NOTE

Synthesis, Crystal Structure and Magnetic Property of a Sandwich-Like Cyanide-Bridged Fe(III)-Mn(II) Complex

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A trinuclear cyanide-bridged Fe(III)-Mn(II) complex has been synthesized with pyridine carboxamide *trans*-dicyanide iron building block and structurally characterized as trinuclear sandwich-like, in which the two cyanide-containing building blocks acting as a monodentate ligand were coordinated face to face to central Mn(II) ion. Investigation over its magnetic property reveals the antiferromagnetic magnetic coupling between the cyanide-bridged neighboring Fe(III) and Mn(II) ions.

Key Words: Cyanide-bridged, Crystal structure, Magnetic property.

As one of the most important magnetic systems, cyanide-bridged complexes have got much attention since their molecular topological structures and magnetic coupling nature between neighboring metal ions through the cyanide bridge can be relatively controlled and predicted[1-3]. Recently, we have reported some low-dimensional heterometallic cyanide-bridged magnetic complexes with various topological structures with a series of rigid *trans*-dicyanide-containinng building blocks based on large in-plane pyridine carboxamide ligands[4-7]. Here, we present the synthesis and magnetic property of a sandwich-like cyanide-bridged Fe(III)-Mn(II) complex based on pyridine carboxamide *trans*-dicyanide iron building block.

To a solution of [Mn(acac)$_2$]Cl (28.9 mg, 0.1 mmol) in methanol (10 mL), K[Fe(bpb)(CN)$_2$] (46.5 mg, 0.10 mmol) [bpb^{2-} = 1,2-*bis*(pyridine-2-carboxamido)benzenate] dissolved in methanol/water (4:1, v:v) (10 mL) was carefully added. The resulting mixture was filtered at once and the filtrate kept undisturbed at room temperature. After several days, dark-brown block crystals were collected by filtration with the yield of 34.2 mg, 60.4 %. Anal. calcd. (%) for C$_{48}$H$_{56}$Fe$_2$MnN$_{12}$O$_{12}$: C, 48.82; H, 4.63; N, 14.85. Found (%): C, 48.74; H, 4.68; N, 14.71.

Elemental analyses of carbon, hydrogen and nitrogen were carried out with an Elementary Vario El. Variable-temperature magnetic susceptibility and field dependence magnetization measurements were performed on a Quantum Design MPMS SQUID magnetometer.

Structure determination: A suitable white block crystal with dimensions of 0.19 mm × 0.23 mm × 0.31 mm was mounted on a glass fiber and the data were collected on a Bruker Smart 1000 CCD diffractometer with a MoK$_\alpha$ radiation (λ = 0.71073 Å) at 293(2) K by using an ω scan mode in the range of $1.60 < \theta < 25.01°$. The hydrogen atoms bound to carbon were located by geometrically calculations and their positions and thermal parameters were fixed during the structure refinement. All non-hydrogen atoms were refined by full-matrix least-squares techniques. All calculations were performed by the SHELXTL 97 program[8]. Crystallographic data and experimental details for structural analyses are summarized in Table-1. CCDC: 864012.

In the sandwich-like complex, two [Fe(bpb)(CN)$_2$]$^-$ units, acting as a monodentate ligand, connect the central Mn(II) ion coordinated by the additional four oxygen atoms coming from four solvent methanol molecules. The coordination sphere for the Mn(II) atom is a octahedron, in which four equatorial positions are occupied by four oxygen atoms from the coordinated methanol molecules and the other two axial ones come from the nitrogen atoms of the bridging cyanide groups. As shown in Table-2, the distances between the Mn atom and the O atoms of the solvent molecules are 2.2042(19) and 2.2191(19) Å, while the Mn-N cyanide bond lengths are 2.159(2) Å, giving further information about the slightly distorted octahedron surrounding of the Mn(II) ion. The angle of C1≡N1-Mn1 is 164.3(2)°, indicating that these three atoms deviate slightly from a linear configuration.

TABLE-1	
CRYSTALLOGRAPHIC DATA AND STRUCTURE REFINEMENT SUMMARY FOR THE COMPLEX	
Empirical formula	$C_{46}H_{52}Fe_2MnN_{12}O_{12}$
Formula weight	1131.64
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions (Å)	a = 8.6044(13), b = 11.7587(17), c = 25.426(4)
Volume ($Å^3$)	2571.8(7)
Z, Calculated density (mg/m^3)	2, 1.461
Absorption coefficient	0.870
$F_{(000)}$	1170
Reflections collected/unique	18287/4494 [$R_{(int)}$ = 0.0329]
Data/restraints/parameters	4494/0/334
Goodness-of-fit on F^2	1.044
Final R indices [I > 2σ(I)]	R_1 = 0.0332, wR_2 = 0.0824
R indices (all data)	R_1 = 0.0444, wR_2 = 0.0897
Largest diff. peak and hole ($e/Å^3$)	0.432 and -0.334

