DALTON
FULL PAPER

Organic–inorganic hybrid materials assembled through weak intermolecular interactions. Synthesis, structures and non-linear optical properties of [4,4′-bipyH$_2$][M(NCS)$_4$] (M = Mn^{2+}, Co^{2+} or Zn^{2+}; 4,4′-bipy = 4,4′-bipyridine)

Hong-Ji Chen,[a] Ling-Zhi Zhang,[a] Zhi-Gang Cai,[b] Guang Yang[a] and Xiao-Ming Chen *[a]

[a] *School of Chemistry and Chemical Engineering, Zhongshan University, Guangzhou 510275, China. E-mail: cescxm@zsu.edu.cn*
[b] *Institute of Laser & Spectroscopy, Zhongshan University, Guangzhou 510275, China*

Received 17th February 2000, Accepted 17th May 2000
Published on the Web 19th June 2000

Three compounds [4,4′-bipyH$_2$][M(NCS)$_4$] (M = Mn^{2+}, Co^{2+} or Zn^{2+}; 4,4′-bipy = 4,4′-bipyridine) were obtained from the reactions of 4,4′-bipy with M(SCN)$_2$ in acidic solution and their crystal structures determined by single-crystal X-ray diffraction. All crystallise isomorphously in the chiral orthorhombic space group $P2_12_12$. The tetrahedral [M(NCS)$_4$]$^{2-}$ anions are inter-connected by S · · · S contacts (*ca.* 3.63 Å) and are hydrogen bonded with the diprotonated [4,4′-bipyH$_2$]$^{2+}$ cations [N · · · S 3.241 Å in **1**; 3.235 Å in **2**; 3.239 Å in **3**] to form two-dimensional, highly wavy networks with hourglass-shaped cavities (*ca.* 12.3 Å long; 9.4 Å wide at the ends, 6.8 Å at the waist). These two-dimensional networks are stacked with each other to furnish a channel accommodating the diprotonated [4,4′-bipyH$_2$]$^{2+}$ cations. The three organic–inorganic hybrid compounds are thermally stable with melting points above 230 °C. The powder second harmonic generation efficiencies were measured as moderate.

Introduction

Supramolecular chemistry and crystal engineering of co-ordination compounds is of current interest. One aspect is the fascinating structural diversity and potential applications as functional materials in selective separation and catalysis.[1,2] So far a wide range of infinite one-, two- and three-dimensional co-ordination frameworks have been found, including helicates,[3] diamondoid,[4,2b] honeycomb,[4a,5] square or rectangular grid,[6] T-shaped,[2c,7] ladder,[8] brick wall,[6a,8a] octahedral[9] and other uncommon frameworks.[1d,10] Another aspect is non-centro-symmetrical organisation of molecular building blocks of co-ordination compounds to yield bulk materials exhibiting second-order non-linear optical (NLO) properties since organic compounds may have good NLO properties and inorganic compounds may have good rigidity and stability.[11,12] Unfortunately, most of the above-mentioned co-ordination polymers are centric. Metal tetrathiocyanates, being in tetrahedral geometry, are potential candidates as acentric centres in crystal engineering. When appropriate counter cations are employed to align the orientation of these tetrahedral cations in a non-centrosymmetrical fashion chiral and acentric solid materials may be generated. The non-centrosymmetrical crystal structure[13] of [4,4′-bipyH$_2$][NO$_3$]$_2$ encouraged us to prepare acentric crystals of metal tetrathiocyanates with protonated 4,4′-bipyridine as counter cations. We isolated three complexes crystallised in the chiral space group $P2_12_12$ and present herewith the synthesis, crystal structures and NLO properties of [4,4′-bipyH$_2$][M(NCS)$_4$] (M = Mn^{2+} **1**, Co^{2+} **2** or Zn^{2+} **3**), which are chiral organic–inorganic hybrid networks constructed by weak S · · · S contacts and hydrogen bonds.

Experimental

All the reagents were commercially available and used as received. The C, H, N microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer. IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Nicolet Impact 420 FT-IR spectrometer.

