

A unique series of dinuclear transition metal–polyradical complexes with a *m*-phenylenediamine spacer and their catalytic reactivity†

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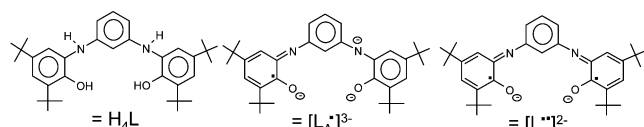
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A series of dinuclear transition metal complexes with either six or four iminosemiquinone radicals, in which the metal centres are separated by a distance of ~6.8 Å, together with their catalytic reactivity is reported.

In the last few years there has been a profusion of studies for the development of molecular magnetic materials¹ based on the hybridization of organic–inorganic molecules in which paramagnetic ions are coordinated to organic open-shell radical ligands.^{1,2} This surge of interest has been also due partly to the relevance of such molecules to biological electron-transfer processes.³

Recently we have described a non-innocent *o*-iminobenzosemiquinone radical ligand based on aniline.⁴ As an obvious and natural progression of our interest in iminosemiquinone ligands we have synthesized a dinucleating ligand H₄L, based on *m*-phenylenediamine.



The ligand H₄L reacts with different metal ions‡ in the presence of a base and air to yield M^{II}₂(L[•])₂ [M = Cu **1**, Ni **2**], M^{III}₂(L[•])₃ [M = Fe **3**, Co **4**, Cr **5**] or Mn^{IV}₂(L_A)₂(L[•]) **6**, in which either four or six iminosemiquinone radicals are present. The structures of the compounds except **2** and **5** have been determined by single crystal X-ray crystallography at 100 K. Fig. 1 shows the structures of Cu^{II}₂(L[•])₂ **1** (left) and Co^{III}₂(L[•])₃ **4** (right) as examples; the structures of Fe^{III}₂(L[•])₃ **3** and Mn^{IV}₂(L_A)₂(L[•]) **6** together with their selected metrical parameters are provided as supplementary information.† Complex **1** contains two distorted square-planar copper ions. The coordina-

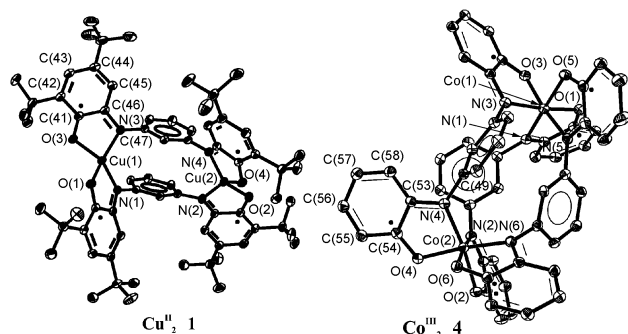


Fig. 1 Structures of **1** and **4**. *tert*-Butyl groups in **4** are omitted for clarity. Cu(1)⋯Cu(2) 6.697 Å, Co(1)⋯Co(2) 6.719 Å. Average bond distances: Cu(1)–O 1.923(9), Cu(1)–N 1.948(3), Cu(2)–O 1.915(13), Cu(2)–N 1.942(7), Co(1)–O 1.899, Co(1)–N 1.925, Co(2)–O 1.899, Co(2)–N 1.934 Å.

† Electronic Supplementary Information (ESI) available: experimental details and crystal data for **1**, **3**, **4** and **6**. See <http://www.rsc.org/suppdata/cc/b3/b300792h/>

tion geometry around the nitrogen donor is planar indicating that this nitrogen is three-coordinated (sp² hybridization) and not protonated; this renders the ligands *o*-iminobenzosemiquinonates, [L[•]]₂²⁻, and consequently, the copper ions are assigned to the oxidation state +II. Thus **1** is the dimer containing *m*-phenylene bridges of the analogous mononuclear Cu(II) complex with the ligand 2-anilino-4,6-di-*tert*-butylphenol.^{4b}

The neutral molecule of **3** or **4** contains two M(N,O)₃-units separated by the *m*-phenylene spacer. The metal centers are hexacoordinated and the geometrical parameters are identical within the experimental error of the analogous mononuclear Fe(III) and Co(III) complexes.⁴

Complex **3** contains two high-spin d⁵ ferric ions and, consequently the Fe–N and Fe–O bond lengths are the longest of the whole series of complexes with Fe–N and Fe–O bond distances at 2.105 ± 0.035 Å and 2.025 ± 0.21 Å. That **3** contains octahedral high-spin ferric ions (d⁵) is clearly established by its zero-field Mössbauer spectrum at 80 K: δ = 0.56 mm s⁻¹ and ΔE_Q = 1.011 mm s⁻¹.

