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Complexed bridging ligand, [M(bpca)$_2$] (M = Mn(II) or Fe(II); Hbpca = bis(2-pyridylcarbonyl)amine), as a building block for linear trinuclear complexes

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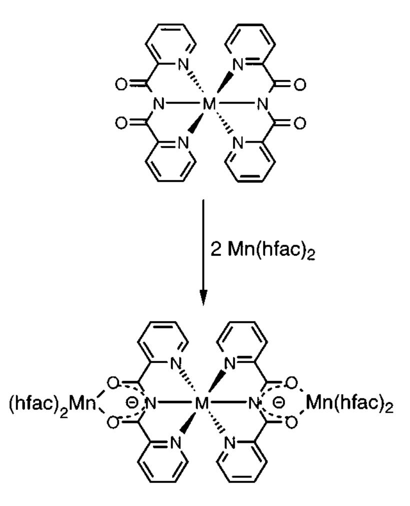
The antiferromagnetically coupled trimanganese complex [Mn^{II}(bpca)$_2${Mn^{II}(hfac)$_2$}$_2$] (Hbpca = bis(2-pyridylcarbonyl)amine; Hhfac = hexafluoroacetylacetone) and its iron–manganese mixed metal derivative, [Fe^{II}(bpca)$_2$-{Mn^{II}(hfac)$_2$}$_2$], were synthesized by the reaction of two equivalents of [Mn(hfac)$_2$(H$_2$O)$_2$] with one equivalent of [M(bpca)$_2$], the latter acting as a bridging complexed-ligand.

The chemistry of multi-metal-centered complexes or metal complex assemblies with highly ordered solid state structures has attracted much attention.[1] In such chemistry, "complexed-ligands" are known to be beneficial in the construction of multi-metal complexes and the control of their properties. Monomeric complexes containing the tridentate ligand bpca$^-$ (Hbpca = bis(2-pyridylcarbonyl)amine), [M(bpca)$_2$] (M = Mn(II),[2] Fe(II),[3] Ni(II),[4] Cu(II),[4] Zn(II)[4]) and [M(bpca)$_2$]X (M = Fe(III); X$^-$ = NO$_3^-$, ClO$_4^-$),[3] could be examples of this type of complexed ligand, although no example has been reported to our knowledge. They have four free C=O groups which may act as two sets of bidentate donors, and, upon reaction with a metal ion M′, they may give a trinuclear complex of the type M′(μ-bpca)M(μ-bpca)M′. It has been reported that oximato and oxamido complexes can act as a complexed ligand to give di-,[5] tri-,[6] and tetra-nuclear complexes.[7] One of the characteristics of the present system is that {M(bpca)$_2$} has a delocalized π-system which might mediate M–M′ interactions in redox and magnetic behaviour in a different way from oxamido complexes. Here we report two examples of trinuclear complexes containing bridging {M(bpca)$_2$}.



[Mn(bpca)$_2$]·H$_2$O[2] or [Fe(bpca)$_2$]·H$_2$O[3] was allowed to react with two equivalents of [Mn(hfac)$_2$(H$_2$O)$_2$] in CHCl$_3$ solution (Hhfac = hexafluoroacetylacetone). Slow evaporation afforded almost quantitatively orange and black crystals of trinuclear complexes, [Mn(bpca)$_2${Mn(hfac)$_2$}$_2$] and [Fe(bpca)$_2${Mn(hfac)$_2$}$_2$], respectively.†

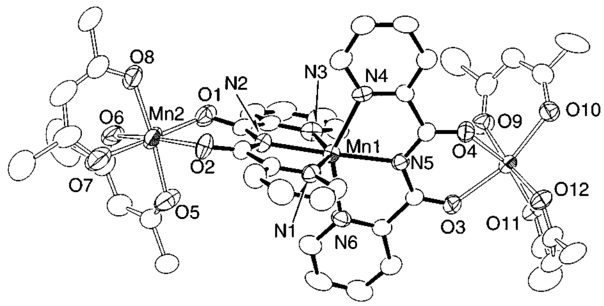


Fig. 1 An ORTEP[8] drawing of [Mn(bpca)$_2${Mn(hfac)$_2$}$_2$] with thermal ellipsoids at 30% probability. Hydrogen atoms and fluorine atoms are omitted for clarity. Selected bond distances (Å): Mn(1)–N(1) 2.246(2), Mn(1)–N(2) 2.196(2), Mn(1)–N(3) 2.221(2), Mn(1)–N(4) 2.262(2), Mn(1)–N(5) 2.203(2), Mn(1)–N(6) 2.242(2), Mn(2)–O(1) 2.153(2), Mn(2)–O(2) 2.176(2), Mn(2)–O(5) 2.146(3), Mn(2)–O(6) 2.163(3), Mn(2)–O(7) 2.126(3), Mn(2)–O(8) 2.113(3), Mn(3)–O(3) 2.171(2), Mn(3)–O(4) 2.190(2), Mn(3)–O(9) 2.152(2), Mn(3)–O(10) 2.147(2), Mn(3)–O(11) 2.120(2), Mn(3)–O(12) 2.122(2), O(1)–C(6) 1.221(3), O(2)–C(7) 1.220(3), O(3)–C(19) 1.251(3), O(4)–C(18) 1.241(3), Mn(1)···Mn(2) 5.6708(6), Mn(1)···Mn(3) 5.6855(6).

