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[Tris(*o*-iminosemiquinone)cobalt(III)]—a radical complex with an $S_t = {}^3/_2$ ground state

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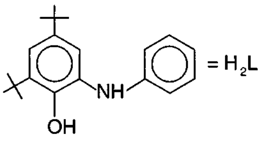
Owing to their topology, three iminosemiquinone radical ligands couple in a ferromagnetic fashion, mediated by a low-spin Co(III) ion.

The realization of the widespread occurrence of radicals in enzyme catalysis has triggered considerable interest and research activity in metal–radical interactions.[1–10] Additionally, investigations relating organic radicals bound to metal ions are relevant to the field of 'molecular magnets'.[11,12]

In earlier reports[13–15] the Ga(SQ)$_3$ complex (SQ = 3,5-di-*tert*-butyl-1,2-semiquinonato) was characterized, both structurally and spectroscopically, and was found to exhibit a weak ferromagnetic exchange interaction (J = +7.8 cm^{-1}) between the three $S = {}^1/_2$ coordinated semiquinone ligands, mediated by a metal centre with empty d orbitals. In pursuit of our interest in coordinated radicals,[16] we now report a compound containing three *ortho*-iminosemiquinone radicals bound to a diamagnetic metal ion, low-spin Co(III), and exhibiting much stronger ferromagnetic interactions than those reported for similar systems.[17]

Treatment of anhydrous CoCl$_2$ in the presence of air with 3 equiv. of the N,O-chelating ligand H$_2$L in acetonitrile yielded a deep blue solution, which on addition of NEt$_3$ turned deep green.



The green solution was refluxed for 0.5 h, followed by stirring at room temperature for an additional 5 h. Slow evaporation of the clear solution afforded X-ray quality deep brown crystals of **1** (yield: 65%).

The most noteworthy features in the IR spectrum of **1** are the absence of both N–H and O–H modes and the appearance of two medium intense ν(CN) bands at 1588, 1577 cm^{-1} and a very strong ν(C–$\dot{\mathrm{O}}$) band at 1433 cm^{-1}. Optical spectra of **1** in solvents such as MeCN, THF and CHCl$_3$ consist of a series of intense bands and shoulders; in particular two extremely intense absorptions at low energies are noteworthy: λ/nm (ε/M^{-1} cm^{-1}) (MeCN) 881(2628), 668(2510); (CHCl$_3$) 902(20300), 676(16400); (THF) 910(16170), 675(13050). The intensity and its dependence on the solvent suggest that allowed electronic transitions of a CT nature dominate the spectra. The intensity of these bands decreases with time indicating the unstable nature of the radicals in solution. Cyclic voltammetric experiments exhibit four quasi-reversible one-electron redox waves for **1** in CH$_2$Cl$_2$ [0.1 M NBu$^n_4$PF$_6$]: $E^1_{1/2}$ = 0.196, $E^2_{1/2}$ = −0.363, $E^3_{1/2}$ = −0.933 and $E^4_{1/2}$ = −1.320 V *vs.* Fc$^+$–Fc. The first three redox potentials are associated with three ligand centred redox processes and $E^4_{1/2}$ must be assigned to the Co(III)–Co(II) couple.

The single crystal X-ray structure of **1** (Fig. 1)† shows that the first coordination sphere of cobalt has a C_2 axis passing through O(2)–Co(1)–N(3); the ligands have lost their aminohydrogen atoms. The structure determination unambiguously shows that cobalt is hexa-coordinated to three deprotonated ligands, each of which contains an iminosemiquinone radical anion, hence indicating a formal +3 oxidation state at the cobalt centre. Thus the distances C3–C4, C5–C6, C23–C24, C25–C26, C43–C44 and C46–C45 at 1.37 ± 0.01 Å are significantly shorter than the other C–C distances in the original phenol ring, 1.43 + 0.01 Å. Correspondingly, the imino C=N bonds at 1.345 ± 0.005 Å are shorter than the C–N bonds to the aniline rings, 1.420 ± 0.005 Å. Similar asymmetric electron density distribution in *ortho*-iminosemiquinone has been observed previously.[16a] Secondary structural confirmation of the intermediate reduction level of the ligand comes from the C–O bond distances, 1.304 ± 0.004(av.), which are much shorter than the 1.35 Å expected of a catechol.[18] They are in the range of those found for other first-row metal semiquinone complexes.[19] The Co–O and Co–N bond distances at 1.88 ± 0.01(av.) and 1.93 ± 0.01(av.) Å, respectively, are in accord with the low-spin description of the cobalt centre.

