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High-Spin Metal Complexes Containing a Ferromagnetically Coupled Tris(semiquinone) Ligand

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The tris-bidentate ligand 1,3,5-tris(5′-*tert*-butyl-3′,4′-dihydroxyphenyl)benzene ($(TBCat)_3Ph$) was synthesized. The reaction of this molecule in basic solution with two paramagnetic acceptors, i.e., a nickel(II)–tetraazamacrocyclic ligand complex (Ni(CTH)) (CTH = *dl*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) and manganese(II)–hydrotris[3-(4′-cumenyl)-5-methylpyrazolyl]borate ($Mn(Tp^{Cum,Me})$), yielded two complexes whose analytical formulas are consistent with those of trinuclear complexes. Spectroscopic and magnetic measurements suggest that these derivatives contain divalent metal ions coordinated to the tris(semiquinone) form of the ligand. Analysis of the magnetic data shows that the π-connectivity of the ligand enforces ferromagnetic coupling between the three semiquinone units of the molecule, giving rise to complexes with $S = 9/2$ ($M = Ni^{II}$) and $S = 6$ ($M = Mn^{II}$) ground states. The coupling within the tris(semiquinone) unit is quite large ($J = -26$ cm^{-1} for the nickel(II) derivative and $J = -40$ cm^{-1} for the manganese(II) one, using the general exchange Hamiltonian $H = \sum J_{ij}S_iS_j$), and it is of the same order of magnitude as that observed in an analogous series of bis(semiquinone) complexes that we recently reported.

Introduction

The possibility to modulate a physical property following a predetermined strategy is of central importance for the development of molecular science. In this sense the lesson we may learn from the synthesis of small molecules is an important step for a future rational design of a multidimensional collection of mutually interacting molecular systems having desirable properties. Molecules that are characterized by high-spin electronic ground states are actively investigated as possible building blocks for molecular magnets since they are attractive candidates for obtaining magnetic solids.[1−5] We are currently attempting the design of appropriate molecular systems with the final goal of obtaining a tridimensional network of paramagnetic centers. Our approach exploits the peculiar electronic properties of metal−semiquinone complexes.[6] The nature of magnetic coupling in complexes formed by 3d and more recently 4f metal ions and paramagnetic *o*-semiquinone ligands is quite well understood.[7,8] We thought that molecules exhibiting designed high-spin electronic ground states could be prepared, provided that appropriate poly-*o*-dioxolene ligands are used.[9−15]

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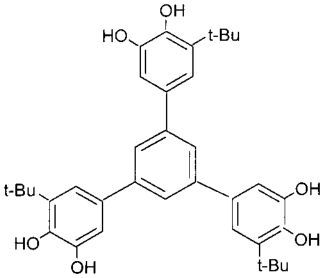
On the basis of simple molecular orbital considerations, it is expected that the 1,3,5-trimethylenebenzene molecule should be characterized by a quartet electronic ground state.[15−18] Bearing this in mind, the potentially tris-bidentate ligand 1,3,5-tris(3′,4′-dihydroxy-5′-*tert*-butyl-phenyl)benzene ((TBCat)$_3$Ph) was synthesized with the aim of isolating a tris(semiquinone) (TBSq)$_3$Ph) derivative in which, according to its topology, the three unpaired electrons are expected to couple ferromagnetically to each other. We thought, therefore, that this topologically predetermined ferromagnetic coupling within the triradical might enforce a high-spin electronic ground state in certain metal complexes of paramagnetic metal ions. To facilitate the analysis of the magnetic data, we have selected two paramagnetic metal ions characterized by nondegenerate electronic ground states. Following our previous studies,[9,19] we used as metal acceptors the nickel(II)−tetraazamacrocycle (Ni(CTH)$^{2+}$, CTH = *dl*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) and the manganese(II)−hydrotris[3-(4′-cumenyl)-5-methylpyrazolyl]borate (Mn(Tp^{Cum,Me})$^+$) complexes. With these acceptors we found that the trianion (TBSQ)$_3$Ph acts as tris-bidentate ligand. These complexes were isolated in the solid state and spectroscopically and magnetically characterized.