Fig. 1 shows the structure of [Mn(bpca)$_2${Mn(hfac)$_2$}$_2$].‡ As expected, a {Mn(bpca)$_2$} unit binds two {Mn(hfac)$_2$} units as a bridging bis-bidentate complexed-ligand. The central Mn ion, Mn1, is surrounded by four pyridyl nitrogens (N1, N3, N4 and N6) with Mn–N distances of 2.221(2)–2.262(2) Å and two amide nitrogens (N2 and N5) with distances of 2.196(2) and 2.203(2) Å. The latter are slightly longer than those in the parent monomeric [Mn(bpca)$_2$] (2.179(7) and 2.169(7) Å).[2] The C=O distances (average 1.233 Å) are definitely longer than those in the monomer, which results in the low frequency shift of C=O stretching (1670 cm^{-1}: an intense band at 1700 cm^{-1} for the parent monomer[2]). These facts suggest that the minus charge of bpca$^-$ is delocalized on the O–C–N–C–O moiety in the trinuclear complex, whereas it is located mainly on the amide nitrogen in [Mn(bpca)$_2$]. Terminal Mn ions, Mn2 and Mn3, are coordinated by six oxygen atoms from two hfac anions and from a {Mn(bpca)$_2$} unit with Mn–O distances of 2.113(3)–2.190(2) Å. These two terminal Mn ions are in a chiral environment with the combination Δ, Λ. The three Mn ions are arranged in an almost linear fashion with separations of 5.6708(6) Å for Mn1···Mn2 and 5.6855(6) Å for Mn1···Mn3, respectively.

The structure of [Fe(bpca)$_2${Mn(hfac)$_2$}$_2$] was isostructural to [Mn(bpca)$_2${Mn(hfac)$_2$}$_2$].§ Overall structural features including delocalization of the O–C–N–C–O moiety are very similar to each other.

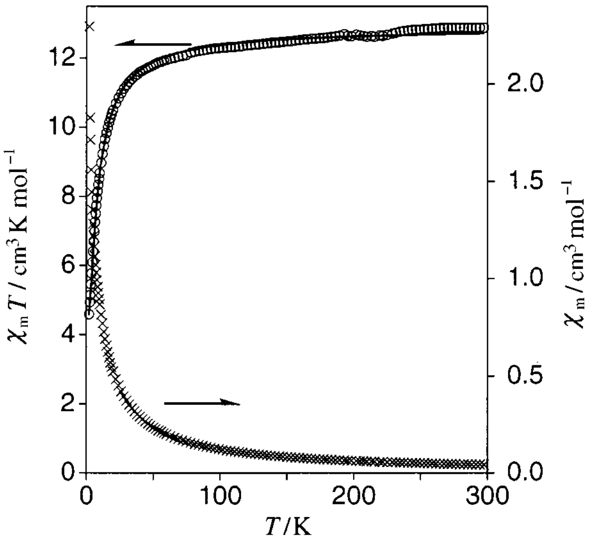


Fig. 2 Plots of χ_mT (o) and χ_m (x) *vs.* T for [Mn(bpca)$_2${Mn(hfac)$_2$}$_2$]. Solid line corresponds to the theoretical curve for which parameters are given in the text.

The temperature dependence of the magnetic susceptibility of the compounds was measured down to 2.0 K. Fig. 2 shows the magnetic susceptibility data for [Mn(bpca)$_2${Mn(hfac)$_2$}$_2$] in the form of χ_mT and χ_m *vs.* T plots. The χ_mT value at room temperature, 12.9 cm³ K mol⁻¹, is slightly smaller than the spin-only value of 13.1 cm³ K mol⁻¹ for the dilute three-spin system with a g value of 2.00. On lowering the temperature, the χ_mT value gradually decreases suggesting antiferromagnetic interaction between adjoining Mn(II) ions through the delocalized π-system. Magnetic data of the trimer was analyzed by the three-spin model with exchange coupling constant J [$H = -2J(S_{Mn1}\cdot S_{Mn2} + S_{Mn1}\cdot S_{Mn3})$].[9] The least squares calculation yielded the best fit parameters of $g = 1.98(1)$ and $J = -0.35(1)$ cm⁻¹. [Fe(bpca)$_2${Mn(hfac)$_2$}$_2$] containing low-spin Fe(II) gave a temperature independent χ_mT value of 8.52 cm³ K mol⁻¹ above 10.0 K. The weak magnetic interaction in [Mn(bpca)$_2${Mn(hfac)$_2$}$_2$] may be related to the Mn–N distances of 2.196(2)–2.262(2) Å, which are longer than the M–N separations of divalent late first row transition metal ions. In fact, [Mn(bpca)$_2${Mn(hfac)$_2$}$_2$] shows no distinct MLCT (from Mn to bpca⁻) band in the absorption spectrum,¶ suggesting weak dπ–pπ interactions.

