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Synthesis, Characterization, and Crystal Structure of a Novel Cyanide-Bridged Heteronuclear Co(III)-Mn(III) Complex Derived from *N*,*N*'-Ethylene-Bis(Chlorosalicylideneimine)[1]

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Abstract—With a bis-Schiff base *N*,*N*'-ethylene-bis(5-chlorosalicylideneimine) (H_2L) and $K_3[Co(CN)_6]$, a novel cyanide-bridged heteronuclear Co(III)–Mn(III) complex was prepared and characterized by elemental analysis, IR spectroscopy and X-ray structure determination (CIF file CCDC no. 1029225). The complex crystallizes in the monoclinic space group $P2_1/c$ with unit cell dimensions $a = 10.741(2)$, $b = 14.015(3)$, $c = 15.074(3)$ Å, $\beta = 94.237(2)°$, $V = 2263.0(8)$ Å^3, $Z = 2$, $R_1 = 0.0441$, and $wR_2 = 0.0999$. Single crystal X-ray diffraction analysis reveals that two $[Mn(L)(OH_2)]^+$ units are linked through a $[Co(CN)_6]^{3-}$ bridge, forming a trinuclear Mn–Co–Mn moiety. The Mn–Co–Mn moieties are further linked through K atoms to form a 1D chain. The chains are stacked through $\pi\cdots\pi$ interactions. The Mn and Co atoms are in octahedral coordination, and the K atom is in square planar geometry.

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INTRODUCTION

Cyanide-bridged complexes have been given much attention by coordination chemists and molecular magnetism chemists due to their versatile structures and interesting magnetic properties [1–5]. Cyanide salts such as KCN and NaCN are well known as potential bridging material [6–8]. However, they are very poisonous. The cyanide groups in $K_3[Fe(CN)_6]$, $K_3[Co(CN)_6]$ and similar compounds can also act as bridging groups to coordinate to other metals, generating homo- or heteronuclear polymeric structures [9–11]. bis-Schiff bases bearing NNOO donor set derived from ethane-1,2-diamine are preferred to construct complexes with various metal atoms [12–15]. In this paper, a novel cyanide-bridged heteronuclear Co(III)–Mn(III) complex derived from *N*,*N*'-ethylene-bis(5-chlorosalicylideneimine) (H_2L) was prepared.

EXPERIMENTAL

Materials and methods. 5-Chlorosalicylaldehyde and ethane-1,2-diamine were purchased from Aldrich. Manganese perchlorate, $K_3[Co(CN)_6]$ and solvents are commercially available and were used without further purification. *N*,*N*'-Ethylene-bis(5-chlorosalicylideneimine) was prepared by condensation of 2 : 1 molar ratio of 5-chlorosalicylaldehyde with ethane-1,2-diamine in methanol [16]. Elemental analyses for carbon, hydrogen, and nitrogen were carried out with an Elementar Vario EL. Infrared spectra were measured on KBr disks with a Hitachi I-5040 FT-IR spectrophotometer.

CAUTION: Perchlorate salts are potentially explosive and should only be handled in small quantities.

Synthesis of the complex. A methanol solution (10 mL) of manganese perchlorate hexahydrate (0.362 g, 1 mmol) was added to a methanol solution (10 mL) of H_2L (0.337 g, 1 mmol). The brown solution was stirred at 60°C for 1 h, and cooled to room temperature. $K_3[Co(CN)_6]$ (0.332 g, 1 mmol) dissolved in 10 mL of water was poured into a glass tube and layered with 5 mL of methanol. Over this, the brown solution containing the Schiff base manganese complex was carefully layered to avoid fast mixing of the reactants. The tube was then sealed with Parafilm to avoid evaporation. After a week deep brown block-shaped single crystals were found at the bottom of the tube. The yield was 72% on the basis of the manganese precursor.

For $C_{38}H_{32}N_{10}O_8Cl_4KMn_2Co$

anal. calcd, %:	C, 41.25;	H, 2.92;	N, 12.66.
Found, %:	C, 41.39;	H, 3.01;	N, 12.50.

IR (KBr; ν, cm^{-1}): 3646 ν(O–H); 2140, 2125, 2116 ν(CN); 1629 ν(C=N).