Experimental Section

General Procedures. Solvent distillations, synthetic procedures, and electrochemistry were carried out under an argon atmosphere. Tetrahydrofuran was distilled from sodium benzophenone ketyl prior to use. Methylene chloride was distilled from calcium hydride. NMR spectra were recorded on a Varian 300 MHz spectrometer using deuteriochloroform as solvent, and referenced to protiochloroform at 7.26 ppm for ^{1}H spectra and 77.0 ppm for ^{13}C spectra.

1,3,5-Tris(5′-*tert*-butyl-3′,4′-dimethoxyphenyl)benzene. To the boronic acid (400 mg, 1.69 mmol) were added ethanol (5 mL), aqueous Na_2CO_3 solution (2 M, 1.68 mL), 1,3,5-tribromobenzene (140 mg, 440 μmol), and palladium tetrakis(triphenylphosphine) (58 mg, 50 μmol). Distilled toluene (15 mL) was added, and the mixture was refluxed overnight under nitrogen. The cooled reaction mixture was concentrated, and run through a plug of silica gel. Following evaporation, the residue was purified by radial chromatography (SiO_2, 20% ether/petroleum ether). The product was collected as a fluorescent fraction that weighed 270 mg (94%) after evaporation. Anal. Calcd for $C_{42}H_{54}O_6$: C, 77.03; H, 8.31. Found: C, 76.77; H, 8.23. ^{1}H NMR ($CDCl_3$): δ 7.64, s (3 H); 7.21, d, J = 1.8 Hz (3 H); 7.10, d, J = 1.8 Hz (3 H); 3.95, s (9 H); 3.92, s (9 H); 1.44, s (27 H). ^{13}C NMR ($CDCl_3$): δ 153.52, 148.41, 143.68, 142.83, 136.25, 125.11, 118.16, 110.16, 60.49, 55.98, 35.32, 30.63.

1,3,5-Tris(5′-*tert*-butyl-3′,4′-dihydroxyphenyl)benzene. 1,3,5-Tris(5′-*tert*-butyl-3′,4′-dimethoxyphenyl)benzene (150 mg, 230 μmol) was dissolved in anhydrous methylene chloride (10 mL) and cooled to −78 °C. Boron tribromide (260 μL, 2.75 mmol, ca. 12 equiv) was added via syringe, and the solution was allowed to slowly warm to room temperature overnight. The pink solution containing precipitate was poured onto ice, washed with saturated aqueous NaCl, dried with Na_2SO_4, filtered, evaporated, and subjected to radial chromatography (SiO_2, ether), to yield 130 mg of an off-white solid that was used directly in the next step. Anal. Calcd for $C_{36}H_{42}O_6$: C, 75.76; H, 7.41. Found: C, 75.62; H, 7.36. ^{1}H NMR ($(CD_3)_2CO$): δ 8.73, br s (3 H, OH); 7.55, s (3 H); 7.21, s, (3 H, OH); 7.14, s (6 H). ^{13}C NMR ($CDCl_3$): δ 145.64, 144.96, 143.64, 136.92, 132.78, 124.03, 117.82, 112.49, 35.46, 29.97. IR (film): 3245 cm^{-1} (ν_{OH}, strong).

$Ni_3(CTH)_3((TBSQ)_3Ph)(PF_6)_3\cdot 1.5H_2O$. The nickel complex was prepared using the same procedure previously described for the DBSQ derivative.[19] A solution of $Ni(CTH)(PF_6)_2$ (0.6 mmol) in methanol was mixed with a solution of 1,3,5-tris(5′-*tert*-butyl-3′,4′-dihydroxyphenyl)benzene (0.184 mmol) in the same solvent under an argon atmosphere, and then solid KOH (1.2 mmol) was added. The resulting solution was gently warmed for 0.5 h, filtered in the presence of air, and then mixed with an aqueous solution of KPF_6. The crude product was recrystallized from dichloromethane/hexane mixtures. Anal. Calcd for $C_{84}H_{147}F_{18}N_{12}Ni_3O_{7.5}P_3$: C, 49.06; H, 7.21; N, 8.17. Found: C, 49.36; H, 7.12; N, 7.86.

