL). Sodium hydroxide (2 mmol) was added, and the resulting solution was gently refluxed for 0.5 h. The addition of an aqueous solution of $NaClO_4$ or KPF_6 led to the precipitation of microcrystalline materials, which were filtered out, washed with water and then recrystallized from acetonitrile/water mixtures. Yields: 70–80%. (Anal. Found for $Mn_2(CTH)_2(DHBQ)(PF_6)_2\cdot H_2O$: C, 40.32; H, 6.90; N, 9.97. Calcd for $C_{38}H_{76}F_{12}Mn_2N_8O_5P_2$: C, 40.57; H, 6.81; N, 9.96. Found for $Fe_2(CTH)_2(DHBQ)(PF_6)_2\cdot H_2O$: C, 40.49; H, 6.65; N, 9.65. Calcd for $C_{38}H_{76}F_{12}Fe_2N_8O_5P_2$: C, 40.51; H, 6.80; N, 9.95. Found for $Fe_2(CTH)_2(DHBQ)(ClO_4)_2\cdot 2H_2O$: C, 43.12; H, 7.28; N, 10.34. Calcd for $C_{38}H_{78}Cl_2Fe_2N_8O_{14}$: C, 43.31; H, 7.46; N, 10.64. Found for $Ni_2(CTH)_2(DHBQ)(PF_6)_2\cdot H_2O$: C, 40.39; H, 6.61; N, 9.68. Calcd for $C_{38}H_{76}F_{12}N_8Ni_2O_5P_2$: C, 40.30; H, 6.76; N, 9.90.)

$[Cr_2(CTH)_2(DHBQ)]Y_3\cdot nH_2O$ (Y = ClO_4, n = 2; Y = PF_6, n = 0). This compound was obtained by following the above procedure with $Cr(CTH)Cl_2$. (Anal. Found for $Cr_2(CTH)_2(DHBQ)(PF_6)_3$: C, 36.73; H, 6.13; N, 8.73. Calcd for $C_{38}H_{74}Cr_2F_{18}N_8O_4P_3$: C, 36.63; H, 5.99; N, 8.99. Found for $Cr_2(CTH)_2(DHBQ)(ClO_4)_3\cdot 2H_2O$: C, 39.92; H, 6.77; N, 9.38. Calcd for $C_{38}H_{78}Cl_3Cr_2N_8O_{18}$: C, 39.98; H, 6.88; N, 9.80.)

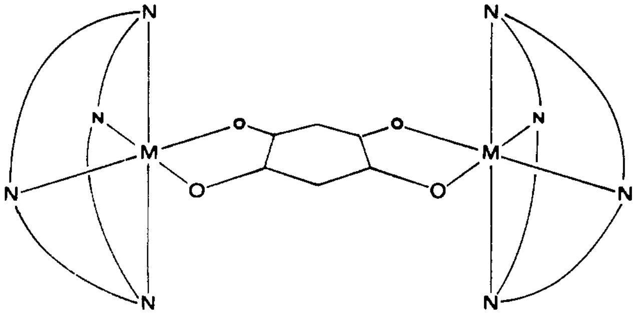
$Fe_2(CTH)_2(DHBQ)(ClO_4)_3\cdot 2H_2O$. A solution of $AgClO_4$ (0.5 mmol) in acetonitrile (15 mL) was slowly added to a stirred solution of $Fe_2(CTH)_2(DHBQ)(ClO_4)_2\cdot 2H_2O$ (0.5 mmol) in the same solvent (30 mL). After 0.5 h the solution was filtered and then mixed with 20 mL of an aqueous solution of $NaClO_4$. The resulting solution was gently concentrated under reduced pressure until crystallization occurred. The precipitate was collected, washed with a small amount of cool water, and then dried over $CaCl_2$. Yield: 45%. (Anal. Found: C, 39.46; H, 6.77; N, 9.54. Calcd for $C_{38}H_{78}Cl_3Fe_2N_8O_{18}$: C, 39.58; H, 6.82; N, 9.72.)