Syntheses

[4,4′-bipyH$_2$][Mn(NCS)$_4$] 1. A hot aqueous solution (15 cm^3) of Mn(NO$_3$)$_2$ (1.06 mmol) and NH$_4$SCN (0.295 g, 4.0 mmol) was added slowly to a hot ethanol solution (20 cm^3) of 4,4′-bipy (0.156 g, 1.0 mmol). After vigorous stirring the solution was adjusted to pH 3.5 by addition of dilute HNO$_3$ solution, and the solution then allowed to evaporate at room temperature. Greenish yellow crystals of complex **1** suitable for X-ray diffraction were deposited in a week (86% yield) (Calc. for C$_{14}$H$_{10}$MnN$_6$S$_4$: C, 37.75; H, 2.26; N, 18.87. Found: C, 37.48; H, 2.32; N, 19.02%). IR data (cm^{-1}): 3210m, 3127m, 3047m, 2984m, 2882m, 2825m, 2077vs, 1628s, 1601s, 1486s, 1344m, 1234w, 1195w, 1063w, 987m, 767s, 723m and 470m. mp = 234 °C (decomp.).

[4,4′-bipyH$_2$][Co(NCS)$_4$] 2. A hot aqueous solution (10 cm^3) of Co(NO$_3$)$_2$·6H$_2$O (0.29 g, 1.0 mmol) and NH$_4$SCN (0.295 g, 4.0 mmol) was slowly added to a hot ethanol solution (50 cm^3) of 4,4′-bipyridinediium dinitrate[13] (0.28 g, 1.0 mmol). The resulting solution (pH 3.5) was allowed to stand at room temperature for 2 days to yield blue crystals of complex **2** (93% yield) (Calc. for C$_{14}$H$_{10}$CoN$_6$S$_4$: C, 37.41; H, 2.24; N, 18.70. Found: C, 37.45; H, 2.03; N, 18.90%). IR data (cm^{-1}): 3212m, 3128m, 3050m, 2987m, 2882m, 2832m, 2094vs, 1630s, 1602s, 1482s, 1342m, 1236w, 1201w, 1060w, 983m, 765vs, 723s and 470m. mp = 260 °C (decomp.).

[4,4′-bipyH$_2$][Zn(NCS)$_4$] 3. This complex was prepared as for **2** using Zn(NO$_3$)$_2$·6H$_2$O (0.30 g, 1.02 mmol) instead of Co(NO$_3$)$_2$·6H$_2$O. Colourless crystals of **3** were deposited in 2 days (88% yield) (Calc. for C$_{14}$H$_{10}$N$_6$S$_4$Zn: C, 36.88; H, 2.21; N, 18.43. Found: C, 37.02; H, 2.18; N, 18.39%). IR data (cm^{-1}): 3212m, 3128m, 3043m, 2980m, 2924m, 2832m, 2101vs, 1630s,

DOI: 10.1039/b001323o

Table 1 Crystallographic data for complexes **1**, **2** and **3**

	1	**2**	**3**
Empirical formula	$C_{14}H_{10}MnN_6S_4$	$C_{14}H_{10}CoN_6S_4$	$C_{14}H_{10}N_6S_4Zn$
M	445.46	449.45	455.89
a/Å	12.755(4)	12.858(4)	12.895(7)
b/Å	13.169(4)	13.019(2)	13.088(4)
c/Å	5.5100(10)	5.452(2)	5.458(2)
V/Å^3	925.5(4)	912.7(5)	915.5(7)
μ(Mo-Kα)/mm^{-1}	1.174	1.408	1.807
Data/parameters	1047, 115	1287, 115	1320, 116
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0387, 0.1011	0.0291, 0.0769	0.0514, 0.1378
all data	0.0458, 0.1093	0.0327, 0.0787	0.0629, 0.1425

Details in common: orthorhombic, space group $P2_12_12$, $Z = 2$.