$Mn_3(Tp^{Cum,Me})_3((TBSQ)_3Ph)$. $MnCl_2\cdot 4H_2O$ (72.8 mg, 0.37 mmol) was dissolved in 10 mL of methanol. To this solution was added K(Tp^{Cum,Me})[20,21](239 mg, 0.37 mmol) dissolved in 5 mL of methanol, and 1,3,5-tris(5′-*tert*-butyl-3′,4′-dihydroxyphenyl)benzene (70 mg, 0.123 mmol) dissolved in 30 mL of CH_2Cl_2. The solution was purged with nitrogen, and KOH (21 mg, 0.037 mmol) was added. After being stirred for 15 min, the reaction mixture was filtered, exposed to air, and stirred for an additional 48 h. After this time, the red-brown solid was filtered off, washed twice with methanol, and air-dried. Anal. Calcd for $C_{153}H_{174}B_3N_{18}Mn_3O_6$: C, 71.82; H, 6.85 N, 9.85. Found: C, 70.85; H, 6.77 N, 9.77.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer BX spectrometer. Electronic spectra were recorded in the range 5000−30000 cm^{-1} on a Perkin-Elmer Lambda spectrophotometer. The electrochemical analysis by cyclic voltammetry was carried out by using an electrochemical unit (Amel model 553 potentiostat equipped with Amel 860, 560, and 568 elements) 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 (SCE). Before each experiment the solution was carefully deaerated with an argon flow. All potentials are reported as referenced versus a ferrocinium/ferrocene couple. Under the experimental conditions used this couple lies at +0.455 V vs SCE.

Magnetic Measurements. The magnetic susceptibility of polycrystalline powder samples of the complexes was measured between

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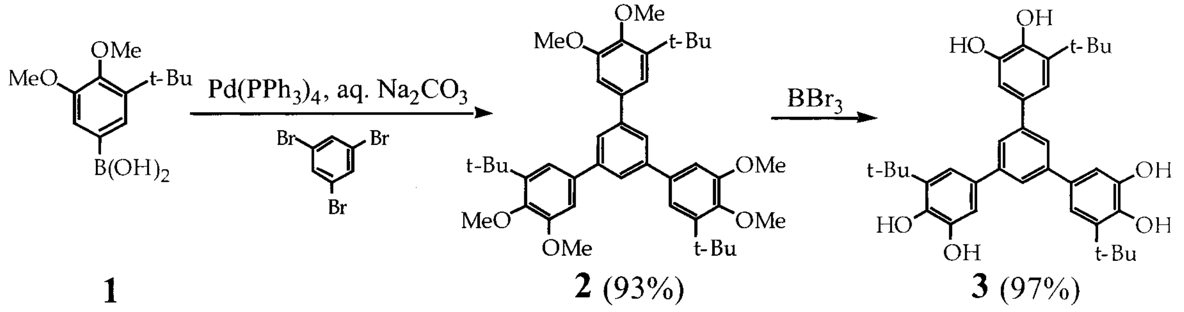
Scheme 1



1 **2** (93%) **3** (97%)

2 and 300 K at an applied magnetic field of 0.1 and 1 T using a Cryogenic S600 SQUID magnetometer. Data were corrected for the magnetism of the sample holder that was determined separately in the same temperature range and field, and the underlying diamagnetism of the samples was estimated from Pascal's constants. Magnetization measurements were performed on the same samples with the same instrument at 2.5 and 4.5 K with a field up to 6.5 T. Finally, the susceptibility data were fitted by minimizing the sum of the squares of the deviation of the computed χT values from the experimental values, using a Simplex minimization procedure. The theoretical susceptibilities were calculated employing CLUMAG,[22] except when stated otherwise.

Results and Discussion

Synthesis. Following a synthetic procedure for obtaining related polyoxolene molecules, the tris(catechol) **3** was prepared according to Scheme 1.[11] Suzuki coupling of **1** and commercially available 1,3,5-tribromobenzene provided **2**. Deprotection of the methyl ethers using BBr_3 gave the tris(catechol) in excellent yield.