X-ray structure determination. Data collection for the complex was performed with a Bruker Apex II CCD diffractometer at 298 K. The structure was solved by di-

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rect methods with SHELXS-97 and refined by full-matrix least squares (SHELXL-97) on F^2 [17]. All non-hydrogens were refined anisotropically. The hydrogen atoms of O(3) water molecule were located from a difference Fourier map and refined isotropically with O–H and H···H distances restrained to 0.85(1) and 1.37(2) Å, respectively. The remaining hydrogens were placed geometrically and refined with a riding model, with isotropic displacement coefficients U(H) = 1.2 U(C). Crystallographic data for the complex are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

Supplementary material for complex has been deposited with the Cambridge Crystallographic Data Centre (no. 1029225; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The complex was prepared by slow diffusion of the Schiff base manganese complex with $K_3[Co(CN)_6]$ in a glass tube. Crystals of **I** are stable in air, and soluble in methanol, ethanol, DMF and DMSO, insoluble in water. The cyanide-bridged heterometallic complex has been characterized by infrared spectroscopy. In the infrared spectrum, three sharp peaks due to the cyanide-stretching vibration were observed at 2140, 2125 and 2116 cm^{-1}, indicating the presence of bridging and non-bridging cyanide ligands in the complex [18]. The intense band at 1629 cm^{-1} can be assigned to the vibration of the azomethine groups, ν(CH=N) [19]. The weak and broad band centered at 3646 cm^{-1} is attributed to the vibration of the water molecules.

The repeat units of complex **I** is shown in Fig. 1. The complex crystallizes in monoclinic space group $P2_1/c$. Two $[Mn(L)(OH_2)]^+$ units are connected by two cyanide groups in a *trans* position of $[Co(CN)_6]^{3-}$ ion to form a hetero trinuclear $[Mn_2(L)_2(OH_2)_2Co(CN)_6]^-$ complex anion. The trinuclear complex anions are further linked by K^+ ion to form an 1D chain along the x axis, as shown in Fig. 2. The chains are stacked through π···π interactions among the planes of Mn(1)–O(2)–C(12)–C(11)–C(10)–N(2), C(1)–C(2)–C(3)–C(4)–C(5)–C(6) and C(11)–C(12)–C(13)–C(14)–C(15)–C(16) with centroids to centroids distances of 3.74–4.82 Å. The coordination sphere for the Mn atom is a distorted octahedral, in which four equatorial positions are occupied by two N atoms and two O atoms from the Schiff base ligand, and the other two axial ones come from the N atoms of the bridging cyanide group and the O atom of the coordinated water molecule. As shown in Table 1, the average distances between the Mn atom and the N, O atoms of the Schiff base ligand (1.982(3) and 1.867(2) Å) are obviously shorter than the $Mn–N_{cyanide}$ and $Mn–O_{water}$ bond lengths with the values 2.333(3) and 2.267(3) Å, which gives further information about the

Table 1. Crystallographic data and and structure refinement for the complex

Parameter	Value
Formula weight	1106.45
Crystal system	Monoclinic
Space group	$P2_1/c$
a, Å	10.741(2)
b, Å	14.015(3)
c, Å	15.074(3)
β, deg	94.237(2)
V, Å^3	2263.0(8)
Z	2
ρ_{calcd}, g cm^{-3}	1.624
F(000)	1116
μ, mm^{-1}	1.301
θ Range, deg	2.39–25.10
Index ranges hkl	$-12 \le h \le 12$, $-14 \le k \le 16$, $-17 \le l \le 17$
Reflections collected/unique	19871/4002
R_{int}	0.0720
Observed with $I > 2\sigma(I)$	2941
Parameters refined	298
Rastraints	4
Final R index ($I > 2\sigma(I)$)	0.0441, 0.0999
R index (all data)	0.0715, 0.1115
Goodness-of-fit on F^2	1.047
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.993/–0.409