Physical Measurements. Polycrystalline powder EPR spectra were recorded with a Bruker ER200 spectrometer working at X-band frequency. Electronic spectra were recorded in the range 5000–40000 cm^{-1} on a Perkin-Elmer Lambda 9 spectrophotometer. Infrared spectra were recorded on a Perkin Elmer 283 spectrophotometer. The electrochemical analysis by cyclic voltammetry was carried out by using an electrochemical unit consisting of an Amel Model 553 potentiostat equipped with Amel 863, 560/A, and 561 elements and an Amel 731 integrator and a classical three-electrode cell. The working electrode was a platinum microsphere, the auxiliary electrode was a platinum disk, and the reference electrode was a calomel electrode in aqueous saturated KCl. Before each experiment the solution was carefully deaerated with a nitrogen flow. All potentials here reported are referenced against ferrocenium/ferrocene (Fc^+/Fc). Variable-temperature magnetic susceptibility measurements were performed by using a fully automatized Aztec DSM5 susceptometer equipped with an Oxford CF1200S continuous-flow cryostat and a Bruker B-E15 electromagnet working at 1.35 T. The apparatus was calibrated by measuring the magnetic susceptibilities of a pure sample of manganese Tutton salt at several temperatures between 4.2 and 300 K. Diamagnetic corrections were estimated from Pascal constants. Mössbauer effect spectra were obtained on a conventional constant-acceleration spectrometer that utilized a room-temperature rhodium matrix cobalt-57 source and was calibrated at room temperature with natural-abundance α-iron foil. The low-temperature measurements were performed in a liquid-helium Harwell cryostat equipped with a variable-temperature sample holder; the temperature was controlled by an Oxford ITC-4 temperature controller. The spectra were fit with Lorentzian line profile doublets in which the line position, width, and areas were varied to give the best agreement to the observed spectra.

Results

Complexes of general formula $M_2(CTH)_2(DHBQ)Y_2\cdot nH_2O$ (M = Mn, Fe, Ni; Y = ClO_4, PF_6) are obtained when solutions containing the dinegative $DHBQ^{2-}$ anion are allowed to react with the appropriate $M(CTH)^{2+}$ derivative.

All the complexes are assumed to contain dinuclear cations in which two metal ions are bridged by the tetraoxolene ligand shown as



with the two macrocycles coordinated in folded configuration in the remaining octahedral coordination sites. Electrochemical, spectroscopic and magnetic data support this suggestion.

The IR spectra of the three compounds are strictly similar to each other and in particular show a very intense band at 1540 cm^{-1} to be assigned to the carbonyl stretching mode of the bridging $DHBQ^{2-}$ ligand.[19] Low-intensity absorptions at 1620 cm^{-1} were also observed and were believed to be indicative of the existence of impurities, such as mononuclear complexes, present in small percentage in the samples.

The electronic spectra of the three compounds show a bands at ca. 29000–31000 cm^{-1}, which is consistent with an internal ligand transition of $DHBQ^{2-}$ (Table I). In addition $Ni_2(CTH)_2(DHBQ)Y_2$ shows the d–d bands typical of octahedral nickel(II), while $Fe_2(CTH)_2(DHBQ)Y_2$ shows intense bands at 10200, 17200, and 22300 cm^{-1}, which are presumably CT in nature (Figure 1).

The room-temperature magnetic moments of 4.4 μ_B for nickel, 7.9 μ_B for iron, and 8.2 μ_B for manganese agree with two substantially uncoupled high-spin metal(II) ions. The nickel and manganese derivatives show a weak temperature dependence of

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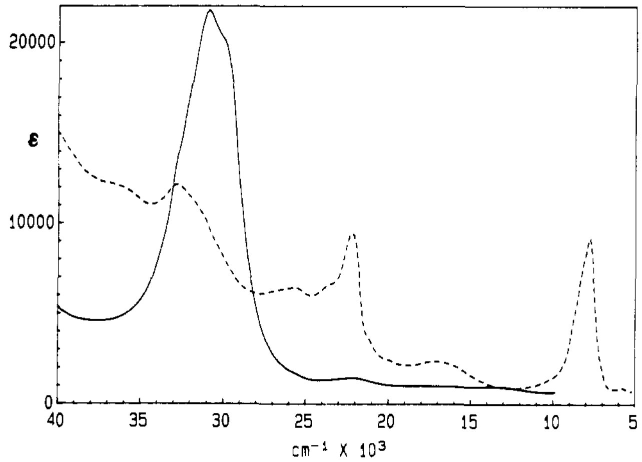

Figure 1. Electronic spectra of $[Fe_2(CTH)_2(DHBQ)]^{2+}$ (—) and $[Fe_2(CTH)_2(DHBQ)]^{3+}$ (- - -) in acetonitrile solution.

the magnetic moment in the range 4.2–300 K, which can be interpreted with an antiferromagnetic coupling, $J = 5$ cm^{-1} for nickel and $J = 0.7$ cm^{-1} for manganese. We use the Hamiltonian in the form $H = JS_1{\cdot}S_2$. Similar values of the coupling constants were previously reported for the complexes of the $DHBQ^{2-}$ ligand.[19,21] In the same temperature range the iron derivative does not show significant variations of the effective magnetic moment.

