

Notes

A New Two-dimensional Cyano-bridged Chromium(III)-Nickel(II) Bimetallic Assembly with Stair-like Layers

SHEN, Xiao-Ping^{*,a}(沈小平) YUAN, Ai-Hua^b(袁爱华) WU, Qiang-Jin^c(吴镛金)
HUANG, Zi-Xiang^c(黄子祥) XU, Zheng^d(徐正) YU, Yun-Peng^a(俞运鹏)

^a Department of Chemistry, Zhenjiang Teacher's College, Zhenjiang, Jiangsu 212003, China

^b Department of Material and Environmental Engineering, East China Shipbuilding Institute, Zhenjiang, Jiangsu 212003, China

^c State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

^d Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, Jiangsu 210093, China

From the reaction of $K_3[Cr(CN)_6]$ and $[NiL](ClO_4)_2$ ($L = 1,8$ -di(hydroxyethyl)-1,3,6,8,10,13-hexaazacyclotetradecane), an infinite stair-like layered assembly $[NiL]_3[Cr(CN)_6]_2 \cdot 6.5H_2O$ is obtained, in which each hexacyanochromate(III) ion connects three nickel(II) ions using three *cis* CN⁻ groups and the bridging cyanide ligands coordinate to the nickel ion in a *trans* fashion forming *trans*-NiL(N≡C)₂ moieties.

Keywords Hexacyanochromate(III) ion, nickel complex, cyano-bridged, crystal structure, two-dimensional assembly

Recently, there has been a growing interest in coordination polymers having a two- (2-D) or three-dimensional (3-D) structure because of the unique physico-chemical properties arising in the bulk of these systems.¹ In particular, much effort has been made for the design of highly ordered structures with paramagnetic metal centers in order to provide molecular-based magnets exhibiting spontaneous magnetization. It is known that Prussian blue analogues, derived from hexacyanometalate ions $[M(CN)_6]^{n-}$ and simple transition metal ions, exhibit magnetic order at considerably high temperatures and form a family of magnetic materials.² In order to clarify the magneto-structural correlation of cyano-bridged bimetallic systems, a wide variety of hybrid Prussian

blue complexes derived from $[M(CN)_6]^{n-}$ ($M = Fe, Cr, Mn$) and coordinatively unsaturated transition metal complexes have been studied structurally and magnetically.³ These complexes assume oligonuclear,^{3b-c} 1-D,^{3d-e} 2-D^{3f-h} and 3-D^{3i-j} structures and exhibit ferro- or metamagnetic behaviour. Their magnetic properties can be chemically tuned by not only varying the metal ions but also the ligands. Among them, the Fe(III)-Ni(II) bimetallic assemblies have been synthesized and characterised in much detail and invariably exhibit a ferromagnetic interaction between the adjacent iron(III) and nickel(II) ions through the CN⁻ bridges. However, due to the difficulty of crystallization, only a few Cr(III)-Ni(II) bimetallic assemblies have been investigated.⁴ We have recently succeeded in preparation of a new cyano-bridged Cr(III)-Ni(II) compound, $[NiL]_3[Cr(CN)_6]_2 \cdot 6.5H_2O$ (**1**) ($L = 1,8$ -di(hydroxyethyl)-1,3,6,8,10,13-hexaazacyclotetradecane), which shows an infinite 2-D layered structure with stair-like sheets.

Complex **1** was obtained as yellow single crystals by slow diffusion of a DMF solution of $[NiL](ClO_4)_2$ ⁵ and an aqueous solution of $K_3[Cr(CN)_6]$ ⁶ in an U-shaped tube. It is insoluble in most inorganic and organic solvents. The IR spectrum of **1** shows two sharp ν_{CN} peaks at 2158 and 2119 cm^{-1} . The shift of ν_{CN} to higher wave

* E-mail: YAH888@public.zj.js.cn

Received December 15, 2000; revised and accepted January 21, 2001.

number relative to that of $K_3[Cr(CN)_6]$ (2128 cm^{-1}) suggests a lowered symmetry about the $[Cr(CN)_6]^{3-}$ entity and the formation of CN^- bridges, as observed for other cyano-bridged systems.

The structure of **1** was determined by X-ray analysis⁷ and the results are shown in Figs. 1–3. Complex **1** exhibits a layered structure with the layers lying perpendicular to the *c*-axis. Within the layers, each $[Cr(CN)_6]^{3-}$ ion is surrounded by three $[NiL]^{2+}$ moieties through $Cr-C\equiv N-Ni$ linkages, whereas each $[NiL]^{2+}$ unit is linked to two hexacyanochromate(III) ions in *trans* positions (Fig. 1), leading to electrical

