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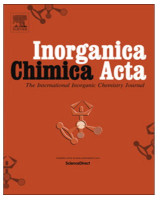

Research paper

Design, syntheses, crystal structures and magnetic properties of a series of cyanide-bridged heterometallic Cr(III)–Mn(III) one-dimensional complexes

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ABSTRACT

Six new cyanide-bridged $Cr^{III}–Mn^{III}$ one-dimensional (1D) complexes $[Mn^{III}(salen)Cr^{III}(bpb)(CN)_2]_n$ (**1**), $[Mn^{III}(5\text{-}Clsalen)Cr^{III}(bpb)(CN)_2{\cdot}0.5CH_3OH{\cdot}H_2O]_n$ (**2**), $[Mn^{III}(5\text{-}Brsalen)Cr^{III}(bpb)(CN)_2{\cdot}0.5CH_3OH{\cdot}H_2O]_n$ (**3**), $[Mn^{III}(5\text{-}MeOsalen)Cr^{III}(bpb)(CN)_2{\cdot}H_2O]_n$ (**4**), $[Mn^{III}(5\text{-}Clsalen)Cr^{III}(bpClb)(CN)_2{\cdot}CH_3CN]_n$ (**5**) and $[Mn^{III}(5\text{-}Brsalen)Cr^{III}(bpClb)(CN)_2{\cdot}2H_2O]_n$ (**6**) have been rationally designed, controlling synthesized and structurally characterized based on $[Mn^{III}(5\text{-}R_1salen)]^+$ and $[Cr^{III}(4\text{-}R_2bpb)(CN)_2]^-$ building blocks [$5\text{-}R_1salen^{2-}$ = *N*,*N*′-ethylenebis(5-R_1-salicylideneaminato)dianion, R_1 = H for $salen^{2-}$, Cl for $5\text{-}Clsalen^{2-}$, Br for $5\text{-}Brsalen^{2-}$ and MeO for $5\text{-}MeOsalen^{2-}$; $4\text{-}R_2bpb^{2-}$ = 1,2-bis(pyridine-2-carboxamido)-4-R_2-benzenate, R_2 = H for bpb^{2-} and Cl for $bpClb^{2-}$]. The single crystal structures of these complexes consist of alternating units of $[Mn^{III}(5\text{-}R_1salen)]^+$ and $[Cr^{III}(4\text{-}R_2bpb)(CN)_2]^-$, forming cyanide-bridged neutral 1D complexes. Investigation over magnetic properties of these complexes reveals the whole relatively weak antiferromagnetic interactions between Mn(III) ion and Cr(III) through cyanide bridge. The magnetic susceptibilities of these complexes were fitted based on the suitable 1D $Cr^{III}–Mn^{III}$ magnetic model. The magneto-structural correlation for cyanide-bridged $Cr^{III}–Mn^{III}$ systems reveals that the cyanide-bridging bond angle is related to the magnitude of magnetic exchange coupling: the larger the $Mn{-}N{\equiv}C$ bond angle, the weaker antiferromagnetic interactions.

1. Introduction

Molecule-based coordination functional materials such as optical, magnetic, electric, hole, catalytic, chiral and their complicated materials have aroused much attentions in the past several decades [1–5]. Of course, the design and assembly of compounds with interesting topological structures and excellent properties will be the main tasks in the fields of coordination chemistry in the future long time. Although the directional design and controlling synthesis of new complexes with interesting properties is the beautifully ultimate goal of crystal engineering and materials science, the control on molecular topological structures of inorganic coordination complexes seems more subtle and unpredictable to some degree, especially for the relatively complicated systems.

Among the many coordination systems, cyanide group exhibits its incomparable advantages not only for its special coordination ability and coordination selectivity, but also for its effective magnetic exchange ability and predictable magnetic coupling nature as well as its unique directional ability of the final molecular topological structures [6–9]. Moreover, cyanide group is the most famous linkage for the heterometallic systems. As a result, a large number of cyanide-bridged complexes with various structural types have been successfully synthesized [10–21]. Cyanide-bridged $Cr^{III}–Mn^{III}$ system shows its special features because the two magnetic carriers have relatively larger spin states. Indeed, some interesting cyanide-bridged $Cr^{III}–Mn^{III}$ systems with polynuclear, 1D and 2D molecular structural have been designed and synthesized [22–24]. Moreover, Gao and Julve groups have reported the magneto-structural correlation based on a series of cyanide-bridged polynuclear and 1D $Cr^{III}–Mn^{III}$ complexes [23a,24a].