Magnetic data (SQUID) with B = 1 T for a polycrystalline sample of **1** are displayed in Fig. 2 as μ_{eff} *vs.* T. On lowering the temperature, μ_{eff} (3.16 μ_B at 290 K) increases monotonically approaching a maximum around 15 K with a value of 3.71 μ_B,

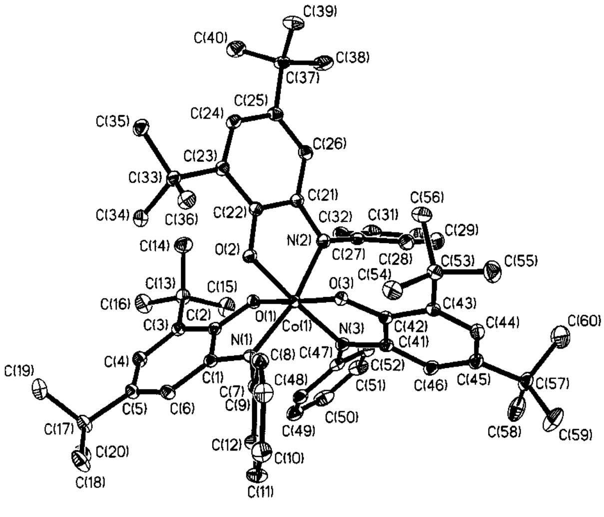


Fig. 1 Structure of the neutral complex CoL$_3$ **1** with selected bond lengths (Å) and angles (°): Co(1)–O(1) 1.878(1), Co(1)–N(1) 1.937(1), Co(1)–O(2) 1.896(1), Co(1)–N(2) 1.946(1), Co(1)–O(3) 1.889(1), Co(1)–N(3) 1.918(1), O(1)–C(2) 1.307(2), N(1)–C(1) 1.350(2), O(2)–C(22) 1.300(2), N(1)–C(7) 1.419(2), O(3)–C(42) 1.305(2), N(2)–C(21) 1.342(2), N(2)–C(27) 1.425(2), N(3)–C(41) 1.348(2), N(3)–C(47) 1.423(2), C(1)–C(6) 1.425(2), C(1)–C(2) 1.438(2), C(2)–C(3) 1.424(2), C(3)–C(4) 1.379(2), C(4)–C(5) 1.434(2), C(5)–C(6) 1.373(2), C(21)–C(26) 1.432(2), C(21)–C(22) 1.435(2), C(22)–C(23) 1.429(2), C(23)–C(24) 1.379(2), C(24)–C(25) 1.436(2), C(25)–C(26) 1.366(2), C(41)–C(46) 1.428(2), C(41)–C(42) 1.440(2), C(42)–C(43) 1.427(2), C(43)–C(44) 1.383(2), C(44)–C(45) 1.430(2), C(45)–C(46) 1.369(2); C(1)–N(1)–C(7) 121.2(1), C(47)–N(3)–C(41) 122.3(1), C(21)–N(2)–C(27) 119.7(1).

