Syntheses, crystal structures, and magnetic properties of a series of cyanide-bridged trinuclear chromate(III)−nickel(II)−chromate(III) complexes based on dicyanidechromate(III) building blocks

Hui Chen, Bao-Xi Miao, Li-Fang Zhang *, Guo-Ling Li, Zhong-Hai Ni *

School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou 221116, Jiangsu Province, PR China

ABSTRACT

Four cyanide-bridged trinuclear Cr^{III}–Ni^{II}–Cr^{III} complexes $[Ni(cyclam)][Cr(bpb)(CN)_2]_2 \cdot 2H_2O$ (**1**) (cyclam = 1,4,8,11-tetraazacyclotetradecane, bpb^{2-} = 1,2-bis(pyridine-2-carboxamido)-benzenate), $[Ni(cyclam)][Cr(bpClb)(CN)_2]_2 \cdot 4H_2O$ (**2**) ($bpClb^{2-}$ = 1,2-bis(pyridine-2-carboxamido)-4-chloro-benzenate), $[Ni(cyclam)][Cr(bpmb)(CN)_2]_2 \cdot 4H_2O$ (**3**) ($bpmb^{2-}$ = 1,2-bis(pyridine-2-carboxamido)-4-methyl-benzenate) and $[Ni(cyclam)][Cr(bpdmb)(CN)_2]_2$ (**4**) ($bpdmb^{2-}$ = 1,2-bis(pyridine-2-carboxamido)-4,5-dimethyl-benzenate) have been synthesized by the reaction of $[Ni(cyclam)](ClO_4)_2$ with a series of dicyanidechromate(III) building blocks. Single crystal X-ray diffraction analyses show that the four complexes have similar trinuclear structures with Cr^{III}–$C\equiv N$–Ni^{II}–$N\equiv C$–Cr^{III} linkages. Magnetic investigations indicate the ferromagnetic coupling between Cr(III) and Ni(II) centers through the cyanide bridge, with J_{CrNi} = 4.64(3) cm^{-1} for **1**, 4.33(4) cm^{-1} for **2**, 3.57(3) cm^{-1} for **3** and 5.3(1) cm^{-1} for **4**. The study on magneto-structural correlation for cyanide-bridged Cr^{III}–Ni^{II} systems reveals that the cyanide-bridging bond angle is related to the strength of magnetic exchange coupling: the larger the Ni–N≡C bond angle, the stronger the Ni· · ·Cr magnetic interaction.

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1. Introduction

In the past decades, there has been continuous interest in cyanide-bridged heterometallic complexes because of their fascinating structural features and excellent magnetic properties [1–9]. Up to now, many interesting cyanide-bridged magnetic complexes with various molecular topological structures, including molecular clusters, 1D chains and 2D or 3D networks, have been successfully prepared based on some suitable cyanide-containing building blocks and some other unsaturated precursors [10–20]. Among them, low-dimensional complexes especially binuclear and trinuclear complexes are the most suitable models for the elucidation of magneto-structural correlations [20a]. Compared with heterometallic Fe^{III}–M (M = Cu(II), Ni(II), Mn(II), Mn(III), et al.) complexes [21–27], heterometallic Cr^{III}–M complexes are still limited due to the shortage of stable and suitable cyanidechromate(III) building blocks [28–32].

As our continuous research work, we have been focusing on the exploitation of cyanide-containing metal building blocks based on pyridinecarboxamide ligands. In this work, we have synthesized four new cyanide-bridged trinuclear Cr^{III}–Ni^{II}–Cr^{III} complexes $[Ni(cyclam)][Cr(bpb)(CN)_2]_2 \cdot 2H_2O$ (**1**), $[Ni(cyclam)][Cr(bpClb)(CN)_2]_2 \cdot 4H_2O$ (**2**), $[Ni(cyclam)][Cr(bpmb)(CN)_2]_2 \cdot 4H_2O$ (**3**) and $[Ni(cyclam)][Cr(bpdmb)(CN)_2]_2$ (**4**) based on $[Ni(cyclam)]ClO_4$ and a series of dicyanidechromate(III) building blocks $K[Cr(L)(CN)_2]$ (L = bpb^{2-}, $bpClb^{2-}$, $bpmb^{2-}$ or $bpdmb^{2-}$) (Scheme 1). Herein, we present the syntheses, crystal structures and magnetic properties of the four complexes. Moreover, the nature of magnetic coupling and magneto-structural correlation of cyanide-bridged Cr^{III}–Ni^{II} complexes are also discussed in detail.

2. Experimental

Elemental analyses (C, H and N) were carried out on an Elementary Vario El instrument. The infrared spectra of solid samples on KBr pellets were recorded on a Nicolet 7199B FT/IR spectrophotometer in the region of 4000–400 cm^{-1}. Magnetic properties measurements on crystal samples were carried out on a Quantum Design MPMS SQUID magnetometer. The experimental susceptibilities were corrected for the diamagnetism estimated based on Pascal's tables.

2.1. General procedures and materials

All chemicals and solvents used during the synthesis were reagent grade. The precursors $[Ni(cyclam)](ClO_4)_2$ [33] and $K[Cr(L)(CN)_2]$ [34] were prepared according to literature methods.

