The first example of a bis-monohelical complex: the crystal and molecular structure of $[Mn_2(dmqpy)_2(H_2O)_2(\mu\text{-}Cl)][ClO_4]_3{\cdot}4H_2O$ (dmqpy = 6,6⁗-dimethyl-2,2′:6′,2″:6″,2‴:6⁗-quinquepyridine)

Youjun Fu,[a] Qi Li,[b] Zhongyun Zhou,[b] Wenning Dai,[a] Defen Wang,[a] Thomas C. W. Mak,[b] Hongwen Hu[a] and Wenxia Tang*[a]

[a] *State Key Lab of Coordination Chemistry, Coordination Chemistry Institute, Nanjing University, Nanjing 210093, P.R. China*
[b] *Chemistry Department, Chinese University of Hong Kong, Shatin, New Territories, Hong Kong*

6,6⁗-Dimethyl-2,2′:6′,2″ 6″,2⁗:6‴,2⁗-quinquepyridine (dmqpy) is found to form a dinuclear complex with manganese(II), the structure of which is not double helical but composed of two shallow monohelical complex cations bridged by a chloride ion.

Oligopyridines can form helical complexes with transition metals in a variety of ways.[1,2] We have been interested in the substituent effects on double helical complex formation and found that both 6,6⁗-Dimethylquinquepyridine (dmqpy) and 6,6⁗-dimethyl-4′,4‴-diphenylquinquepyridine (dmdpqpy) form double helical complexes with silver(I),[3] while unsubstituted qpy produces only a mononuclear, near-planar five-coordinate complex under the same conditions,[4] These results indicate that substituents can control the assembly of double helical complexes. Nevertheless we found in this work that dmqpy forms a dinuclear rather than a double helical complex with manganese(II) in the presence of coordinating chloride ions.

The ligand dmqpy was prepared as previously reported.[3] When dmqpy was suspended in a methanolic solution of $MnCl_2{\cdot}4H_2O$ and refluxed, a clear yellow solution was obtained. Addition of $LiClO_4$ and cooling gave pale yellow microcrystals of $[Mn_2(dmqpy)_2(H_2O)_2(\mu\text{-}Cl)][ClO_4]_3{\cdot}4H_2O$. Single crystals were obtained by slow diffusion of diethyl ether vapour into an acetonitrile solution of the complex.

The molecular structure was determined† and the molecule was found to be centrosymmetric. A dinuclear formulation is confirmed but the two dmqpy molecules in the structure do not adopt double helical configurations about the two manganese(II) atoms. Instead, they form two monohelical complex cations which are bridged by a single chloride ion (Fig. 1). The coordination geometry at each Mn^{II} ion is distorted pentagonal-bipyramidal with one dmqpy molecule twisting to form the equatorial plane and one of the apical positions occupied by a water molecule, and the other by a bridging chlorine atom. The metal–metal distance is 4.726 Å, Mn(1), Cl(1) and Mn(2) form an angle of 134.9°. This nonlinearity results in two important structural features: (*i*) the two helices have different axial orientations and the equatorial planes of the two pentagonal bipyramids do not lie parallel to each other but have a dihedral angle of 37.4°. The plane defined by Mn(1), Cl(1), M(2) has different dihedral angles (57, 46°) with the two equtorial planes. (*ii*) Although helical directions in a given molecule are the same (left- or right-handed), the two ligands are positioned differently as shown by the two central pyridyl rings which are located at opposite sides of the plane defined by Mn(1)Mn(2)Cl(1), which has dihedral angles of 50.4 and 60.2° with planes Mn(1)Mn(2)N(3) and Mn(1)Mn(2)N(8) respectively. The orientations of the two helices results in two stacking systems, one between rings 3 and 10 with a distance of 3.92 Å and the other between rings 1 and 8 with a distance of 4.04 Å; thus the molecule is asymmetric. While Mn(1) is bonded more tightly to the two apical donor atoms [Cl(1) O(1w)], Mn(2) has a shorter average bond length with the five equatorial nitrogen donor atoms of dmqpy (2.337 *vs.* 2.384 Å). The helical configurations of the ligands are achieved by two different series of twists of the ligands about the C–C bonds between adjacent pyridine rings. The dihedral angles between planes: 1/2, 11.4; 2/3, 9.2; 3/4, 7.1; 4/5, 18.2° at Mn(1) and 6/7, 9.9; 7/8, 13.6; 8/9, 4.4; 9/10, 13.3° at Mn(2) (the pyridine ring planes are numbered according to the nitrogen atom) indicate that the two ligand molecules adopt similar but slightly different helical conformations. Compared to $[Co(pt_2qpy)Cl_2]$,[5] [pt_2qpy = 4′,4‴-bis(propylthio)-2,2′:6′,2″:6″,2‴: 6⁗,2⁗- quinquepyridine] the degree of twisting is increased. This is in accord with a greater steric effect caused by the introduction of terminal substituents. No intermolecular stacking interactions are observed in the crystal structure, but the six water molecules (both coordinating and those of crystallization) and the perchlorate anions participate in several hydrogen bonding systems,‡ which link the molecules to form infinite chains along the *z* direction.