The six equidistant, short Co–O distances at 1.899 ± 0.004 Å together with short Co–N distances at 1.930 ± 0.009 Å in **4** containing two *fac*-CoO₃N₃ units are compatible with the low-spin d⁶ configuration of the Co(III) ions coordinated to six iminosemiquinone radicals.

Fig. 2 shows the magnetic behaviour (μ_{eff} vs. *T*) together with the model used for the simulation of the experimental data for **4**. We note that the model used is a simplified one. As a preliminary result the parameters obtained from the simulation are: J₁ = -9.7 cm⁻¹, J₂ = +13.0 cm⁻¹, g = 2.0 (fixed). The solid line in Fig. 2 represents the simulation using the Hamiltonian given as the inset. Complexes **2** and **5** are diamagnetic, whereas complex **1** contains two uncoupled Cu(II) centers. The magnetic behaviour of **3** is provided in Figure S1 (supplementary material).†

A novel series of dinuclear (iminosemiquinone)metal complexes is described that provides a suitable basis for further research in a systematic way, especially on the metal–radical interactions and their impact on the oxidative catalytic reactions. Indeed, **1** and **6** can catalyze the aerial oxidation of

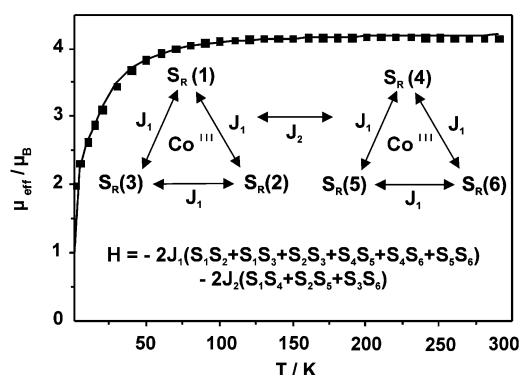
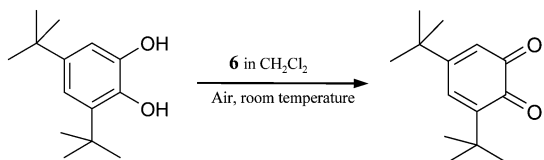
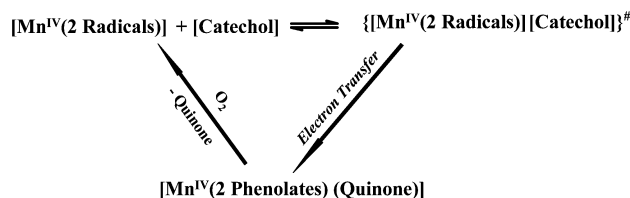


Fig. 2 The magnetic moment (μ_{eff}) vs. temperature (*T*) plot for **4** together with the model and the Hamiltonian used. The solid line represents the best fit.

catechol to quinone; the dimanganese(IV) compound, **6**, is a better catalyst than the dicopper(II) complex, **1**, for the aerial oxidation of catechol to quinone, thus mimicking the function of catechol oxidase.⁵



Oxidative catalytic reactions were investigated by using 2×10^{-7} mole of **6** in dichloromethane (25 cm³), in which different amounts of the substrate 3,5-di-*tert*-butylcatechol (2×10^{-6} to 20×10^{-6} mole) was added to be stirred in air at ambient temperature and the progress of the reaction was monitored with time by liquid chromatography and UV-vis spectroscopy. To unequivocally establish the identity of the quinone the retention time and spectral data were compared to those of the commercially available compound. The rate law observed is first order in both substrate and catalyst. No product other than the corresponding quinone was detected and **6** has been proved to be a very good catalyst for the aerial oxidation of catechol with 100% conversion and a turnover number expressed in mole product per mole catalyst of 500 after 24 h. Presumably an outer-sphere electron-transfer mechanism is operative.