Once deprotonated, this molecule is part of a seven-component ((diox)$_3$Ph) redox chain, the trinegative anion being expected to behave as tris(semiquinone) (TBSQ)$_3$Ph. Since in the past it was shown that the Ni(CTH)(DBSQ)Y complex (DBSQ = 3,5-di-*tert*-butylsemiquinone; Y = ClO_4, PF_6) was characterized by a quartet electronic ground state arising from a strong ferromagnetic coupling between the metal ion and the radical ligand,[19] we have prepared the Ni(CTH) adduct of **3** to characterize the magnetic properties of solid compounds containing the $Ni_3(CTH)_3(TBSQ)_3Ph)^{3+}$ cation. The reaction of **3** with a stoichiometric amount of $Ni(CTH)(PF_6)_2$ in basic methanol under argon followed by aerial oxidation gave a brown microcrystalline powder of analytical formula $Ni_3(CTH)_3$(tris(diox)Ph)$(PF_6)_3\cdot 1.5H_2O$ (**4**). We postulate that this compound contains three six-coordinate nickel(II) cations bridged by the tris-bidentate dioxolene ligand.

In a similar fashion the Mn(Tp^{Cum,Me}) adduct of **3** was synthesized since it has been previously found that the tris(pyrazolyl)borate ligand may allow the isolation of M^{II}–semiquinone adducts.[21,23] These complexes are expected to be five-coordinated on the basis of steric constraints of the ligand and characterized by a quintet electronic ground state arising from a strong antiferromagnetic coupling between the S =5/2 metal ion and the radical ligand.[7,24] On the basis of previous results for Zn^{II}, Cu^{II}, and Co^{II},[21] we believe that Mn_3(Tp^{Cum,Me})$_3$((diox)$_3$)Ph) **(5)** contains five-coordinated manganese cations bridged by this dioxolene ligand.

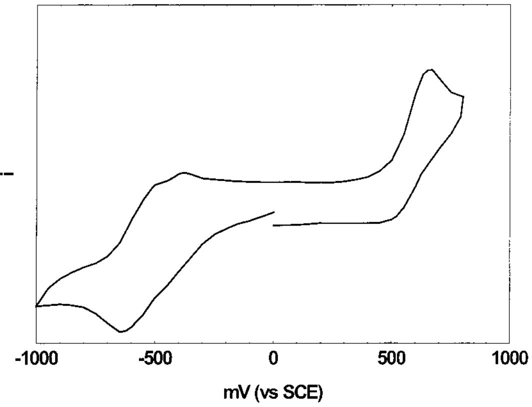


Figure 1. Cyclic voltammogram of the $Ni_3(CTH)_3((TBSQ)_3Ph)(PF_6)_3$ complex in 1,2-dichloroethane and 0.1 M NBu_4PF_6 at 25 °C.

All attempts at obtaining crystals suitable for structural analysis were unsuccessful. However, the formulation of the obtained compound as a metal(II)–semiquinone derivative is clearly indicated from its electronic spectrum, electrochemical properties, and magnetic data discussed below.

Electronic Spectra and Electrochemistry. The features of the electronic spectrum of the nickel complex **4**, which shows bands at 12300, 20200, and 26300 cm^{-1}, are the same as those observed for the mononuclear Ni(CTH)(DBSQ)Y and some related complexes.[9,19] The bands at 12300 and 26300 cm^{-1} can be assigned as internal semiquinone transitions, whereas the band at 20200 cm^{-1} can be assigned as a metal-to-ligand charge-transfer transition. The cyclic voltammogram of a deaerated 1,2-dichloroethane solution of this compound (Figure 1) shows three sequential one-electron reversible redox processes at −1.08, −0.97, and −0.86 V and one irreversible redox process at +0.1 V vs a ferrocenium/ferrocene reference couple. In agreement with the electrochemical properties of the mononuclear and dinuclear analogue[9] derivatives, the three reversible processes can be assigned to the semiquinone/catecholate couple whereas the irreversible one can be assigned to the quinone/semiquinone couple. It is rather clear from these data that the species obtained working under aerobic conditions is the suggested tris(semiquinonato) one. As a further consideration, it is also

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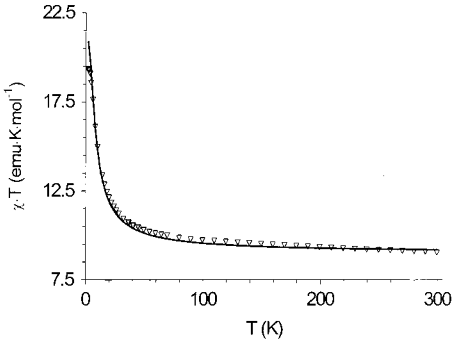


Figure 2. χT vs T curve for the complex $Mn_3(Tp^{Cum,Me})_3(TBSQ)_3$ (empty triangles). The continuous line is the result of the best fit obtained with both the models described in the text, which yielded superimposable curves. The best fit parameters for the two models are reported in the text.