The effective magnetic moments (μ_{eff}) per manganese ion measured down to 4.27 K are plotted in Fig. 2 and indicate a weak antiferromagnetic coupling of the $S = 10/2$ spin systems in each dinuclear unit. Assuming isotropic exchange, the exchange Hamiltonian is $H = -2JS_1{\cdot}S_2$ with $S_1 = S_2 = 5/2$.[6] With a molecular-field correction,[7] the data were fitted by a least-squares method using the disagreement factor $R = [\Sigma(\mu_{obs}\text{-}\mu_{calc})^2/\Sigma\mu_{obs}{}^2]^{1/2}$ and best fit parameters: J =

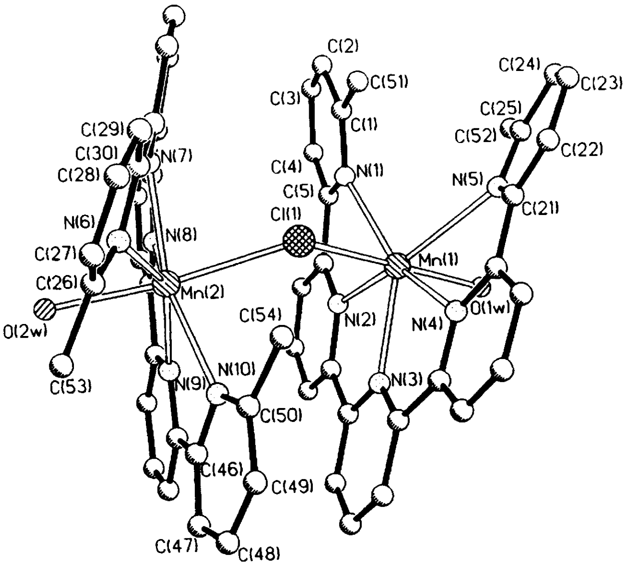

Fig. 1 The crystal and molecular structure of $[Mn_2(dmqpy)_2(H_2O)_2(\mu\text{-}Cl)]^{3+}$ with atom numbering scheme (bond lengths in Å, angles in °): Mn(1)–Cl(1) 2.531(2), Mn(1)–O(1w) 2.208(4), Mn(2)–Cl(1) 2.587(2), Mn(2)–O(2w) 2.274(3), range Mn(1)–N 2.297(4)–2.557(4), range Mn(2)–N 2.279(4)–2.432(4), Cl(1)–Mn(2)–O(2w) 170.8(1), Mn(1)–Cl(1)–Mn(2) 134.9(1)

$-0.188\ \mathrm{cm^{-1}}$, $zJ' = -0.081\ \mathrm{cm^{-1}}$, $g = 2.07$, $R = 1.8 \times 10^{-5}$ were obtained. The results indicate that a single chloride bridge with a bond angle of 134.9° provides only a weak coupling pathway for magnetic exchange between the two manganese(II) cations.

Complexes of manganese have been studied most extensively in modelling the possible active site of Photosystem II.[8] Although seven-coordinate manganese(II) complexes have been reported,[9] this is, to our knowledge, the first example of a dinuclear manganese(II) complex in which both of the two metal atoms are seven-coordinate with pentagonal-bipyramidal geometry. In addition, this is also the first structurally characterized dinuclear manganese complex containing a single bridging chloride ion.

This work was supported by the China National Science Foundation and Hong Kong Research Grants Council Earmarked Grant CUHK 311/94P.