The temperature dependence of magnetic susceptibility for the complex measured in the temperature range of 2-300 K in the applied field of 2000 Oe is given in Fig. 1. The room temperature χ_m T values of the complex is 5.13 emu K mol^{-1}, which is consistent with the spin only value of 5.125 emu K mol^{-1} for uncoupled Mn(II) (S = 5/2) and two low spin Fe(III) (S = 1/2) based on g = 2.00. With the temperature decreasing, the χ_m T value decreases gradually and attains the value of 4.95 emu K mol^{-1} at *ca.* 50 K, then decreases sharply to their lowest value of 2.46 emu K mol^{-1} at 2 K. This is characteristic of antiferromagnetic coupling in the trimeric Fe(III)$_2$Mn(II) cluster, which is also proven by the Brillouin curves (Fig. 1). The magnetic susceptibility for the complex conforms well to Curie-Weiss law in the range of 2-300 K and give the negative Weiss constant θ = -3.27 K and Curie constant C = 5.18 emu K mol^{-1}.

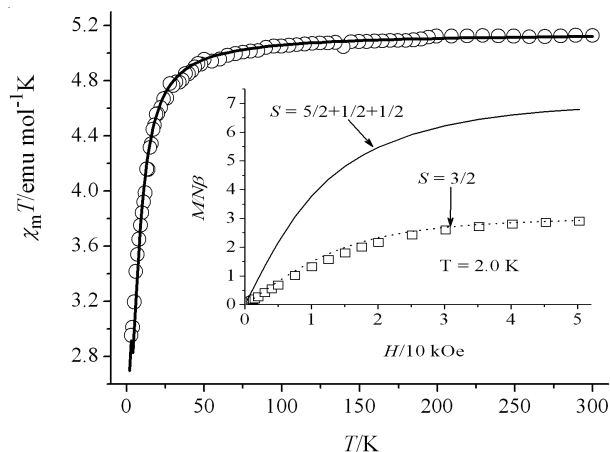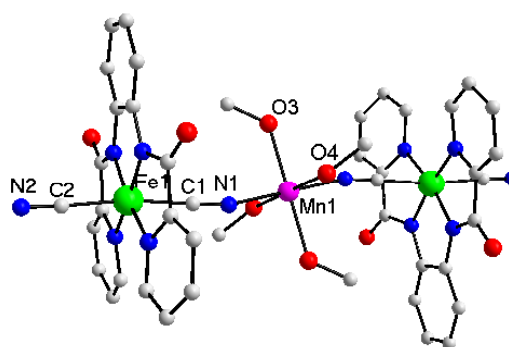Fig. 1. Trinuclear structure of the complex and its magnetic property

TABLE-2					
SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR Fe(III)-Mn(II) COMPLEX					
Bond	Dist.	Bond	Dist.	Bond	Dist.
Mn1-N1	2.159(2)	Mn1-O3	2.2042(19)	Mn1-O4	2.2191(19)
Fe1-C1	1.972(2)	Fe1-C2	1.979(2)	Fe1-N3	1.8962(19)
Fe1-N4	1.8850(19)	Fe1-N5	1.995(2)	Fe1-N6	1.9976(19)
Angle	(°)	Angle	(°)	Angle	(°)
Mn1-C1-N1	164.3(2	C1-Fe1-C2	172.25(10)	Fe1-C1-N1	178.6(2)

REFERENCES

1. J.N. Rebilly and T. Mallah, *Struct. Bond*, **122**, 103 (2006).
2. R. Lescouezec, L.M. Toma, J. Vaissermann, M. Verdaguer, F.S. Delgado, C. Ruiz-Perez, F. Lloret and M. Julve, *Coord. Chem. Rev*., **249**, 2691 (2005).
3. H. Miyasaka, A. Saitoh and S. Abe, *Coord. Chem. Rev*., **251**, 2622 (2007).
4. Z.H. Ni, H.Z. Kou, L.F. Zhang, C. Ge, A.L. Cui, R.J. Wang, Y. Li and O. Sato, *Angew. Chem. Int. Ed*., **44**, 7742 (2005).
5. Z.H. Ni, H.Z. Kou, Y.H. Zhao, L. Zheng, R.J. Wang, A.L. Cui and O. Sato, *Inorg. Chem*., **44**, 2050 (2005).
6. Z.H. Ni, L.F. Zhang, V. Tangoulis, W. Wernsdorfer, A.L. Cui, O. Sato and H.Z. Kou, *Inorg. Chem*., **46**, 6029 (2007).
7. D.P. Zhang, H.L. Wang, Y.T. Chen, Z.H. Ni, L.J. Tian and J.Z. Jiang, *Inorg. Chem*., **48**, 5488 (2009).
8. G.M. Sheldrick, SHELXTL97, Program for the Refinement of Crystal Structure, University of Göttingen, Germany (1997).