Although this mechanism is in accord with the electrochemical data[†] for **6**, we could not detect the fate of O₂ involved in the catalytic cycle. Probably the catalase-like activity of **6** disproportionates hydrogen peroxide produced during the reaction.

In summary, we have reported a rational synthesis of dinuclear transition metal-iminosemiquinone radical complexes as an obvious progression of our earlier report⁴ and demonstrated that the Mn(IV)-radical complex **6** can catalyze the oxidation of catechol with molecular oxygen as the sole oxidant to afford quinone in excellent yield under mild conditions to mimic the function of the copper-containing enzyme catechol oxidase.

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Note added to proof: We reported the metal complexes of the present ligand H₄L first in ICCO 35 (Heidelberg) and then in ICMC'2002 (Valencia). Recently the same ligand has also been described in *Inorg. Chem.*, 2003, **42**, 701, but unfortunately without giving any prior reference.

Notes and references

[†] **1**: The ligand H₄L (0.3 g, 0.6 mmol), prepared in an analogous manner described earlier by us,⁴ CuCl (0.06 g, 0.6 mmol) and NEt₃ (0.4 cm³) were

dissolved under argon in CH₃CN-CH₃OH (1 : 1) and the resulting solution was refluxed for 1 h and filtered in the air. Slow evaporation of the filtrate afforded green microcrystals of **1**. Recrystallization from THF-CH₃OH (4 : 1) afforded X-ray quality crystals. Yield: 0.40 g (~53%).

Crystal data for 1·1.5(C₄H₈O): C₆₈H₈₈O₄N₄Cu₂·C₆H₁₂O_{1.5}. *M_r* = 1260.66, monoclinic, space group *P*2₁/*c*, *a* = 15.2345(12), *b* = 18.903(2), *c* = 24.840(3) Å, β = 90.51(2)°, *V* = 7153.1(13) Å³, *Z* = 4, *T* = 100(2) K, λ(MoKα) = 0.71073 Å, 46103 reflections collected, 19375 independent reflections (*R*_{int} = 0.0438), data/restraints/parameters = 19318/0/808, ShelXTL software package, *F*² refinement, *R*₁ = 0.0472, *R*₂ = 0.1307 (all data).

For 3: The ligand H₄L (0.3 g, 0.6 mmol), FeCl₂·4H₂O (0.08 g, 0.44 mmol) and NEt₃ (0.4 cm³) were dissolved in a solvent mixture (40 cm³) of CH₂Cl₂-CH₃CN (4 : 5) and the resulting solution was refluxed for 0.5 h and filtered. Slow evaporation of the filtrate afforded green crystals of **3**. Recrystallization from acetone afforded X-ray quality crystals. Yield: 0.18 g (~54%).

Crystal data for 3·0.5CH₃COCH₃: C₁₀₂H₁₃₂Fe₂N₆O₆·0.5C₃H₆O. *M_r* = 1678.88, monoclinic, space group *P*2₁/*n*, *a* = 25.374(2), *b* = 15.7754(12), *c* = 26.287(2) Å, β = 106.40(1)°, *V* = 10094.2(13) Å³, *Z* = 4, *T* = 100(2) K, λ(MoKα) = 0.71073 Å, 33764 reflections measured at an intensity threshold of 2σ(*I*), 14847 independent reflections (*R*_{int} = 0.0768) analyzed, data/restraints/parameters = 14670/0/1081, ShelXTL software package, *F*² refinement, *R*₁ = 0.0658, *R*₂ = 0.1303 (all data).

For 4: The same protocol as that for **3** using Co(ClO₄)₂·6H₂O (0.16 g, 0.4 mmol) yielded dark brown crystals. Yield: 0.27 g (80%).