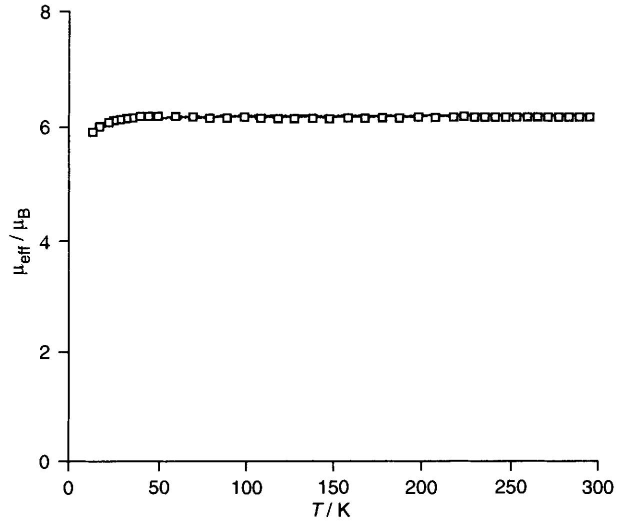

Fig. 2 Temperature dependence of the magnetic moment (μ_{eff}); the solid line is the theoretical least-squares fit

---

Footnotes

† *Crystal data*: $[\mathrm{Mn_2(dmqpy)_2(H_2O)_2(\mu\text{-}Cl)}][\mathrm{ClO_4}]_3\cdot 4\mathrm{H_2O}$, $M = 1382.8$, pale yellow crystals, monoclinic, space group $P2_1/n$, $a = 15.983(3)$, $b = 14.580(3)$, $c = 25.129(6)$ Å, $\beta = 92.06(3)°$, $Z = 4$, $D_c = 1.569\ \mathrm{Mg\ m^{-3}}$, $F(000) = 2840$, $\lambda(\text{Mo-K}\alpha) = 0.71073$, $\mu = 0.696\ \mathrm{mm^{-1}}$. 18544 reflections were collected at 292 K on a Siemans R3m/V diffractometer in the variable ω-scan technique, of which 11378 were unique ($R_{\mathrm{int}} = 0.0459$). The 5687 observed reflections $[|F_o| > 4.0\sigma(|F_o|)]$ were used in the structure solution, using the SHELXTL PC program package[10] on a PC486 computer. The refinement of the coordinates and anisotropic thermal parameters of the non-hydrogen atoms was carried out by full-matrix least-squares analysis on F^2. The final R indices were $R1 = 0.0642$, $wR = 0.1068$ $[w^{-1} = \sigma^2(F) + 0.0006F^2]$ for observed data and $R = 0.1500$, $wR = 0.1419$ for all data. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/96.

‡ Hydrogen-bonding distances (Å): O(1w)–O(2) 2.781, O(1w)–O(7) 3.34, O(1w)–O(8) 2.830, O(3w)–O(4w) 2.635, O(3w)–O(6w) 3.861, O(4w)–O(5w) 2.753, O(4w)–O(6w) 2.608, O(5w)–O(6w) 2.942, O(5w)–O(5) 2.791, O(2)–O(8) 3.622.

References

1 E. C. Constable, *Tetrahedron*, 1992, **48**, 10013.
2 E. C. Constable, *Prog. Inorg. Chem.*, 1994, **42**, 67.
3 Y. Fu, J. Sun, Q. Li, Y. Chen, W. Dai, D. Wang, T. C. W. Mak, W. Tang and H. Hu, *J. Chem. Soc., Dalton Trans.*, in the press.
4 E. C. Constable, M. C. B. Drew, C. Forsyth and M. D. Ward, *J. Chem. Soc., Chem. Commun.*, 1988, 1450.
5 K. A. Cheysen, K. T. Potts, H. C. Hurrel and H. D. Abruna, *Inorg. Chem.*, 1990, **29**, 1589.
6 S. L. Lambert and D. N. Hendrickson, *Inorg. Chem.*, 1979, **18**, 2683.
7 J. J. Borras-Almenar, R. Burriel, E. Coronado, D. Gatteschi, C. J. Gomez-Garcia and C. Zanchini, *Inorg. Chem.*, 1991, **30**, 947.
8 K. Wieghardt, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1153.
9 N. Nakasuka, S. Azuma, C. Katamaya, M. Honda and J. Tanaka, *Acta Crystallogr., Sect. C*, 1985, **41**, 1176.
10 G. M. Sheldrick, in *Computational Crystallography*, ed. D. Sayre, Oxford University Press, New York, 1982, pp. 506–514.

Received, 15th January 1996; Com. 6/00294C