Only the manganese derivative gives an EPR spectrum, which is centered at $g \approx 2$.

Mössbauer spectra of $Fe_2(CTH)_2(DHBQ)(PF_6)_2$ reported at room and liquid-nitrogen temperature show (Figure 2 and Table II), besides minor components due to impurities, a quadrupole-split doublet with parameters that are typical of high-spin iron(II) compounds. The two iron sites are identical within the Mössbauer time scale, as proved by the value of the line width. While the temperature dependence of the isomer shift can be easily accounted for by second-order Doppler shift, the increase of the quadrupole splitting on going from room temperature to 78 K is larger than expected. Spectra obtained at intermediate temperatures, namely 214 and 150 K, show a progressive increase of the quadrupole splitting value, ruling out the possibility of the interconversion of two different components as a function of the temperature.

Cyclic voltammetry experiments in deaerated acetonitrile solutions show that manganese, iron, and nickel derivatives undergo three reversible one-electron redox processes, suggesting the formation of $[M_2(CTH)_2(DHBQ)]^{n+}$ species, with $n = 1$–4. All the complexes exhibit a reversible electron-transfer process in the range −1.30/−1.42 V vs ferrocenium/ferrocene (Fc^+/Fc) couple (Figure 3 and Table III), which can be suggested to be associated with a ligand-centered electron-transfer reaction with the tetraoxolene bridging two metal–macrocycle moieties, because it remains practically constant throughout the series.

Table I. Electronic Spectral Data for $[M_2(CTH)_2(DHBQ)]^{n+}$ in Acetonitrile Solutions[a]

complex	spectral data
$[Cr_2(CTH)_2(DHBQ)]^{3+}$	14 050 (400), 14 850 (2450), 15 450 (380), 16 150 (950), 16 900 (530), 19 950 (13 750), 20 400 sh, 21 850 (8060), 22 000 sh, 26 700 sh, 28 400 (4560), 30 600 (8900), 33 400 sh, 35 300 sh, 36 200 (5350)
$[Mn_2(CTH)_2(DHBQ)]^{2+}$	20 000 (500), 29 600 sh, 30 600 (34 350)
$[Fe_2(CTH)_2(DHBQ)]^{2+}$	10 200 (1200), 14 300 sh, 17 200 (1750), 22 300 (2800), 29 800 sh, 31 800 (21 730)
$[Fe_2(CTH)_2(DHBQ)]^{3+}$	7780 (9200), 8100 sh, 10 200 sh, 15 900 sh, 17 200 (2350), 19 900 sh, 21 100 (9430), 22 400 sh, 23 500 sh, 25 800 (6450), 26 900 sh, 32 800 (12 150), 36 500 sh
$[Ni_2(CTH)_2(DHBQ)]^{2+}$	10 600 (40), 18 000 sh, 20 000 sh, 21 500 sh, 28 400 (18 250), 31 600 (18 400), 32 500 sh

[a] Absorption maxima in cm^{-1}; ε (mmol^{-1} cm^2) in parentheses; sh = shoulder.

Table II. Mössbauer Spectral Data

complex	T	δ^c	ΔE_Q	$\Gamma_1/\Gamma_2{}^a$	$A_1/A_2{}^a$
$Fe_2(CTH)_2(DHBQ)(PF_6)_2$	295	1.005	2.082	1.0^b	1.0^b
	78	1.118	2.875	1.0^b	1.0^b
$Fe_2(CTH)_2(DHBQ)(PF_6)_3$	295	0.46	1.04	0.70	1.00
	78	0.54	0.84	0.35	1.20

[a] Low- to high-velocity ratio. [b] Values constrained to 1/1 ratio. [c] Referenced to room temperature α-iron foil.

All the complexes show additionally two reversible one-electron redox processes at more positive potentials, whose values depend on the nature of the metal ions. For manganese and nickel the