Table 2 Selected bond lengths (Å) and bond angles (°) for complexes **1**, **2** and **3**

	1	**2**	**3**
M–N(1)	2.061(5)	1.956(3)	1.953(8)
M–N(2)	2.075(5)	1.975(3)	1.965(7)
N(1a)–M–N(1)	113.0(3)	109.4(2)	110.7(5)
N(1a)–M–N(2)	107.8(2)	109.99(13)	109.0(3)
N(1)–M–N(2)	113.0(2)	111.36(13)	111.1(3)
N(2)–M–N(2a)	101.9(3)	104.6(2)	105.9(5)
C(1)–N(1)–M	170.3(4)	172.7(3)	171.0(7)
C(2)–N(2)–M	161.3(5)	164.5(3)	163.4(8)

Symmetry code: a) $-x + 1, -y + 2, z$.

1602s, 1482s, 1236w, 1201w, 1060w, 990m, 765vs, 723s and 470m. mp = 235 °C (decomp.).

Crystallography

Crystallographic data for the three complexes are summarised in Table 1. The data collections were carried out on a Siemens R3m diffractometer using graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation at 293(2) K; the crystal class, orientation matrix, and cell dimensions were determined according to established procedures. The intensity data were collected using the ω-scan mode. Absorption corrections were applied by fitting a pseudoellipsoid to the ψ-scan data of selected strong reflections over a range of 2θ angles.[14]

The structure solutions and full-matrix least-squares refinements based on F^2 were performed with the SHELXS 97 and SHELXL 97 program packages, respectively.[15,16] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the organic ligands were generated geometrically (C–H 0.96 Å) and all the hydrogen atoms were assigned isotropic thermal parameters and included in the structure-factor calculations. Analytical expressions of neutral-atom scattering factors were employed. Anomalous dispersion corrections were incorporated.[17] The absolute structures have been determined by Flack parameters of 0.00(6), 0.03(3) and 0.05(5) for complexes **1**, **2** and **3**, respectively.[18] The drawings were produced with SHELXTL.[19]

CCDC reference number 186/1990.

See http://www.rsc.org/suppdata/dt/b0/b001323o/ for crystallographic files in .cif format.

Non-linear optical property measurement

According to the principles proposed by Kurtz and Perry the strength of the second harmonic generation (SHG) efficiency of the compounds was estimated by measuring the powder (76–154 μm diameter) in the form of pellets (0.8 mm thickness).[20] The pressure used in compacting the pellet was 300 MPa. The experimental arrangement included high-power mode-locked Nd : YAG laser with 200 ps pulse at a repetition rate of 5 Hz at a selected wavelength of 1064 nm. The laser beam is split into two parts, one to generate the second harmonic signal in the sample and the other to generate the second harmonic signal in the reference (urea pellet). The SHG effects of 4,4′-bipyridinediium dinitrate, **1** and **3** have been estimated to be 0.92×10^{-3}, 1.5×10^{-3} and 0.21 times that of urea based upon the experimental data, respectively.

Results and discussion

Structures of $\{(4,4'\text{-bipyH}_2)[M(NCS)_4]\}_n$ (M = Mn^{2+} 1, Co^{2+} 2 or Zn^{2+} 3)

Selected bond distances and bond angles for complexes **1**, **2** and **3** are listed in Table 2.

X-Ray analysis revealed that the three complexes **1**, **2** and **3** are isomorphous, crystallising in the chiral space group $P2_12_12$ (see Table 1). As expected, the metal atom (Mn^{2+}, Co^{2+} or Zn^{2+}) is tetrahedrally co-ordinated by four nitrogen atoms from four monodentate thiocyanate groups; the longest average M–N bond length is 2.068 Å for complex **1**, being slightly longer than those of 1.966 and 1.959 Å for **2** and **3**, respectively, which can be attributed to the larger ionic radius of Mn^{II}. The N–M–N bond angles are in the ranges of 101.9(3)–113.0(3), 104.6(2)–111.36(13)°, and 105.9(5)–111.1(3)°, respectively, showing moderate distortions of the MN_4 tetrahedra. All the thiocyanate groups bind the metal atoms in a virtually linear fashion, with the C–N–M bond angles in the range of 161.3(5)–172.7(3)°.