[Ni(cyclam)]$^{2+}$
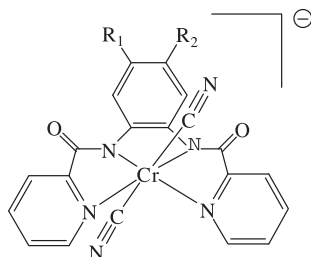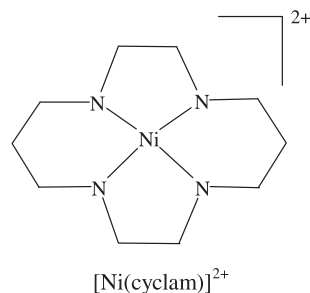
[Cr(L)(CN)$_2$]$^-$ [L = bpb (R$_1$ = R$_2$ = H), bpClb (R$_1$ = Cl, R$_2$ = H),

bpmb (R$_1$ = H, R$_2$ = CH$_3$) or bpdmb (R$_1$ = R$_2$ = CH$_3$)]

Scheme 1. The building blocks for complexes **1–4**.

Caution! Cyanides are very toxic and perchlorate salts of metal complexes with organic ligands are potentially explosive which should be handled with great caution.

2.2. Preparation of complexes **1–4**

All four target complexes were prepared using one similar procedure. Therefore, a representative method for preparing complex **1** is described herein. Dark red block single crystals of complex **1** was prepared at room temperature by carefully mixing a methanol/aqueous solution of [Ni(cyclam)](ClO$_4$)$_2$ (0.1 mmol, 44.5 mg)

and a red methanol solution (5 mL) of K[Cr(bpb)(CN)$_2$] (0.1 mmol, 42.0 mg), and the crystals were carefully collected after about 3 days.

2.2.1. Complex **1**
Yield: 0.044 g, 62%. *Anal.* Calc. for NiCr$_2$C$_{50}$H$_{52}$N$_{16}$O$_6$: C, 52.88; H, 4.61; N, 19.73. Found: C, 52.48; H, 4.69; N, 19.38%. Selected IR frequencies (KBr disk, cm^{-1}): 2156, v(C≡N); 2136, v(C≡N).

2.2.2. Complex **2**
Yield: 0.045 g, 58%. *Anal.* Calc. for NiCr$_2$C$_{50}$H$_{54}$N$_{16}$O$_8$Cl$_2$: C, 51.34; H, 4.65; N, 19.16. Found: C, 51.60; H, 4.91; N, 19.52%. Selected IR frequencies (KBr disk, cm^{-1}): 2158, v(C≡N); 2138, v(C≡N).

2.2.3. Complex **3**
Yield: 0.043 g, 59%. *Anal.* Calc. for NiCr$_2$C$_{52}$H$_{60}$N$_{16}$O$_8$: C, 52.05; H, 5.04; N, 18.68. Found: C, 52.15; H, 5.24; N, 18.73%. Selected IR frequencies (KBr disk, cm^{-1}): 2153, v(C≡N); 2134, v(C≡N).

2.2.4. Complex **4**
Yield: 0.055 g, 64%. *Anal.* Calc. for NiCr$_2$C$_{54}$H$_{56}$N$_{16}$O$_4$: C, 52.11; H, 4.88; N, 9.39. Found: C, 52.16; H, 4.80; N, 9.33%. Selected IR frequencies (KBr disk, cm^{-1}): 2154, v(C≡N), 2133, v(C≡N).

2.3. X-ray data collection and structure refinement

Single crystals of complexes **1–4** with suitable size for X-ray diffraction were obtained as described above. The structures were obtained by the direct methods (SHELXS-97) and refined by full-matrix least-squares methods (SHELXL-97) on F^2. Structural measurements were performed on a Bruker APEX II CCD using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) and the ω-scan techniques at room temperature. Anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms. Hydrogen atoms were added geometrically and refined using a riding model. Images were created by using DIAMOND program. The crystal and structure refinement parameters and the conditions for data collection are listed in Table 1.

Table 1
Crystal data and structure refinement parameters for complexes **1–4**.

	1	**2**	**3**	**4**
Chemical formula	NiCr$_2$C$_{50}$H$_{52}$N$_{16}$O$_6$	NiCr$_2$C$_{50}$H$_{54}$N$_{16}$O$_8$Cl$_2$	NiCr$_2$C$_{52}$H$_{60}$N$_{16}$O$_8$	NiCr$_2$C$_{54}$H$_{56}$N$_{16}$O$_4$
Formula weight	1135.79	1240.70	1199.87	1155.86
Temperature (K)	123(2)	123(2)	123(2)	123(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	14.443(3)	15.643(3)	15.716(3)	9.0535(18)
b (Å)	14.416(3)	13.601(3)	13.648(3)	14.211(3)
c (Å)	13.379(3)	12.889(3)	12.753(3)	20.331(4)
α (°)	90.00	90.00	90.00	90.00
β (°)	95.96(3)	92.78(3)	93.04(3)	90.37(3)
γ (°)	90.00	90.00	90.00	90.00
V (Å^3)	2770.6(10)	2740.1(10)	2731.6(10)	2615.8(9)
Z	2	2	2	2
ρ_{calc} (g cm^{-3})	1.361	1.511	1.459	1.467
Mo Kα (mm^{-1})	0.783	0.900	0.801	0.828
$F(000)$	1172	1280	1248	1200
θ (°)	2.83–25.10	3.00–25.10	2.99–25.00	3.01–26.55
Unique reflections	4802	4820	4774	5679
Reflections ($I > 2\sigma$)	4501	4614	4651	5303
GOF on F^2	1.071	1.213	0.979	0.948
R_1 [I > sigma(I)]	0.0383	0.0822	0.0686	0.0488
wR_2 (all data)	0.0816	0.2138	0.1715	0.1362
ρ_{max}/ρ_{min}(e Å^{-3})	0.501/−0.300	2.100/−1.046	1.169/−0.463	0.535/−0.521