To deliberately synthesize cyanide-bridged magnetic systems with the desired structures, several effective factors such as the number and position of cyanide groups, the number and nature of charge of the cyanide-containing building blocks, and the steric effect of the reactants must be taken into account. In the present work, $[Cr^{III}(4\text{-}R_2bpb)(CN)_2]^-$ [$4\text{-}R_2bpb^{2-}$ = 1,2-bis(pyridine-2-carboxamido)-4-R_2-benzenate, R_2 = H for bpb^{2-} and Cl for $bpClb^{2-}$]

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were selected as the cyanide-containing precursors and $[Mn^{III}(5\text{-}R_1salen)]^+$ [$5\text{-}R_1salen^{2-}$ = *N,N′*-ethylenebis(5-R_1-salicylideneaminato)dianion, R_1 = H for $salen^{2-}$, Cl for $5\text{-}Clsalen^{2-}$, Br for $5\text{-}Brsalen^{2-}$ and MeO for $5\text{-}MeOsalen^{2-}$] were selected the corresponding reactants (Scheme 1). The resulting molecular structures of the final complexes based on the above building blocks are very limited and nearly can be anticipated according to the basic rules of coordination chemistry and cyanide chemistry. Indeed, six new cyanide-bridged 1D heterometallic Cr^{III}–Mn^{III} complexes have been prepared. Herein, we report the design, syntheses, crystal structures and magnetic properties of these complexes.

2. Experimental

2.1. Materials and physical measurements

Elemental analyses of carbon, hydrogen, and nitrogen were carried out with an Elementary Vario El. The infrared spectroscopy on KBr pellets was performed on a Magna-IR 750 spectrophotometer in the 4000–400 cm^{-1} region. The powder XRD data were measured on a Bruker D8 Advance X-ray diffractometer equipped with a Cu-Kα radiation (λ = 0.15418 nm, cathode voltage 40 kV and cathode current 30 mA). Variable-temperature magnetic susceptibilities were performed on a Quantum Design MPMS SQUID magnetometer. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's tables).

All the chemicals were obtained commercially. The four $[Mn^{III}(5\text{-}R_1salen)]ClO_4$ precursors and the two cyanide-containing building blocks $K[Cr^{III}(4\text{-}R_2bpb)(CN)_2]$ prepared by the procedures reported previously [21a,25b]. *WARNING*: Cyanides are extremely toxic and should be handled with caution.

2.2. Syntheses of complexes **1–6**

The six complexes were prepared by a similar method, therefore only the synthesis of complex **1** was described in detail as the representative. $K[Cr^{III}(bpb)(CN)_2]$ (0.1 mmol) dissolved in 15 mL water/methanol (v/v = 1/5) was added to the CH_3OH/CH_3CN (v/v = 2/1) solution (15 mL) containing $[Mn^{III}(salen)]ClO_4$ (0.1 mmol). The mixture was filtered and the filtrate was allowed to evaporate at the room temperature without disturbing. Dark brown crystals suitable for X-ray diffraction analysis can be obtained after about two days. Yield: 45.6 mg (60.9%). Anal. Calcd. for $C_{36}H_{26}CrMnN_8O_4$ (**1**): C, 58.31; H, 3.53; N, 13.67. Found: C, 58.15; H, 3.58; N, 15.02. Main IR bands (cm^{-1}): 2148 ($\nu C{\equiv}N$), 2126 ($\nu C{\equiv}N$).

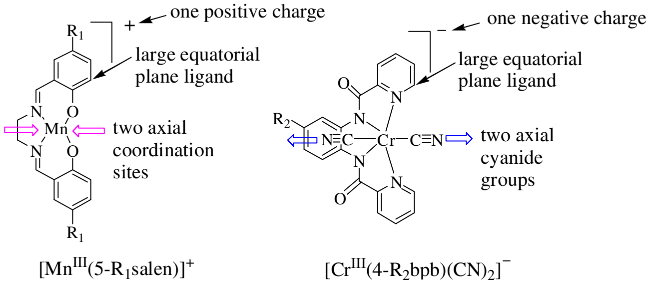
Complex **2**: Yield: 38.2 mg (45.3%). Anal. Calcd. for $C_{36.50}H_{28}Cl_2CrMnN_8O_{5.50}$: C, 51.91; H, 3.34; N, 13.26. Found: C, 51.68; H, 3.46; N, 12.98. Main IR bands (cm^{-1}): 2145 ($\nu C{\equiv}N$), 2138 ($\nu C{\equiv}N$).