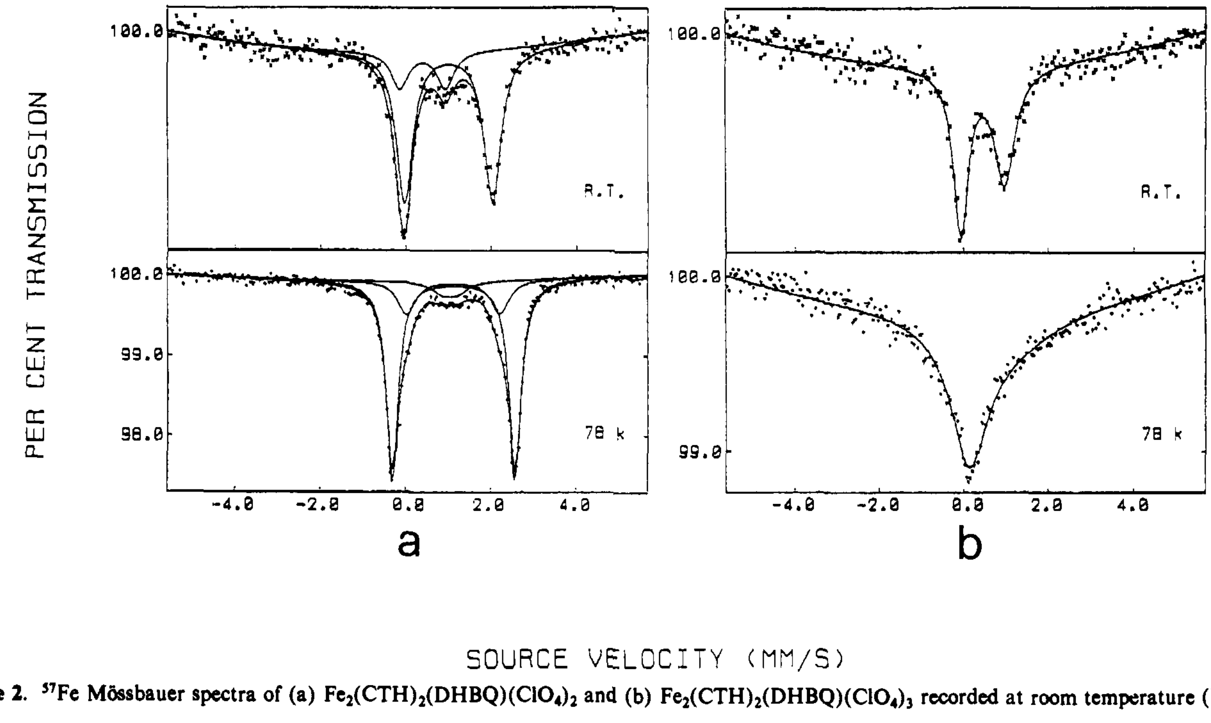

Figure 2. ^{57}Fe Mössbauer spectra of (a) $Fe_2(CTH)_2(DHBQ)(ClO_4)_2$ and (b) $Fe_2(CTH)_2(DHBQ)(ClO_4)_3$ recorded at room temperature (RT) and 78 K.

Table III. Electrochemical Potentials (V) of the $[M_2(CTH)_2(DHBQ)]^{n+}$ Complexes (M = Cr, Mn, Fe, Ni) in Acetonitrile, 0.1 M NBu_4PF_6[a,b]

M	*n*		
	2+/1+	3+/2+	4+/3+
Cr	-1.04	-0.01	
Mn	-1.30	0.17	0.36
Fe	-1.31	-0.22	0.35
Ni	-1.42	0.68	0.88

[a] All potentials are referenced to the ferrocenium/ferrocene couple. The potentials are the average anodic and cathodic peak potentials in cyclic voltammograms recorded at 100 mV s^{-1}. [b] At 25 °C for ca. 10^{-3} M solutions.

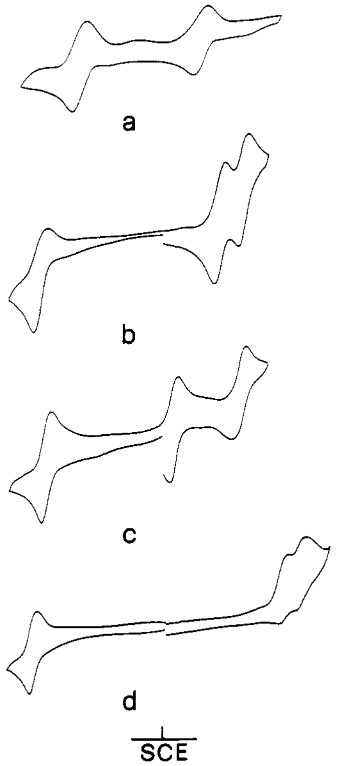

Figure 3. Cyclic voltammograms of $M_2(CTH)_2(DHBQ)Y_n$ in acetonitrile, 0.1 M NBu_4PF_6, where M = Cr (a), Mn (b), Fe (c), and Ni (d). Scan rates are 0.1 V s^{-1}.

difference between the two redox steps is not large (0.19 and 0.20 V, respectively), so that the disproportionation constant associated with the equilibrium

$$2[M_2(CTH)_2(DHBQ)]^{3+} \rightleftharpoons [M_2(CTH)_2(DHBQ)]^{4+} + [M_2(CTH)_2(DHBQ)]^{2+}$$

is ca 10^{-3}. This means that it is quite difficult to isolate pure solids containing the tripositive cation. The iron derivative on the other hand exhibits well-separated redox processes (-0.22 and +0.37 V vs Fc^+/Fc), and the value of the associated disproportionation constant is small (10^{-10}).