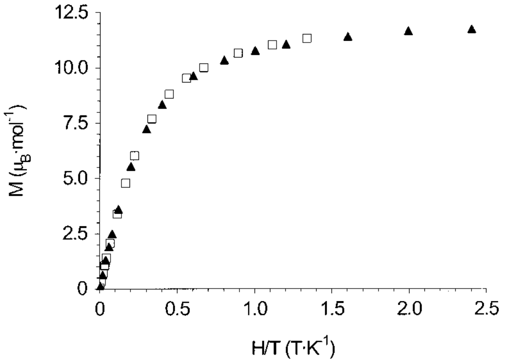


Figure 3. Reduced magnetization data for $Mn_3(Tp^{Cum,Me})_3(TBSQ)_3$, measured at 2.5 K (full triangles) and 4.5 K (empty squares), respectively. The presence of only a small zero-field splitting is evidenced by the almost perfect coincidence of the two curves.

clear that it is not possible to characterize species containing mixed-valent forms of the ligand, i.e., one catecholate and two semiquinones or two semiquinones and one catecholate, without a significant presence of its reduced and oxidized species. In fact the comproportionation constant for the equilibrium

$$Ni_3CTH_3((SQ)_2(Cat)Ph)^{2+} + Ni_3CTH_3((Cat)_3Ph) \rightarrow 2Ni_3CTH_3((SQ)(Cat)_2Ph)^{+}$$

is about 33, according to the electrochemical data. Similar considerations hold for the comproportionation constant of the formation of the second intermediate species, namely, $Ni_3CTH_3((SQ)_2(Cat)Ph)^{2+}$. These data show that the energies of the frontier orbitals of the three dioxolene fragments of the ligand are the same, taking into account the differences in the solvation free energy changes and statistical factors.

The electronic spectrum of the manganese derivative **5** shows a pattern of transitions in the red region of the spectrum (11600, 12900, and 14200 cm^{-1}) which are usually found to characterize the semiquinone ligands. The shoulder at 24100 cm^{-1} could be also consistent with a semiquinone ligand-centered transition. A strong absorption is also detected at 21300 cm^{-1} and can probably be assigned to a charge-transfer transition. The features of the spectrum therefore are consistent with the formulation of this manganese compound as tris(semiquinone) derivative $Mn_3(Tp^{Cum,Me})_3((TBSQ)_3Ph)$.

Magnetic Properties. The χT vs T curve for the $Mn_3(Tp^{Cum,Me})_3((TBSQ)_3Ph)$ complex is shown in Figure 2. At room temperature (300 K) the experimental value of χT is 9.07 emu K mol^{-1}, and its tendency is to slowly increase with decreasing temperature. This value is much lower than that expected for three spins of 5/2 and three spins of 1/2 uncorrelated ($\chi T_{theor} = 14.25$ emu K mol^{-1}), while it is in perfect agreement with what is expected for three $S = 2$ centers with $g = 2.00$ (3×3.00 emu K mol^{-1}). This is then a clear indication that each Mn^{II} is strongly antiferromagnetically coupled to each semiquinone radical, while the interaction between the radicals is not evident at this temperature. On lowering T, χT increases, and at low temperature (2 K), it reaches a value of 19.7 emu K mol^{-1}. It should however be noted that the value is still growing at this temperature. This behavior suggests the existence of a ferromagnetic coupling between paramagnetic centers. The observed χT value is consistent with an $S = 6$ ground state (theoretical value 21 emu K mol^{-1}), and the low observed value can be again explained by assuming an incomplete population of the ground state, even at low temperature. This interpretation is confirmed by the M vs H curves at low T (2.5 and 4.5 K, shown as reduced magnetization in Figure 3), which at 6 T are almost saturated to the expected value of 12 μ_B. The plot of M vs H/T clearly shows that the two curves are almost perfectly superimposed, and this suggests that only a very small zero-field splitting exists in this complex. This result is in agreement with the presence in the system of very isotropic species, namely, Mn^{II} (a ^6S ion) and semiquinone radicals. Interestingly, the X-band EPR spectra show the presence of a fine structure due to a small zero-field splitting: preliminary interpretation of the HF-EPR spectra confirms the $S = 6$ ground state and a value of $D < 0.1$ cm^{-1}.