Complex **3**: Yield: 31.7 mg (34.0%). Anal. Calcd. for $C_{36.50}H_{28}Br_2CrMnN_8O_{5.50}$: C, 46.97; H, 3.02; N, 12.00. Found: C, 47.02; H, 3.23; N, 11.75. Main IR bands (cm^{-1}): 2144 ($\nu C{\equiv}N$), 2136 ($\nu C{\equiv}N$).

Complex **4**: Yield: 36.6 mg (44.6%). Anal. Calcd. for $C_{38}H_{32}CrMnN_8O_7$: C, 55.68; H, 3.96; N, 13.67. Found: C, 55.46; H, 3.89; N, 13.55. Main IR bands (cm^{-1}): 2146 ($\nu C{\equiv}N$), 2138 ($\nu C{\equiv}N$).

Complex **5**: Yield: 42.8 mg (48.3%). Anal. Calcd. for $C_{38}H_{26}Cl_3CrMnN_9O_4$: C, 51.52; H, 2.96; N, 14.23. Found: C, 51.42; H, 3.02; N, 14.01. Main IR bands (cm^{-1}): 2146 ($\nu C{\equiv}N$), 2139 ($\nu C{\equiv}N$).

Complex **6**: Yield: 45.6 mg (47.0%). Anal. Calcd. for $C_{36}H_{27}Br_2ClCrMnN_8O_6$: C, 44.58; H, 2.81; N, 11.55. Found: C, 44.42; H, 2.73; N, 11.62. Main IR bands (cm^{-1}): 2145 ($\nu C{\equiv}N$), 2137 ($\nu C{\equiv}N$).



Scheme 1. The structures of building blocks $[Mn^{III}(5\text{-}R_1salen)]^+$ (R_1 = H, Cl, Br and MeO) and $[Cr^{III}(4\text{-}R_2bpb)(CN)_2]^-$ (R_2 = H and Cl).

2.3. X-ray crystallography data and structure refinement

The collection of crystallographic data for the four complexes was carried out on a Bruker Smart-1000 CCD diffractometer, using graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å) at 123(2) K. The structures were solved by direct method and expanded using Fourier difference techniques with the SHELXTL-97 program. All of the nonhydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were assigned isotropic displacement coefficients U(H) = 1.2U(C) or 1.5U(C), and their coordinates were allowed to ride on their respective carbons using SHELXL97, except some of the H atoms of the solvent water molecules. Details of the crystal parameters, data collection and refinement are summarized in Table 1.

3. Results and discussion

3.1. Synthesis and general characterization

Generally, cyanide-bridged heterometallic complexes are prepared by the reaction between the cyanide-containing building block and the other metal or metal compound containing coordination reacting sites. As depicted in Scheme 1, $[Mn^{III}(5\text{-}R_1salen)]^+$ precursors contain mac rocyclic planar Schiff base ligands at the equatorial plane of the central Mn(III) ions. The two *trans* axial sites are weakly occupied by water oxygen atoms which can be replaced by other strong coordination atoms such as cyanide nitrogen and carbons atoms, azide nitrogen atoms et al. Salen-like ligands herein are well known ligands for stabilizing the high-spin Mn(III) ion. The corresponding cyanide-containing reactants were selected bicyanidechromate(III) building blocks also with large planar pyridinecarboxamide ligand bpb^{2-} or $bpClb^{2-}$ at the equatorial plane. Two cyanide carbons coordinate to the two *trans* positions of the central Cr(III) ion. Taking into the above characteristics of $[Mn^{III}(5\text{-}R_1salen)]^+$ and $[Cr^{III}(4\text{-}R_2bpb)(CN)_2]^-$ building blocks together with the opposite equal charge nature, the reaction of the two building blocks can yield low-dimensional structural complexes, especially 1D complexes. Indeed, six new Cr^{III}–Mn^{III} 1D complexes were assembled based on the above building blocks. These complexes are expected and can be comparable to those of the reported cyanide-bridged 1D or wheel-like Fe^{III}–Mn^{III} complexes based on similar building blocks [25]. The results in this paper further indicate that the structures of cyanide-bridged complexes can be controlled and anticipated to some degree and the *trans*-dicyanidemetal building blocks facilitate the formation of 1D structure when reacting with metal units containing planar equatorial ligands.

It is noteworthy that the yields for the six complexes herein are moderate in order to prepared high-purity samples for magnetic study. The PXRD diagrams (Figs. S1 and S2) of complexes **1–6** are well agree with the calculated curves, indicating the samples are