One-electron oxidation of $Fe_2(CTH)_2(DHBQ)Y_2$ with $AgClO_4$ leads to the isolation of a compound of formula $Fe_2(CTH)_2(DHBQ)(ClO_4)_3$, which in principle can be formulated in several different ways: $Fe^{II}(DHBQ^{2-})Fe^{III}$, $Fe^{III}(DHBQ^{3-})Fe^{III}$, or $Fe^{II}(DHBQ^{-})Fe^{II}$. The observed dependence of the redox potential on the nature of the metal ion suggests that the last possibility must be excluded. Indeed the nickel and manganese derivatives exhibit redox couples at significantly more positive values. IR spectra of $Fe_2(CTH)_2(DHBQ)(ClO_4)_3$ show that the band at 1540 cm^{-1}, which was used[19] as diagnostic or bridging $DHBQ^{2-}$, decreases drastically in intensity compared to that of $Fe_2(CTH)_2(DHBQ)(ClO_4)_2$.

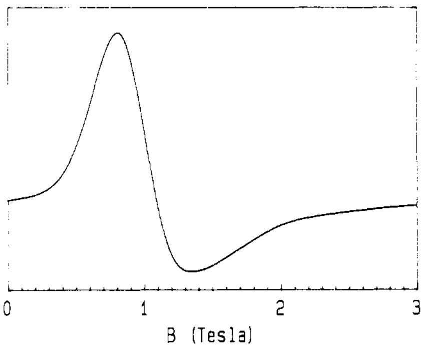

Figure 4. Polycrystalline powder EPR spectrum of $Fe_2(CTH)_2(DHBQ)(ClO_4)_3$ at 4.2 K.

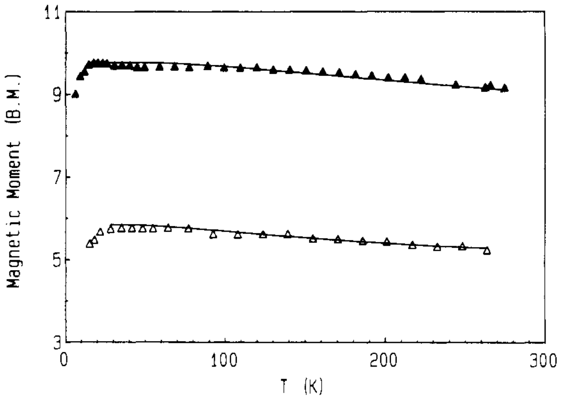

Figure 5. Variation of the magnetic moment with temperature in the range 4-298 K for $Fe_2(CTH)_2(DHBQ)(ClO_4)_3$ (▲) and for $Cr_2(CTH)_2(DHBQ)(ClO_4)_3$ (△). The curves represent the best fit (see text).

The Mössbauer spectrum at room temperature shows (Figure 2 and Table II) an asymmetric doublet with parameters that are typical of high-spin iron(III) derivatives. Therefore, the formulation $Fe^{III}(DHBQ^{3-})Fe^{III}$ is strongly supported. The asymmetry is mainly attributable to differences in line widths rather than in the areas of the peaks. With a decrease of temperature, the asymmetry increases with the high velocity component broadening out until, at about 78 K, the doublet nearly collapses to a broad single line with non-Lorentzian line shape. This behavior suggests the presence of paramagnetic relaxation on the Mössbauer time scale of 10^{-8} s. In order to study the nature of this relaxation process in more detail, Mössbauer effect measurements as a function of temperature extended in the liquid-helium range are in progress.

The electronic spectrum of this compound is shown in Figure 1. This spectrum is rich with very intense absorptions, whose assignments are not straightforward. The comparison with the spectrum of the chromium(III) derivative, which contains the same radical anion as bridging ligand (see below), suggests that the band occurring at 21 100 cm^{-1} might be assigned to an internal transition of the $DHBQ^{3-}$ ligand. The strong band occurring at 7800 cm^{-1} is not present in the spectrum of the chromium(III) complex and therefore is assigned to a charge-transfer transition.