Following this preliminary interpretation, two fits of the χT data were attempted. We assumed C_3 symmetry for the exchange interactions, which, given the lack of a crystal structure, cannot be experimentally confirmed. However, the following discussion will show that even with the use of a reduced number of parameters we could get a very reasonable explanation of the observed magnetic properties of the $Mn_3(Tp^{Cum,Me})_3((TBSQ)_3Ph)$ complex.

In the first simple model we assumed the manganese(II)−semiquinone antiferromagnetic coupling to be so strong to consider the system as virtually built up by three $S = 2$ ferromagnetically interacting spins, and we then employed only one J value to analyze the data. The exchange Hamiltonian describing the system is then that of a regular triangular spin structure:

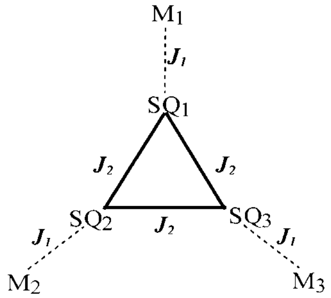
$$H = J(S_1S_2 + S_2S_3 + S_1S_3) \qquad (1)$$

In this approach, the energy of each state is a function of total spin only:

$$E(S_T) = (J/2)S_T(S_T + 1) \qquad (2)$$

The derivation of the analytic expression of the Van Vleck

Chart 1



equation is then straightforward:[2]

$$\chi T = \frac{Ng^2\beta^2}{k_B}\,\frac{546e^{21x} + 660e^{15x} + 540e^{10x} + 336e^{6x} + 150e^{3x} + 18e^{x}}{13e^{21x} + 22e^{15x} + 27e^{10x} + 28e^{6x} + 25e^{3x} + 9e^{x} + 1} \tag{3}$$

where $x = J/k_BT$. The best fit (shown in Figure 2) was obtained by using a value of J of 1.12 ± 0.05 cm^{-1} and gave an agreement factor, $R = 1/(N - n_P)[\sum(\chi_{calcd}T - \chi_{obsd}T)^2/\sum(\chi_{obsd}T)^2]^{1/2}$, of 6.7 × 10^{-4}, where N is the number of experimental points and n_P is the number of parameters. The error on the calculated coupling constant is obtained assuming a $Dx = 90\%$ and an error on the experimental χT values equal to the square root of the mean quadratic error.[25]

Even if this fit is satisfactory and confirms our qualitative analysis, it does not give us any indication about the value of the "real" coupling between the semiquinones. To get an estimate of this parameter, we then turned to a more refined model and considered as variable parameters both the coupling constant between the radicals and Mn and the coupling constant between each pair of semiquinones. The Hamiltonian of the system is then the one describing the pattern of Chart 1:

$$H = J_1(S_1S_2 + S_3S_4 + S_5S_6) + J_2(S_1S_3 + S_3S_5 + S_1S_5) \tag{4}$$

where S_1, S_3, and S_5 label the radical spins and S_2, S_4, and S_6 indicate the metal centers.

The best fit parameters gave the following results: g = 2.00 (fixed), $J_1 > 350$ cm^{-1}, in agreement with the predicted strong antiferromagnetic coupling between Mn and the semiquinone, and $J_2 = -40$ cm^{-1}, with an agreement factor R of 5.7 × 10^{-4}. Notwithstanding a certain systematic deviation from the experimental value, the correlation between the parameters is very small and the fit is very stable. Varying J_1 from 350 to 500 cm^{-1} results in a variation of J_2 of less than 0.3 cm^{-1}, without an appreciable effect on the calculated curve. It is also interesting to note here that the two models yielded the same theoretical curve: indeed, a comparison of the energies of the low-lying spin levels shows very good agreement between the two fitting models (see Table 1).

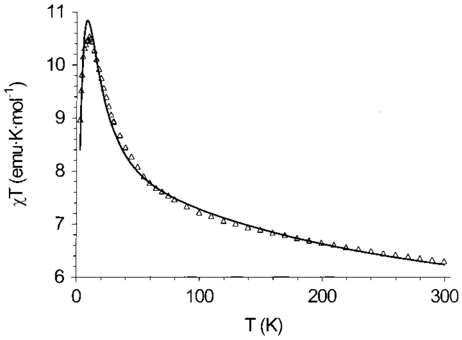


Figure 4. χT vs T curve for the complex $Ni_3(CTH)_3((TBSQ)_3Ph)(PF_6)_3$ (empty triangles). The continuous line is the result of the best fit obtained with the parameters reported in the text.