Table 2. Selected bond distances (Å) and angles (deg) for the complex

Bond	*d*, Å	Bond	*d*, Å
K(1)–N(4)	2.774(4)	K(1)–O(4)	2.863(5)
Mn(1)–O(1)	1.867(2)	Mn(1)–O(2)	1.887(2)
Mn(1)–N(1)	1.982(3)	Mn(1)–N(2)	1.986(3)
Mn(1)–O(3)	2.267(3)	Mn(1)–N(3)	2.333(3)
Co(1)–C(18)	1.890(4)	Co(1)–C(17)	1.900(4)
Co(1)–C(19)	1.911(4)		
Angle	**ω, deg**	**Angle**	**ω, deg**
N(4)K(1)O(4)	95.40(13)	O(1)Mn(1)N(1)	92.58(11)
O(1)Mn(1)O(2)	92.45(10)	O(1)Mn(1)N(2)	174.66(11)
O(2)Mn(1)N(1)	174.93(12)	N(1)Mn(1)N(2)	82.64(12)
O(2)Mn(1)N(2)	92.32(11)	O(2)Mn(1)O(3)	93.10(10)
O(1)Mn(1)O(3)	89.41(10)	N(2)Mn(1)O(3)	87.93(10)
N(1)Mn(1)O(3)	86.30(11)	O(2)Mn(1)N(3)	94.58(11)
O(1)Mn(1)N(3)	93.00(12)	N(2)Mn(1)N(3)	89.01(12)
N(1)Mn(1)N(3)	85.81(12)	C(17)Co(1)C(19)	89.64(15)
O(3)Mn(1)N(3)	171.84(11)	C(18)Co(1)C(17)	90.00(14)
		C(18)Co(1)C(19)	88.33(15)

elongation octahedron surrounding the Mn^{3+} ion, typically accounting for the well-known Jahn–Teller effect. The Mn–N and Mn–O bond lengths are in good agreement with the manganese complexes with bis-Schiff bases [20–22]. The bond angle of O(3)Mn(1)N(3), 171.8(1)° clearly indicates that the three atoms are in a linear configuration, while the angle of C(17)≡N(3)–Mn(1) is much bent and deviates obviously from a linear configuration with the value of 144.3(3)°. The intramolecular Mn(III)–Mn(III) separation through bridging $[Co(CN)_6]^{3-}$ is 10.22 Å, and the intramolecular Mn(III)–Co(III) separation through bridging cyanide group is 5.11 Å. The dihedral angle between the two benzene rings of the Schiff base ligand is 7.7(3)°. In the $[Co(CN)_6]^{3-}$ fragment, the Co atom is surrounded by six cyanide ligands, exhibiting an octahedral coordination geometry. The bond lengths of Co–C vary from 1.890(4) to 1.911(4) Å. These Co–C bond lengths are in good agreement with the reported complexes bearing $Co(CN)_6$ bridges [10, 23]. The K atom is coordinated by two cyanide N at-

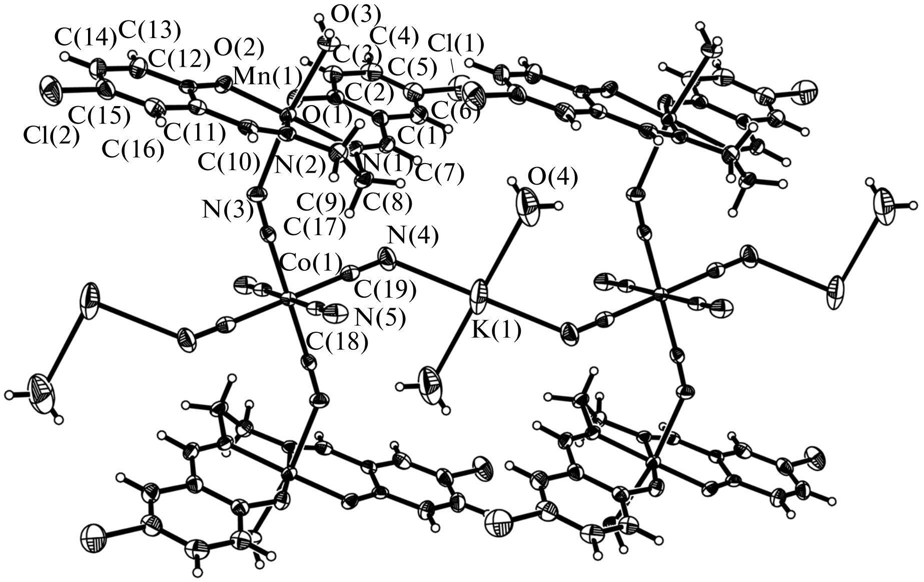

Fig. 1. The repeated fragments of the complex with 30% probability thermal ellipsoids.