The most important feature in the three complexes is the role of the sulfur atoms. In the solid, each sulfur atom of the $[M(NCS)_4]^{2-}$ anion has a weak S · · · S contact with a sulfur atom from an adjacent $[M(NCS)_4]^{2-}$ anion. The distances of these contacts, being 3.64, 3.63 and 3.63 Å for complexes **1**, **2** and **3**, respectively, are slightly shorter than the sum of the van der Waals radii of two sulfur atoms, indicating weak interaction.[21] The sulfur atoms also form acceptor hydrogen bonds with the diprotonated $[4,4'\text{-bipyH}_2]^{2+}$ cations [N · · · S 3.241 Å in **1**; 3.235 Å in **2**; 3.239 Å in **3**].[22] With these S · · · S contacts and hydrogen bonds, the $[M(NCS)_4]^{2-}$ anions are arranged into two-dimensional, highly wavy networks concentrated about the (001) planes with hourglass-shaped cavities (*ca.* 12.3 Å long; 9.4 Å wide at the ends, 6.8 Å at the waist), as shown in Fig. 1; these two-dimensional networks are stacked with each other to furnish a channel structure in the solid. The diprotonated $[4,4'\text{-bipyH}_2]^{2+}$ cations are accommodated in the channels, as illustrated in Fig. 2. Such an arrangement constructs a unitary graph set $C^2_2(19)$,[23,24] and a big ring [graph set = $R^2_2(25)$] with two S · · · S contacts.

Examination of the detailed structural data reveals that there is only weak π–π stacking interaction between the aromatic rings of adjacent $[4,4'\text{-bipyH}_2]^{2+}$ cations since the adjacent $[4,4'\text{-bipyH}_2]^{2+}$ cations from adjacent layers are arranged in a highly offset fashion with face-to-face distances of *ca.* 3.1 Å.

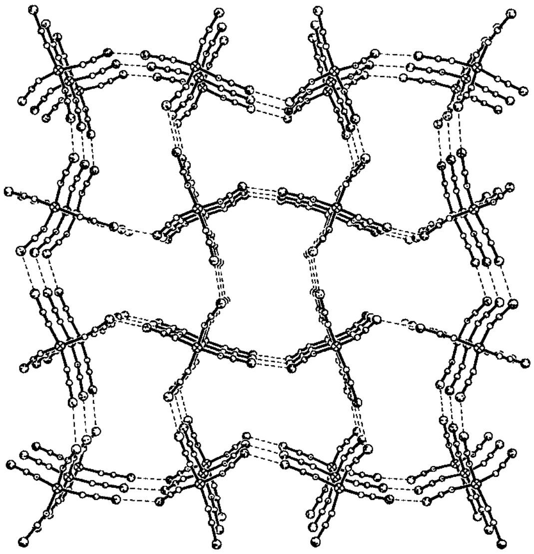

Fig. 1 Two-dimensional networks formed by $[M(NCS)_4]^{2-}$ anions through weak S · · · S contacts (viewed along the *c* axis).

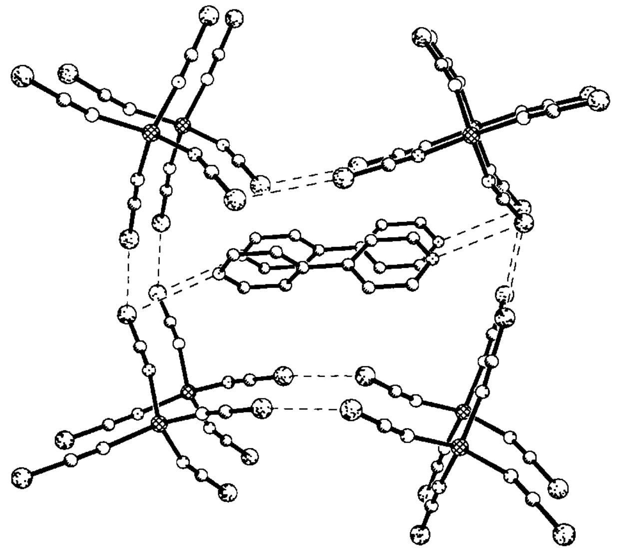

Fig. 2 Encapsulation of the $[4,4'\text{-bipyH}_2]^{2+}$ cations in the two-dimensional networks viewed along the *c* axis.