Table 1. Difference in Energy between Subsequent Levels Obtained by the Best Fit of the χT Data for Mn_3SQ_3 with Models 1 and 2

	ΔE (cm^{-1})			ΔE (cm^{-1})	
	model 1	model 2		model 1	model 2
$S = 6$	ground state	ground state	$S = 2 - S = 3$	3.36	3.5
$S = 5 - S = 6$	6.72	6.5	$S = 1 - S = 2$	2.24	2.3
$S = 4 - S = 5$	5.6	5.7	$S = 0 - S = 1$	1.12	1.15
$S = 3 - S = 4$	4.48	4.6			

Finally, we introduced a lower symmetry (C_2) for the exchange pattern in both the models employed, but this did not lead to an improvement of the fit, thus confirming that the assumption of a 3-fold symmetry for the exchange is completely justified.

Given this result, we employed the same exchange pattern of Chart 1 for the interpretation of the magnetic data of the $Ni_3(CTH)_3((TBSQ)_3Ph)(PF_6)_3$ complex, whose χT vs T curve is shown in Figure 4. The room-temperature value (6.25 emu K mol^{-1}) is higher than expected for three uncoupled nickel(II) ions and three semiquinones (theoretical value 4.7 emu K mol^{-1}, assuming $g = 2.2$ for Ni ions). However, we point out that the mononuclear $[Ni(CTH)(DBSQ)]PF_6$ complex shows a χT value of 2.28 emu K mol^{-1} at 300 K[19] as a result of a strong ferromagnetic interaction between the paramagnetic metal ion and the radical ligand. Thus, a value equal to 6.7−6.8 emu K mol^{-1} (3 × 2.28 emu K mol^{-1}) was expected for the present trinuclear derivative if the coupling between the metal and semiquinonato had not changed. The observed value at room temperature then suggests that, while there is a ferromagnetic coupling between nickel(II) and the semiquinonato which is effective even at room temperature, this is smaller than in the mononuclear parent derivative. On decreasing the temperature, the value of χT increases, thus indicating that a ferromagnetic coupling is active between the three semiquinone radicals, as found in our manganese(II) derivative. The curve passes through a maximum of 10.53 emu K mol^{-1} at 10 K, and then decreases. It has to be stressed that the value of the maximum is substantially lower than expected for a completely populated $S = 9/2$ state (13.6 emu K mol^{-1}) but can be explained by population of spin states with lower multiplicity. A magnetization measurement performed at low temperatures yielded a value of 8.70 μ_B at 6.5 T and 2.5 K, where the sample is still unsaturated (Figure 5). This is again in agreement with a ground $S = 9/2$ spin state and near excited state of lower

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(25) For more details on the Dx definition, see: *Numerical Recipes*; Cambridge University Press: Cambridge, 1986.

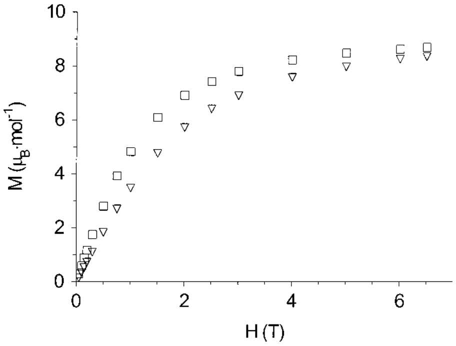

Figure 5. Magnetization curves for the $Ni_3(CTH)_3((TBSQ)_3Ph)(PF_6)_3$ complex, measured at 2.5 K (empty squares) and 4.5 K (empty triangles).

spin multiplicity, whose population reduces the magnetization to a value lower than expected for an $S = 9/2$ spin state (theoretical M_{sat} value around 9.6 μ_B assuming $g = 2.15$; see below). The picture emerging from the interpretation of the magnetic data is then consistent with our hypothesis of an $S = 9/2$ ground spin state, due to the expected ferromagnetic coupling between nickel and the semiquinone and the smaller ferromagnetic coupling between the three unpaired electrons of the ligand.