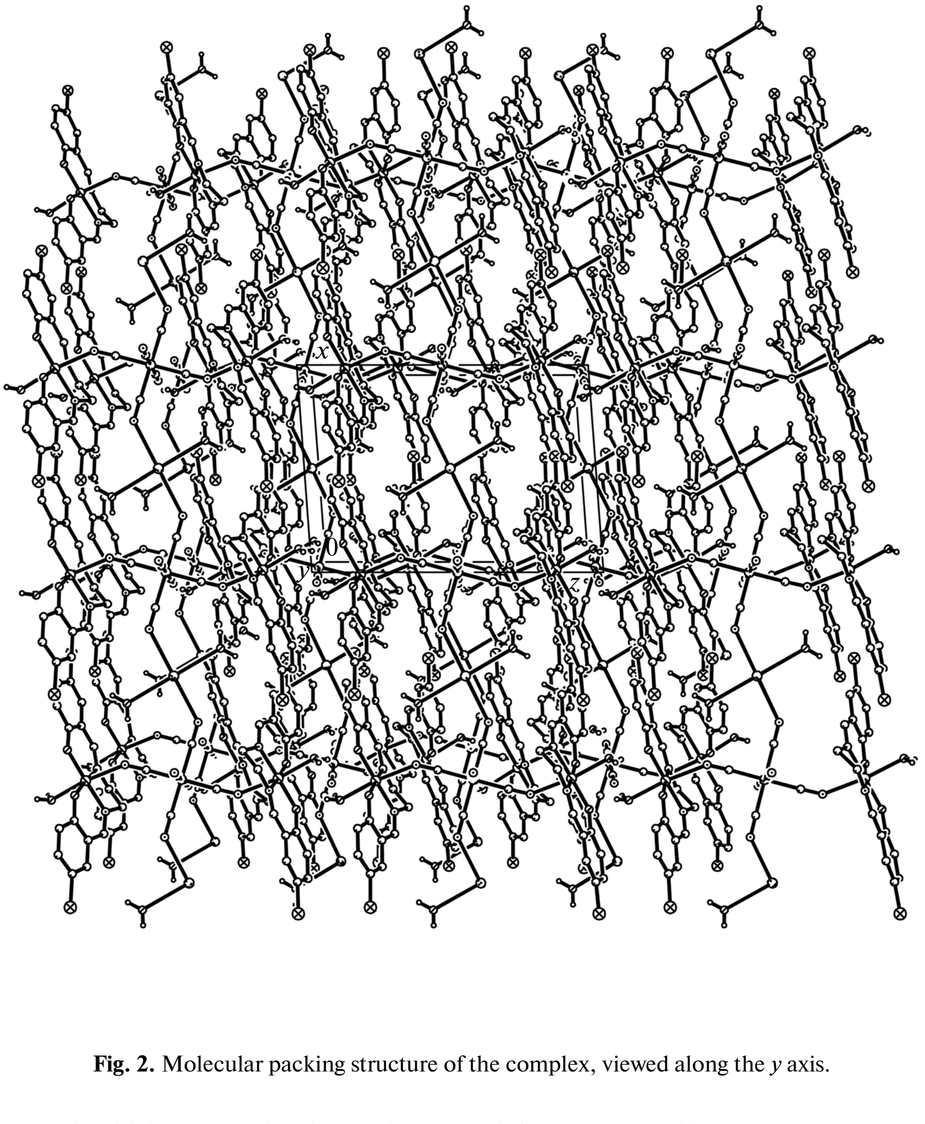

Fig. 2. Molecular packing structure of the complex, viewed along the *y* axis.

oms and two water O atoms, forming a square planar geometry.

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