The complex $Fe_2(CTH)_2(DHBQ)(ClO_4)_3$ is EPR silent at room temperature, but it shows a broad feature centered about $g = 6.3$ at 4.2 K, as shown in Figure 4. The effective magnetic moment of this compound at room temperature is 9.1 μ_B, corresponding to 6.5 μ_B per iron, which is indicative of extensive magnetic coupling within the dimer. In fact the expected value for uncoupled iron(III) and radical species would be 8.5 μ_B. The magnetic moment is temperature dependent, increasing on decreasing temperature, and reaches a plateau at ca. 9.8 μ_B below 30 K (Figure 5). These data clearly indicate that a ground state with $S = {}^9/_2$ is populated at low temperature.

$Cr_2(CTH)_2(DHBQ)(ClO_4)_3$, which can be obtained by reaction of $Cr(CTH)^{2+}$ with $DHBQ^{2-}$, has an IR spectrum similar to that of $Fe_2(CTH)_2(DHBQ)(ClO_4)_3$, suggesting that it can be formulated as $Cr^{III}(DHBQ^{3-})Cr^{III}$. The electronic spectrum shows a sharp and intense band at 14 850 cm^{-1}, with a bandwidth of ca.

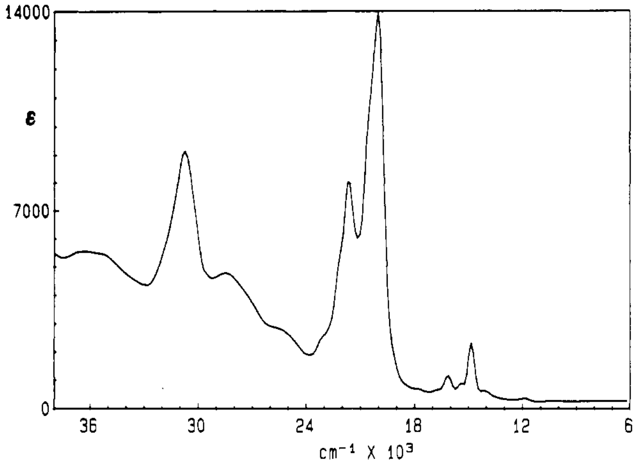

Figure 6. Electronic spectrum of $[Cr_2(CTH)_2(DHBQ)]^{3+}$ in acetonitrile solution.

300 cm^{-1} (Figure 6), which compares well with that reported for a chromium(III)–semiquinonate species, confirming the above formulation.[14]

The room-temperature effective magnetic moment is 5.3 μ_B, and it is temperature dependent, increasing on decreasing temperature and reaching a plateau at ca. 5.8 μ_B below 50 K (Figure 5). These data suggest that the spins of the chromium and of the radical are coupled and give some indication of a ground $S = {}^5/_2$ state.

The EPR spectrum of $Cr_2(CTH)_2(DHBQ)(ClO_4)_3$ shows an isotropic feature at $g \cong 4$, which does not show any significant change on decreasing temperature.

Cyclic voltammetry experiments show that this complex undergoes two reversible one-electron-transfer processes at −1.03 and −0.01 vs Fc$^+$/Fc (Figure 3 and Table III). Electronic and EPR spectra suggest that the latter process is associated with the ligand-centered electron-transfer process $DHBQ^{2-}/DHBQ^{3-}$.

Solutions containing the two $M_2(CTH)_2(DHBQ)^{3+}$ cations (M = Fe, Cr) are unstable and slowly decompose, yielding mononuclear $M(CTH)(DHBQ)^+$ complexes. This prevents the possibility of obtaining suitable crystals for X-ray analysis.

Discussion

The spectral and magnetic properties of the complexes of the bivalent metal ions confirm what was already known[19,21] about the ability of the $DHBQ^{2-}$ ligand to transmit the exchange interaction. The redox potentials here reported show that, with the exception of iron, the bivalent metal ions require too low potentials to yield radical species; therefore, they are not suitable for the metal–radical approach to molecular based ferromagnets. When the +3 oxidation state of the metal is readily available, the radical states can be conveniently stabilized, as shown by the chromium(III) and iron(III) derivatives. The latter is particularly interesting, because, although the iron(II) dimer can undergo one-electron oxidation, the product is not the mixed-valence $Fe^{II}(DHBQ^{2-})Fe^{III}$ species but the iron(III) dimer bridged by the $DHBQ^{3-}$ radical; i.e., both the metal ions are oxidized and the ligand is reduced. For comparison the oxidation of $[Ru_2(bpy)_4(tetrox)]^{2+}$ yields the mixed-valent $Ru^{II}(tetrox^{2-})Ru^{III}$ species, rather than the radical-stabilized $Ru^{III}(tetrox^{3-})Ru^{III}$ species.[17] Among the possible causes of the different behaviors, we may suggest the higher covalency of the ruthenium derivative, which stabilizes the species with lower charge separation. Processes that are accompanied by extensive charge redistributions within the metal dioxolene species, as observed for the Fe–DHBQ–Fe system, were previously reported.[15,26-29]