On the other hand, weak van der Waals interaction between the pyridyl rings and the thiocyanate groups are found, with shortest contacts of *ca.* 3.7 Å between the thiocyanate sulfur atom and the pyridyl carbon atoms. These S · · · C contacts may cause a highly twisted geometry of the pair of pyridyl rings in the cation with the dihedral angles of the two pyridyl rings being *ca.* 63, 67 and 68° for complexes **1**, **2** and **3**, respectively, and which are rarely observed[25] and are unfavourable for π–π stacking interaction. Since all the intermolecular interactions, including the S · · · S contact, hydrogen bonding and so on, are relatively weak, the crystal packing of the three complexes may be attributed to the combined effect of these weak interactions.

Discussion

When we performed an analogous reaction to the synthesis of complex **1** using $Ni(NO_3)_2$ instead of $Mn(NO_3)_2$ we isolated an interesting centrosymmetrical hydrogen-bonded two-dimensional network with octahedral $[Ni(NCS)_4(H_2O)_2]^{2-}$ anions, nitrate anions and $[4,4'\text{-bipyH}_2]^{2+}$ cations. We have also found that it is not possible to use other diamines, such as 4,4′-diaminobiphenyl, in generating complexes analogous to the present compounds. Therefore, this work demonstrates not only that tetrahedral transition-metal centres are able to generate two-dimensional networks, which are usually made of square-planar or octahedral transition metal centres,[6] but also that tetrahedral co-ordination centres are important in the formation of acentric and chiral crystals of metal complexes, since crystal structures of multi-dimensional co-ordination networks with square-planar or octahedral transition metal centres are commonly centric.[6] This work implies that the anions are also important in the formation of the acentric networks.

It is noteworthy that pH of the reaction system of 4,4′-bipy with metal thiocyanates is critical. When reaction mixtures of $Mn(NO_3)_2$ and NH_4SCN with 4,4′-bipy, $Co(SCN)_2$ with 4,4′-bipyridinediium dinitrate, and $Zn(SCN)_2$ with 4,4′-bipyridinediium dinitrate were adjusted in the pH ranges of 3.0–4.5, 2.5–5.0, and 3.5–4.5, respectively, complexes **1**, **2** and **3** were obtained. In contrast, the staircase polymer $[Mn(NCS)_2(H_2O)_2(4,4'\text{-bipy})]\cdot 4,4'\text{-bipy}$ was prepared by a reaction of $Mn(NO_3)_2$ and NH_4SCN with 4,4′-bipy in an ethanol solution at pH 4.5–6.5.[8e]

The results show that complex **3** has a higher SHG effect (0.21 times that of urea) than those of 4,4′-bipyridinum dinitrate and **1** (0.92×10^{-3}, 1.5×10^{-3} times that of urea, respectively). Complexes **1** and **3** are isomorphous, belonging to the chiral $P2_12_12$ space group. Therefore, the significantly different SHG effects of complexes **1** and **3** may be attributed the effect of the metal atoms in the tetrahedral $[M(NCS)_4]^{2-}$ anions. The smaller SHG effect of complex **1** may possibly be attributed to the fact that Mn^{II}, though a harder acid, may easily be oxidised to Mn^{III} and thus is less effective in polarising the π system in the thiocyanate group. Stable Zn^{II} can be more effective in the polarising the π system and hence gives a larger SHG effect. Finally, the melting points (mp > 230 °C) of these organic–inorganic hybrid materials indicate that they are thermally stable.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 29625102, 29971033) and the Higher Education Bureau of Guangdong Province. We thank the Chemistry Department of The Chinese University of Hong Kong for donation of the diffractometer.