Crystal data for 4·3CH₂Cl₂: C₁₀₂H₁₃₂Co₂N₆O₆·3CH₂Cl₂, *M_r* = 1910.77, triclinic, space group *P*1̄, *a* = 15.5627(8), *b* = 16.2417(12), *c* = 23.5948(2) Å, α = 74.09(1)°, β = 76.48(1)°, γ = 66.45(1)°, *V* = 5205.1(6) Å³, *Z* = 2, *T* = 100(2) K, λ(MoKα) = 0.71073 Å, 47876 reflections measured at an intensity threshold of 2σ(*I*), 29002 independent reflections (*R*_{int} = 0.0441) analyzed, data/restraints/parameters = 26325/0/1105. Residual electron density peaks and holes are located at Cl. ShelXTL software package, *F*² refinement, *R*₁ = 0.0881, *R*₂ = 0.1275 (all data).

6: To a solution of the ligand (0.52 g, 1 mmol) in CH₃OH (25 cm³) containing [Bu₄N]OCH₃ (0.9 cm³, 2.5 mmol) "manganese(III) acetate" (0.13 g, 0.2 mmol) was added to produce a brown solution, which was refluxed in air for 0.5 h and filtered to remove any solid particles. The deep brown microcrystalline solid separated after cooling was recrystallized from CH₂Cl₂-CH₃CN (1 : 1). Yield: 0.32 g (60%).

Crystal data for 6·0.5CH₂Cl₂: C₁₀₂H₁₃₂Mn₂N₆O₆·0.5CH₂Cl₂. *M_r* = 1690.48, monoclinic, space group *P*2₁/*n*, *a* = 25.0716(9), *b* = 15.7152(6), *c* = 26.2842(12) Å, β = 105.43(1)°, *V* = 9982.8(7) Å³, *Z* = 4, *T* = 100(2) K, λ(MoKα) = 0.71073 Å, 56918 reflections collected, 13020 independent reflections (*R*_{int} = 0.0922), data/restraints/parameters = 12926/0/1072, ShelXTL software package, *F*² refinement, *R*₁ = 0.0592, *R*₂ = 0.1444 (all data). CCDC reference numbers: 207577, 199328-199330 for **1**, **3**, **4** and **6**, respectively. See <http://www.rsc.org/suppdata/cc/b3/b300792h/> for crystallographic data in .cif format.

- (a) *Magnetic Properties of Organic Materials*, ed. P. M. Lahti, Marcel Dekker, New York, 1999; (b) *Molecular Magnetism: New Magnetic Materials*, ed. K. Itoh and M. Kinoshita, Gordon & Breach, Amsterdam, The Netherlands, 2000; (c) H. Iwamura, K. Inoue and T. Hayamizu, *Pure Appl. Chem.*, 1996, **68**, 243; (d) O. Kahn, *Molecular Magnetism*, VCH, New York, 1993; (e) D. A. Dougherty, *Acc. Chem. Res.*, 1991, **24**, 88; (f) H. Iwamura and N. Koga, *Acc. Chem. Res.*, 1993, **26**, 346; (g) A. Racja, *Chem. Rev.*, 1994, **94**, 871.
- (a) C. G. Pierpont and C. W. Lange, *Prog. Inorg. Chem.*, 1994, **41**, 331; (b) C. G. Pierpont, *Coord. Chem. Rev.*, 2001, **216-217**, 99.
- (a) J. Stubbe and W. A. van der Donk, *Chem. Rev.*, 1998, **98**, 705; (b) R. H. Holm and E. I. Solomon, Guest Editors, *Chem. Rev.*, 1996, **96**, No. 7.
- (a) C. N. Verani, S. Gallert, E. Bill, T. Weyhermüller, K. Wieghardt and P. Chaudhuri, *Chem. Commun.*, 1999, 1747; (b) P. Chaudhuri, C. N. Verani, E. Bill, E. Bothe, T. Weyhermüller and K. Wieghardt, *J. Am. Chem. Soc.*, 2001, **123**, 2213; (c) H. Chun, C. N. Verani, P. Chaudhuri, E. Bothe, E. Bill, T. Weyhermüller and K. Wieghardt, *Inorg. Chem.*, 2001, **40**, 4157.
- C. Gerdemann, C. Eicken and B. Krebs, *Acc. Chem. Res.*, 2002, **35**, 183.