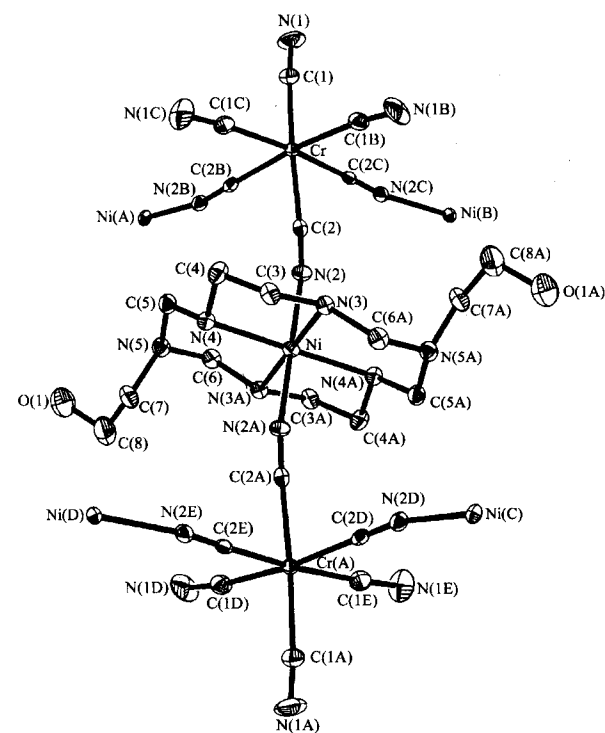


Fig. 1 An ORTEP drawing of complex **1** with the atom numbering scheme.

neutrality of the layer. The three NiL units adopt a facial configuration around the chromium ion, leaving three terminal cyano groups. The $Cr-Ni$ distance through the cyanide bridge is 0.5254 nm , close to that observed for Prussian blue analogues.⁸ The $Ni-N-C$ bond angle is $166.3(5)^\circ$, slightly deviating from linearity. The $Cr-C$ distance for the bridging CN^- ($0.2070(7)\text{ nm}$) is slightly shorter than that for non-bridging CN^- ($0.2080(7)\text{ nm}$), and the $C-N$ distance of the bridging CN^- ($0.1138(8)\text{ nm}$) is almost equal to that of non-bridging CN^- ($0.1135(9)\text{ nm}$). The bond angles of $Cr-C$

(1)— $N(1)$ and $Cr-C(2)-N(2)$ are $172.8(7)$ and $177.2(6)^\circ$, respectively, which do not deviate significantly from linearity. Four secondary amine nitrogen atoms of the macrocycle **L** coordinate to the nickel center with $Ni-N$ distances of $0.2055(5)$ and $0.2076(5)\text{ nm}$. The geometry around the nickel atoms is elongated octahedral; the $Ni-N(CN)$ distances (apical positions) are slightly longer ($0.2088(5)\text{ nm}$) than the equatorial ones. The particular local molecular arrangement leads to a honeycomb-like structure, as viewed along the *c*-axis (Fig. 2). The repeating hexagonal-like unit adopt a chair configuration. The layer can be described as an infinite stair with the chromium ions lying at the edges of the steps and the nickel ions within the steps (Fig. 3). The shortest interlayer $Cr\cdots Cr$, $Cr\cdots Ni$ and $Ni\cdots Ni$ separations are 0.9411 , 0.7821 and 0.9411 nm , respectively. All pendant groups CH_2CH_2OH of macrocycle **L** are positioned in the hexagonal-like units, which result in hydrophilic cavities. The water molecules are contained in the hydrophilic cavities and linked to OH groups of CH_2CH_2OH pendant groups *via* hydrogen bonding.

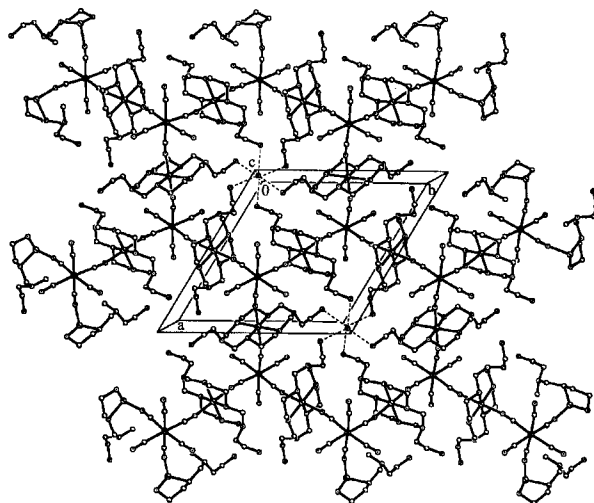


Fig. 2 Projection along the *c*-axis, showing the polymeric layer including Cr_6Ni_6 hexagons and hydrogen bonds (---).

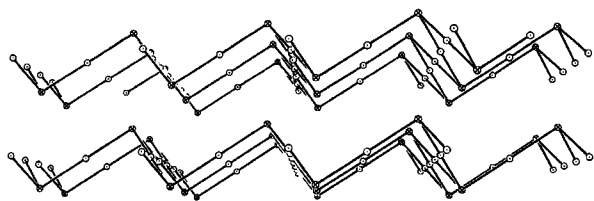


Fig. 3 View of two sheets showing the stair-like structure; only metal ions are shown for clarity: \oplus Cr, \ominus Ni.