References

1 (*a*) B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1990, **112**, 1564; (*b*) A. Stein, S. W. Keller and T. E. Mallouk, *Science*, 1993, **259**, 1558; (*c*) M. Fujita, Y. J. Kwon, S. Washizu and K. Ogurs, *J. Am. Chem. Soc.*, 1994, **116**, 1151; (*d*) S. R. Batten and R. Robson, *Angew. Chem.*, *Int. Ed.*, 1998, **37**, 1460.

2 (*a*) O. M. Yaghi and G. Li, *Angew. Chem.*, *Int. Ed. Engl.*, 1995, **34**, 207; (*b*) O. M. Yaghi and J. Li, *J. Am. Chem. Soc.*, 1995, **117**, 10401; (*c*) O. M. Yaghi and H. Li, *J. Am. Chem. Soc.*, 1996, **118**, 295; (*d*) O. M. Yaghi, H. Li, C. Davis, D. Richardson and T. L. Groy, *Acc. Chem. Res.*, 1998, **31**, 474.

3 K. Biradha, C. Seward and M. J. Zaworotko, *Angew. Chem.*, *Int. Ed.*, 1999, **38**, 492; M.-L. Tong, X.-M. Chen, B.-H. Ye and S. W. Ng, *Inorg. Chem.*, 1998, **37**, 5278.

4 (*a*) M. Hayashi, Y. Miyamoto, T. Inoue and N. Oguni, *J. Chem. Soc.*, *Chem. Commun.*, 1992, 1752; (*b*) L. R. MacGillivray, S. Subramanian and M. J. Zaworotko, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 1325; (*c*) L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 2755.

5 G. B. Gardner, D. Venkataraman, J. S. Moore and S. Lee, *Nature* (*London*), 1995, **374**, 792.

6 For examples, (*a*) J. Li, H. Zeng, J. Chen, Q. Wang and X. Wu, *Chem. Commun.*, 1997, 1213; (*b*) L. R. MacGillivray, R. H. Groeneman and J. L. Atwood, *J. Am. Chem. Soc.*, 1998, **120**, 2676; (*c*) L.-M. Zheng, X. Feng, K. H. Lii, H.-H. Song, X.-Q. Xin, H.-K. Fun, K. Chinnakali and I. A. Razak, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 2311; (*d*) D. Hagrman, R. P. Hammond, R. Haushalter and J. Zubieta, *Chem. Mater.*, 1998, **10**, 2091; (*e*) Z. Wang, R.-G. Xiong, B. M. Foxman, S. R. Wilson and W. Lin, *Inorg. Chem.*, 1999, **38**,

1523; (*f*) C. V. K. Sharma and R. D. Rogers, *Chem. Commun.*, 1999, 83; (*g*) M.-L. Tong, X.-M. Chen, X.-L. Yu and T. C. W. Mak, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 5; M.-L. Tong, B.-H. Ye, J.-W. Cai, X.-M. Chen and and S. W. Ng, *Inorg. Chem.*, 1998, **37**, 2645.

7 F. Robinson and M. J. Zaworotko, *J. Chem. Soc.*, *Chem. Commun.*, 1995, 2413; H. Gudbjartson, K. Biradha, K. M. Poirier and M. J. Zaworotko, *J. Am. Chem. Soc.*, 1999, **121**, 2599.

8 For examples, (*a*) T. L. Hennigar, D. C. MacQuarrie, P. Losier, R. D. Rogers and M. J. Zaworotko, *Angew. Chem.*, *Int. Ed. Engl.*, 1997, **36**, 972; (*b*) A. J. Blake, N. R. Champness, A. Khlobystov, D. A. Lemenovkii, W.-S. Li and M. Schröder, *Chem. Commun.*, 1997, 2027; (*c*) O.-S. Jung, S. H. Park, K. M. Kim and H. G. Jang, *Inorg. Chem.*, 1998, **37**, 5781; (*d*) J. Lu, C. Yu, T. Niu, T. Paliwala, G. Crisci, F. Somosa and A. J. Jacobson, *Inorg. Chem.*, 1998, **37**, 4637; (*e*) L. Carlucci, G. Ciani and D. M. Proserpio, *Chem. Commun.*, 1999, 449; (*f*) M.-X. Li, G.-Y. Xie and Y. D. Gu, *Polyhedron*, 1995, **14**, 1235.