The fitting model in this case includes a correction to account for the decrease in χT below 10 K, assuming intermolecular antiferromagnetic interactions: $\chi_{corr} = \chi'/(1 - \Theta\chi)$, with $\Theta = 2zJ_{inter}/Ng^2\beta$.[25] It has to be stressed here that the use of a phenomenological molecular field correction does not necessarily imply the presence of magnetic interactions between neighboring molecules. The same effect may in fact be due to zero-field splitting terms which were not included in the Hamiltonian, and that are likely to play a nonnegligible role on the low-temperature part of the χT curve, given the anisotropy of nickel(II) ions. Unfortunately, HF-EPR spectra only showed an uninformative very broad band around $g = 2.2$, thus not allowing the determination of the anisotropy of the system. It should be noted that in the case of our manganese(II) derivative there was no need for intermolecular interaction correction because the intermolecular interactions are supposed to be reduced to a minimum by the bulky ancillary ligand we used and that system is virtually without zero-field splitting.

In addition to this phenomenological correction, we assumed the presence of a small amount of paramagnetic impurity, which is expected to play a relevant role in agreement with the trinuclear nature of the system. The best fit curve (Figure 4, continuous line) obtained in such a way yielded the following parameters for the spin Hamiltonian: $J_1 = -173$ cm^{-1}, $J_2 = -26.5$ cm^{-1}, $g = 2.14$, and $\Theta = -0.25$ K with a factor R of 3.9×10^{-4}. With these values of the coupling constants, the lowest excited states are doubly degenerate $S = 7/2$, 12 cm^{-1} higher in energy with respect to the ground state. The g value 2.14 is in agreement with what is expected for nickel(II) and a semiquinonato ferromagnetically coupled. Indeed, for a system with such a coupling scheme the global g value may be related to the individual ones by the relation $g = (2/3)g_{Ni} + (1/3)g_{SQ}$.[26,27] Then, if one assumes $g_{SQ} = 2.00$, a global g of 2.14 implies $g_{Ni} = 2.21$, which is a well-established value for the nickel(II) ion.[28]

It has to be noted that the nickel(II)−semiquinonato ferromagnetic coupling is strongly reduced with respect to that of the single-center systems.[19] Such a difference between the metal−semiquinone interaction in a 1:1 adduct and the metal−polysemiquinone interaction has already been observed,[9] and points out that while the qualitative behavior of this metal−radical interaction can be easily predicted, its intensity can vary largely on passing from one family to another.

The semiquinonato−semiquinonato coupling within the triradical is, as expected, ferromagnetic, and the value of the coupling between the semiquinonato units of the radical is the same of that reported for the homologous biradical.[9] A comparison of the obtained values for the coupling between radicals in the two derivatives shows that it is higher in the manganese complex than in the nickel(II) one, thus suggesting that a variation in the dihedral angle between the plane of the semiquinone is likely to occur on passing from the nickel(II) complex to the manganese(II) one.[7,9,29,30] This is probably due to the different diamagnetic ligands employed in the two cases, which imply a pentacoordinated manganese(II) and a hexacoordinated nickel(II) and then a different accommodation of the paramagnetic ligands as well.

Conclusions

Our present results show that the 1,3,5-tris(dioxolene)-benzene may be used to create a tris(semiquinone) ligand characterized by a quartet ground state. It should be stressed that the strategy based on the substitution of some sp^2 radical carbons of a non-Kekulè hydrocarbon with other radical groups has been in general used for obtaining ferromagnetically coupled biradicals.[17] As we have previously shown with a bis(semiquinonato), *m*-xylylene-substituted analogue,[9] the coordination of paramagnetic metal ions to the present ligand enforces high-spin ground states in the resulting metal complexes. Here the magnetic coupling induces an $S = 9/2$ electronic ground state in the nickel(II) complex and an $S = 6$ electronic ground state in the manganese(II) complex according to our expectations, thus showing how an appropriate linker between the paramagnetic centers may propagate the desired magnetic interactions. At this step there is therefore the problem concerning the utility of these metal−polyoxolene complexes as building blocks for a network coordination polymer. It has been suggested that to achieve this goal the chemist should predetermine the structure of the network, and in this sense simpler units to be assembled than those we propose should be required.[31]

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