The structure of complex **1** demonstrates the versatility of hexacyanometalates in building molecule-based assemblies of tunable dimensionality from discrete species to three-dimensional networks, *via* low-dimensional systems. At present, the study of its magnetic property and inclusion ability to other hydrophilic molecules (such as methanol, ethanol and acetone *etc.*) is underway.

References and notes

- 1 (a) Chen, C. T.; Suslick, K. S. *Coord. Chem. Rev.* **1993**, *128*, 293.
 (b) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1460.
 (c) Yuan, A. H.; Zou, J. Z.; Li, B. L.; Zha, Z. G.; Duan, C. Y.; Liu, Y. J.; Xu, Z.; Keizer, S. *Chem. Commun.* **2000**, 1297.
 (d) Gatteschi, D. *Adv. Mater.* **1994**, *6*, 635.
 (e) Gatteschi, D.; Kahn, O.; Miller, J. S.; Palacio, F. *Molecular Magnetic Materials*, Netherlands, **1992**, pp. 35–52.
 (f) Kou, H. Z.; Liao, D. Z.; Cheng, P.; Jiang, Z. H.; Wang, G. L. *Acta Chim. Sinica* **1999**, *57*, 409 (in Chinese).
- 2 (a) Mallah, S.; Thiebaut, S.; Verdager, M.; Veillet, P. *Science* **1993**, *262*, 1554.
 (b) Ently, W. R.; Girolani, G. S. *Science* **1995**, *268*, 397.
 (c) Kahn, O. *Nature* **1995**, *378*, 667.
 (d) Verdager, M. *Science* **1996**, *272*, 698.
- 3 (a) Ohba, M.; Okawa, H. *Coord. Chem. Rev.* **2000**, *198*, 313.
 (b) Miyasaka, H.; Ieda, H.; Matsumoto, N.; Re, N.; Crescenzi, R.; Floriani, C. *Inorg. Chem.* **1998**, *37*, 255.
 (c) Scuiller, A.; Mallah, T.; Verdager, M.; Niv-rozkhin, A.; Tholence, J.; Veillet, P. *New J. Chem.* **1996**, *20*, 1.
 (d) Ohba, M.; Maruono, N.; Okawa, H.; Enoki, T.; Latour, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 11566.
 (e) Kou, H. Z.; Wang, H. M.; Liao, D. Z.; Cheng, P.; Jiang, Z. H.; Yan, S. P.; Huang, X. Y.; Wang, G. L. *Aust. J. Chem.* **1998**, *51*, 661.
 (f) Kou, H. Z.; Bu, W. M.; Liao, D. Z.; Jiang, Z. H.; Yan, S. P.; Fan, Y. G.; Wang, G. L. *J. Chem. Soc., Dalton Trans.* **1998**, 4161.
 (g) Miyasaka, H.; Matsumoto, N.; Okawa, H.; Re, N.; Gallo, E.; Floriani, C. *J. Am. Chem. Soc.* **1996**, *118*, 981.
 (h) Ohba, M.; Okawa, H.; Ito, T.; Ohto, A. *Chem. Commun.* **1995**, 1545.
 (i) El Fallah, S. M.; Rentschler, E.; Caneschi, A.; Sessoli, R.; Gatteschi, D. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1947.
 (j) Fukita, N.; Ohba, M.; Okawa, H.; Matsuda, K.; Iwamura, H. *Inorg. Chem.* **1998**, *37*, 842.
- 4 Ohba, M.; Usuki, N.; Fukita, N.; Okawa, H. *Inorg. Chem.* **1998**, *37*, 3349.
- 5 Suh, M. P.; Kang, S. G. *Inorg. Chem.* **1988**, *27*, 2544.
- 6 Schaap, W. B.; Krishnamurthy, R.; Wakefield, D. K.; Coleman, W. F. In *Coordination Chemistry*, Ed.: Kirschner, S., Plenum Press, New York, **1969**, p. 177.
- 7 Crystal data for **1**: $C_{48}H_{103}Cr_2N_{30}Ni_3O_{12.50}$, $M_r = 1580.73$, trigonal, space group P-3c1, $a = b = 1.5109(2)$, $c = 1.8821(4)$ nm, $V = 3.7212(10)$ nm³, $Z = 2$, $D_c = 1.411$ Mg/m³, $F(000) = 1666$, Enraf-Nonius CAD4 diffractometer, $\mu(Mo-K\alpha) = 1.101$ mm⁻¹, $\lambda = 0.071073$ nm, ω - 2θ scan, $T = 293(2)$ K, crystal size $1.2 \times 1.1 \times 1.0$ mm; 7171 reflections measured ($2.67 \leq \theta \leq 25.97^\circ$) and 2414 considered unique. The structure was solved by direct methods (SHELXTL-94) and refined on F^2 by full-matrix least squares methods to $R_1 = 0.0620$ and $wR_2 = 0.1396$ for 149 variable parameters.
- 8 Ludi, A.; Gudel, H. U. *Struct. Bonding (Berlin)* **1973**, *14*, 1.