The present results confirm that both the di- and the tetraoxolene molecules have frontier orbitals with energies comparable to those of the transition-metal ions, and the nature of the reduced and oxidized species depends on the additional ligands that are present in the coordination environment.

Both $Cr_2(CTH)_2(DHBQ)(ClO_4)_3$ and $Fe_2(CTH)_2(DHBQ)(ClO_4)_3$ have effective magnetic moments that increase on decreasing temperature. This behavior is that expected for two spins with $S > {}^1/_2$ which are antiferromagnetically coupled to a central spin with $S = {}^1/_2$. In fact the μ (or χT) vs T plot for this kind of molecules is expected to decrease initially from high temperature, go through a minimum, and increase again at low temperatures.[30] The fact that for both the chromium and iron derivatives μ_{eff} increases on decreasing temperature is indicative that the temperature of the minimum is higher than room temperature, suggesting that in both cases J is large. The temperature dependence of χT was quantitatively fit with $J = 372$ (28) cm^{-1} and $g = 1.98$ (1) for the iron and $J = 273$ (19) cm^{-1} and $g = 1.98$ (1) for the chromium derivative. The calculated values are determined only with limited precision because the experimental temperature dependence of the effective magnetic moments is small.

The strong antiferromagnetic couplings can be justified with the overlap of the π^* orbital of $DHBQ^{3-}$ with the T_{2g} orbitals of both chromium(III) and iron(III). It is interesting to notice that larger couplings were observed for chromium(III)–semiquinonato complexes,[14] presumably due to the fact that the electron is more highly delocalized in the tetraoxolene molecule compared to dioxolene.

The ground state for $Fe_2(CTH)_2(DHBQ)(ClO_4)_3$ is thus $S = {}^9/_2$, and this rather unusual ground state is now rather well documented. In fact a ground $S = {}^9/_2$ was observed as originated by the ferromagnetic coupling of one gadolinium(III), $S = {}^7/_2$, and two copper(II) ions,[30] by the ferromagnetic coupling of one manganese(II) ion and four nitronyl nitroxide radicals,[31] by the ferromagnetic coupling in a dinuclear manganese(II)–manganese(III) complex,[32] and by the antiferromagnetic coupling of two manganese(II) ions bridged by a copper(II).[33] It is apparent that the last compound is very similar to the present one as far as the scheme of magnetic interaction is concerned.

Finally, it is important to refer here to recent reports of mixed-valent iron(III)–iron(II) species, in which the metal ions are bridged by three hydroxyl ions[34] or by two phenoxo groups.[35] In these cases the ground $S = {}^9/_2$ state is largely determined by the electron delocalization in the class III mixed-valence species, which was confirmed by Mössbauer spectra. Again, the same ground state is found in a tetranuclear mixed-valence manganese(III)–manganese(IV) derivative.[36]

High-spin molecules are currently actively investigated, and it is useful that the spectral properties of these are well understood, also with the aim to use them as analytical tools in order to confirm the nature of the ground state. The EPR spectra of $Fe_2(CTH)_2(DHBQ)(ClO_4)_3$ are at first sight puzzling, because only one broad feature is observed at $g \approx 6$. However, a hint to the understanding of this kind of spectra comes from those of Cr_2-

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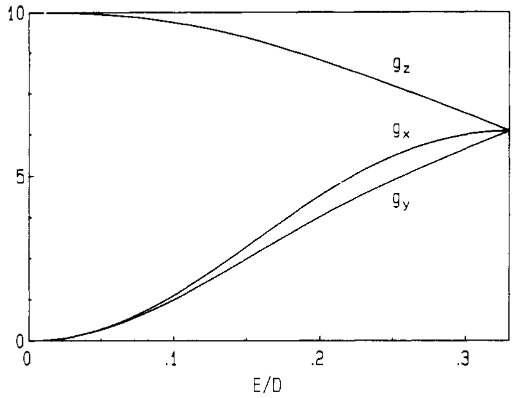

Figure 7. Variation of the principal values of the **g** tensors for the ground state of a $S = {}^9/_2$ system as a function of the E/D parameter.