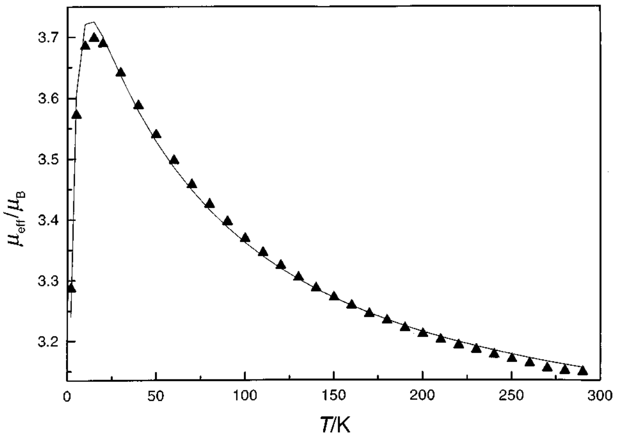


Fig. 2 A plot of μ_{eff} *vs.* T for **1**. The solid line represents the simulation of the experimental data.

which is close to the spin-only value for $S_t = 3/2$, expected as the ground state for three ferromagnetically coupled iminosemiquinone radicals. Below 15 K there is a decrease in μ_{eff}, which reaches a value of 3.30 μ_B at 2 K due to saturation effects and/or intermolecular antiferromagnetic interactions. A full-matrix diagonalization approach[20] was employed to fit the experimental data. We have found that the experimental data could not be fitted with only one 'J' as satisfactorily as with two 'J' values. Two exchange coupling constants have to be considered for the simulation based on the Hamiltonian

$$H = -2J(S_1 \bullet S_2 + S_2 \bullet S_3) - 2J_{13}(S_1 \bullet S_3)$$

with $S_1 = S_2 = S_3 = 1/2$ and the best fit shown as the solid line in Fig. 2 yields $J = J_{12} = J_{23} = +9.1$ cm^{-1}, $J_{13} = +59.5$ cm^{-1}, $g_1 = g_2 = g_3 = 2.005$ (fixed), TIP = 100×10^{-6} cm^3 mol^{-1} (fixed). Thus the quartet ground state is separated from the first doublet state by 27 cm^{-1} owing to the exchange interactions.

The quartet ground state is stabilized by the topology of the three magnetic orbitals of the iminosemiquinone radicals. In an idealized C_2 symmetry the three π*-magnetic orbitals are orthogonal to each other, thus rationalizing the observed ferromagnetic coupling. The superexchange mechanism is most probably mediated by the metal 3d π-orbitals. A rationale for the relative strengths of the two 'J' values might be sought in the orthogonality of the planes of the three ligands including the central cobalt in the coordination polyhedron. The dihedral angle between the two ligand planes containing O2 and O3 is 92.7°, accounting for the stronger coupling J_{13}. On the other hand, the dihedral angles between the planes containing O1 and O3 (79.4°) and between the planes containing O1 and O2 (82.8°) deviate significantly from 90°, thus rendering an appreciable antiferromagnetic contribution to the overall coupling. As a result the latter couplings, $J = J_{12} = J_{23}$, are weaker than the former one J_{13}.

The results reported here show that much larger ferromagnetic coupling can be achieved with suitably designed organic radicals by using appropriate diamagnetic acceptors. A novel tris(iminosemiquinone)metal(III) complex is described that can provide a suitable basis for further research in a systematic way, especially on the electronic properties of other metal(III)–radical complexes.

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Notes and references

† *Crystal data:* $C_{60}H_{75}N_3O_3Co$, monoclinic, space group $P2_1/n$, a = 15.043(1), b = 13.953(1), c = 27.594(2) Å, β = 103.62(2)°, V = 5629.0(7) Å^3, Z = 4, D_c = 1.115 g cm^{-3}, T = 100(2) K, F(000) = 2028, λ(Mo-Kα) = 0.71073 Å, μ = 0.348 mm^{-1}. Brown–black crystal, size 0.66 × 0.59 × 0.39 mm, Siemens SMART CCD, 53106 reflections collected. Structure solution by using the Siemens ShelXTL software package (G. M. Sheldrick, Universität Göttingen) from 16129 independent reflections; full-matrix least-squares refinement on F^2, using 16074 and 622 parameters, refinement converged at R_1 = 0.042 and R_2 = 0.064 (all data).

CCDC 182/1362. See http://www.rsc.org/suppdata/cc/1999/1747/ for crystallographic files in .cif format.

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