9 T. Soma, H. Yuge and T. Iwamoto, *Angew. Chem.*, *Int. Ed. Engl.*, 1994, **33**, 1665; S. Subramanian and M. J. Zaworotko, *Angew. Chem.*, *Int. Ed. Engl.*, 1995, **34**, 2127.

10 M. Kondo, T. Yoshitomi, K. Seki, H. Matsuzaka and S. Kitagawa, *Angew. Chem.*, *Int. Ed. Engl.*, 1997, **36**, 1725; C. J. Kepert and M. J. Rosseinsky, *Chem. Commun.*, 1999, 375; M.-L. Tong, S.-L. Zheng and X.-M. Chen, *Chem. Commun.*, 1999, 561; M.-L. Tong, X.-M. Chen, B.-H. Ye and L. N. Ji, *Angew. Chem.*, *Int. Ed.*, 1999, **38**, 2237; M.-L. Tong, H.-K. Lee, X.-M. Chen, R.-B. Huang and T. C. W. Mak, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 3657.

11 J.-G. Qin, D.-Y. Liu, C.-Y. Dai, C.-T. Chen, B.-C. Wu, C.-L. Yang and C.-M. Zhan, *Coord. Chem. Rev.*, 1999, **188**, 23.

12 W.-B. Lin, O. R. Evans, R.-G. Xiong and Z.-Y. Wang, *J. Am. Chem. Soc.*, 1998, **120**, 13272.

13 D. J. Barker, J. S. Buckleton, G. R. Clark, R. P. Cooney and C. E. F. Rickard, *J. Mol. Struct.*, 1990, **239**, 249.

14 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr.*, *Sect. A*, 1968, **24**, 351.

15 G. M. Sheldrick, SHELXS 97, Program for Crystal Structure Determination, Göttingen University, 1997.

16 G. M. Sheldrick, SHELXL 97, Program for Crystal Structure Refinement, Göttingen University, 1997.

17 *International Tables for Crystallography*, Kluwer, Dordrecht, 1992, vol. C, Tables 4.2.6.8 and 6.1.1.4.

18 H. D. Flack, *Acta Crystallogr.*, *Sect. A*, 1983, **39**, 876.

19 G. M. Sheldrick, SHELXTL, Version V, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1998.

20 S. K. Kurtz and T. T. Perry, *J. Appl. Phys.*, 1968, **39**, 3798.

21 M. Munakata, T. Kuroda-Sowa, M. Maekawa, A. Hirota and S. Kitagawa, *Inorg. Chem.*, 1995, **34**, 2705; J. Die, M. Munakata, T. Kuroda-Sowa, Y. Suenaga and L.-P. Wu, *Inorg. Chim. Acta*, 1997, **255**, 163.

22 Q.-M. Wang, X.-T. Wu, W.-J. Zhang, T.-L. Shang, P. Lin and J.-M. Li, *Inorg. Chem.*, 1999, **38**, 2223.

23 J. Bernstein, R. E. Davis, L. Shimoni and N.-L. Chang, *Angew. Chem.*, *Int. Ed. Engl.*, 1995, **34**, 1555.

24 G. R. Desiraju, *Angew. Chem.*, *Int. Ed. Engl.*, 1995, **34**, 2311.

25 M. Ayhan, Z. Xiao, M. J. Lavery, A. M. Hamer, K. W. Nugent, S. D. B. Scrofani, M. Guss and A. G. Wedd, *Inorg. Chem.*, 1996, **35**, 5902; P. M. Boorman, X.-L. Gao and M. Parvez, *J. Chem. Soc.*, *Chem. Commun.*, 1992, 1656.