$(CTH)_2(DHBQ)(ClO_4)_3$. In fact this compound has a ground $S = {}^5/_2$ state and one isotropic g value at $g \approx 4$. It is well-known from the EPR spectra of high-spin iron(III) complexes that when the metal ion is in a completely rhombic coordination environment, only the transitions within the middle Kramers doublet of the zero-field-split $S = {}^5/_2$ manifold are observed:[37] these are isotropic with $g = 4.3$. We assume that the origin of the EPR spectrum of $Cr_2(CTH)_2(DHBQ)(ClO_4)_3$ is the same, with the small reduction in the g value determined by the fact that the chromium ion has a g value that is slightly lower than 2.

If this interpretation is correct, it is tempting to assume that also for the $S = {}^9/_2$ state the origin of the spectra is similar; i.e., they are due to transitions within a Kramers doublet in rhombic symmetry. By using the spin Hamiltonian approach, it is easy to show that an isotropic g feature arising from the middle Kramers doublet is not peculiar to $S = {}^5/_2$ states, but it can be extended to all the $S = (4n + 1)/2$ states that split into an odd number of Kramers doublets. In the limit of maximum rhombic splitting, which corresponds to $E/D = \pm{}^1/_3$, the Kramers doublets of $S = {}^9/_2$ have energies $\pm(11.7D + 1.8E)$, $\pm(4.6D + 1.2E)$, and 0 and the central Kramers doublet has an isotropic g value of $35g_s/11$, where g_s is the value for the spin multiplet. For $g_s = 2$, g is 6.3. For the interest of researchers who may stumble on high-spin states, the isotropic g value for $S = {}^{13}/_2$ is 8.3, for $S = {}^{17}/_2$ is 10.2, and for $S = {}^{21}/_2$ it is 12.0. These values are calculated in the assumption $g_s = 2$.

When the E/D ratio decreases from the limit value of ${}^1/_3$ for $S = {}^9/_2$, two g values move toward zero, while the third tends to 10 at $E/D = 0$. The dependence of the g values on the E/D ratio is shown in Figure 7.

Assuming that the EPR spectra of $Fe_2(CTH)_2(DHBQ)(ClO_4)_3$ are given by transitions within the middle doublet, they can be fitted to the polycrystalline powder spectrum of an effective $S = {}^1/_2$ with g values $g_1 = 5.5$, $g_2 = 5.0$, and $g_3 = 7.3$. These values show that the splitting of the $S = {}^9/_2$ manifold is not completely rhombic, suggesting $E/D = 0.28$.

Conclusion

The present results have shown that the radical species $DHBQ^{3-}$ can be stabilized with trivalent cations, such as iron(III) and chromium(III). $DHBQ^{3-}$ behaves essentially as an innocent ligand, which can yield reasonably strong antiferromagnetic coupling with the metal ions but smaller than that of simple *o*-semiquinones. It is hoped that by using this kind of ligands it is possible to build molecular based ferromagnets.

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Quasirelativistic Effects in the Electronic Structure of the Thiomolybdate and Thiotungstate Complexes of Nickel, Palladium, and Platinum

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In this paper, we present a comparative study of the thiomolybdate and the thiotungstate complexes of the formula $[M'(MS_4)_2]^{2-}$ (M' = Ni, Pd, Pt; M = Mo, W). The electronic structure and the bonding properties of these complexes are discussed by using the quasirelativistic multiple scattering Xα method. We have repeated the calculations for the $[Pt(WS_4)_2]^{2-}$ complex ion without incorporating the mass velocity and the Darwin corrections around the Pt sphere, and certain conclusions are obtained regarding the relativistic and the nonrelativistic effects on these complex ions. Transition and ionization energies are also discussed.

Introduction

The thioanions $[MS_4]^{2-}$ (M = Mo, W), which act as bidentate chelating ligands with transition metals, have been of great interest for many years.[1,2] They have a bioinorganic significance, particularly in the ligand-exchange processes in aqueous solutions.[3,4] The thiomolybdate complex ion plays an important role in the nitrogenase problem and Cu-Mo antagonism.[5] These anions have been studied spectroscopically[6-12] and theoretically.[13-15] Various theoretical calculations have been conducted on the $[MoS_4]^{2-}$ complex ion,[15] and most of these studies have indicated that the HOMO is essentially of S(p) character. This orbital can act as a donor in complexes that contain a transition metal, as may be verified in Figure 1, which is a correlation diagram for $[MoS_4]^{2-}$ in a tetrahedral environment. Tetrathiomolybdates and tetrathiotungstates can produce multimetal complexes of the type

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