This study shows that [M(bpca)$_2$]$^{n+}$ could be a potential building block for supramolecular compounds. In fact, similar trinuclear complexes [M(bpca)$_2${Mn(hfac)$_2$}$_2$] (M = Ni(II), Cu(II)) have been isolated *via* similar reactions, in which {M(bpca)$_2$} is acting as a building block.[10] Such studies are now in progress in our laboratories.

Acknowledgements

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Notes and references

† Elemental analysis: **1**, found: C, 36.37; 1.62; N, 5.85. Calc. for $C_{44}H_{18}N_6O_{12}Mn_3F_{24}$: C, 36.61; H, 1.26; N, 5.82%. **2**, found: C, 36.59; H, 1.53; N, 5.77. Calc. for $C_{44}H_{18}N_6O_{12}FeMn_2F_{24}$: C, 36.59; H, 1.26; N, 5.82%.

‡ Crystal data: $C_{44}H_{18}N_6O_{12}Mn_3F_{24}$, $M = 1443.44$, orthorhombic, space group $Pna2_1$ (no. 33), $a = 17.142(9)$, $b = 20.552(3)$, $c = 16.233(4)$ Å, $U = 5718(3)$ Å³, $Z = 4$, $D_c = 1.676$ g cm⁻³, $F(000) = 2940.00$, μ(Mo-Kα) = 12.30 cm⁻¹, 3953 unique reflections ($I > 2.0\sigma(I)$) collected at room temperature with Mo-Kα radiation ($\lambda = 0.71069$ Å) up to $2\theta = 55.0°$ on a Rigaku AFC 7S diffractometer. Final R value is 0.058 for observed data. CCDC reference number 186/1132. See http://www.rsc.org/suppdata/dt/1998/3351/ for crystallographic files in .cif format.

§ Crystal data: $C_{44}H_{18}N_6O_{12}FeMn_2F_{24}$, $M = 1444.35$, orthorhombic, space group $Pna2_1$ (no. 33), $a = 16.701(6)$, $b = 20.134(7)$, $c = 16.353(5)$ Å, $U = 5498(2)$ Å³, $Z = 4$, $R = 0.052$.

¶ Electronic spectrum in CHCl$_3$ solution: $\lambda_{max} = 290$ nm ($\varepsilon = 60500$ dm³ mol⁻¹ cm⁻¹) and *ca.* 420 nm (shoulder, *ca.* 600 dm³ mol⁻¹ cm⁻¹).

1 For example, H. O. Stumpf, L. Ouahab, Y. Pei, D. Grandjean and O. Kahn, *Science*, 1993, **261**, 447; S. L. Suib, *Chem. Rev.*, 1993, **93**, 803.
2 D. Marcos, J.-V. Folgado and D. Beltrán-Porter, *Polyhedron*, 1990, **9**, 2699.
3 S. Wocadlo, W. Massa and J.-V. Folgado, *Inorg. Chim. Acta*, 1993, **207**, 199.
4 D. Marcos, R. Martinez-Mañe, J.-V. Folgado, A. Beltrán-Porter, D. Beltrán-Porter and A. Fuertes, *Inorg. Chim. Acta*, 1989, **159**, 11.
5 F. Birkelbach, M. Winter, U. Flörke, H.-J. Haupt, C. Butzlaff, M. Lengen, E. Bill, A. X. Trautwein, K. Weighardt and P. Chaudhuri, *Inorg. Chem.*, 1994, **33**, 3990; P. Basu, S. Pal and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, 1991, 3217; A. Escuer, R. Vicente, J. Ribas, R. Costa and X. Solans, *Inorg. Chem.*, 1992, **31**, 2627.
6 For example, S. Chattopadhyay, P. Basu, S. Pal and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, 1990, 3829; R. Costa, A. Garcia, R. Sanchez, J. Ribas, X. Solans and V. Rodriguez, *Polyhedron*, 1993, **12**, 2697.
7 C. Krebs, M. Winter, T. Weyhermüller, E. Bill, K. Wieghardt and P. Chaudhuri, *J. Chem. Soc., Chem. Commun.*, 1995, 1913; F. Corazza, E. Solari, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc., Chem. Commun.*, 1986, 1562.
8 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
9 O. Kahn, *Molecular Magnetism*, VCH Publishers, Weinheim, 1993; S. Ménage, S. E. Vitols, P. Bergerat, E. Codjovi, O. Kahn, J.-J. Girerd, M. Guillot, X. Solans and T. Calvet, *Inorg. Chem.*, 1991, **30**, 2666.
10 T. Noguchi, T. Kajiwara and T. Ito, unpublished work.

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