PERGAMON

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polyhedron 22 (2003) 789–794

POLYHEDRON

www.elsevier.com/locate/poly

Supramolecular solid-state architectures constructed from 4,4′-bipyridine-N,N′-dioxide and dicyanamido tectons. Synthesis and crystal structures of $[M(bpno)_2\{N(CN)_2\}_2(H_2O)_2]$ (M = Co, Mn) and $[Cu(bpno)\{N(CN)_2\}_2(H_2O)]$

Aneta Nedelcu[a], Zdirad Žak[b], Augustin M. Madalan[a], Jiri Pinkas[b], Marius Andruh[a,*]

[a] Inorganic Chemistry Laboratory, Faculty of Chemistry, University of Bucharest, Str. Dumbrava Rosie nr. 23, 70254 Bucharest, Romania
[b] Department of Chemistry, Faculty of Sciences, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic

Received 28 June 2002; accepted 30 August 2002

Abstract

The reaction between transition metal salts, $M(ClO_4)_2 \cdot 6H_2O$ (M = Co, Mn, Cu), sodium dicyanamide, $NaN(CN)_2$, and 4,4′-bipyridine-N,N′-dioxide, bpno, leads to three new complexes: $[Co(bpno)_2\{N(CN)_2\}_2(H_2O)_2]$ **1**, $[Mn(bpno)_2\{N(CN)_2\}_2(H_2O)_2]$ **2**, and $[Cu(bpno)\{N(CN)_2\}_2(H_2O)]$ **3**. In the three compounds, the $N(CN)_2^-$ ions act as monodentate ligands through one of the CN groups. Compounds **1** and **2** are isomorphous. Both bpno molecules are terminal ligands. The metal ions, cobalt(II) and manganese(II), display an octahedral stereochemistry and are located on an inversion center. In compound **3,** the bpno molecules act as bridging ligands and support the formation of infinite chains. The copper(II) ions are pentacoordinated. The packing diagrams of the three compounds reveal interesting supramolecular solid-state architectures. Compounds **1** and **2** are two-dimensional hydrogen bonded polymers, which are formed by the interaction of the bpno and dicyanamido ligands with the aqua ligands of neighboring $[M(bpno)_2\{N(CN)_2\}_2(H_2O)_2]$ units. The crystal structure of **3** consists of infinite chains of copper(II) ions connected through the bpno bridges. The distance between the copper atoms within the chain is 12.00 Å. The copper(II) ions exhibit a distorted square-pyramidal stereochemistry. The apical position is occupied by a water molecule. Hydrogen bond interactions between the aqua ligands and the terminal dicyanamido ligands lead to a complex 2-D structure.

Keywords: Cobalt complexes; Manganese complexes; Copper complexes; 4,4′-Bipyridine-N,N′-dioxide; Extended structures

1. Introduction

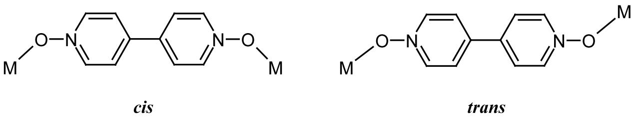
In contrast to 4,4′-bipyiridine [1], the potentialities of 4,4′-bipyridine-N,N′-dioxide (bpno) in crystal engineering and in the construction of coordination networks have been only little exploited. The systematic investigation of its role in designing extended structures has started very recently [2–4]. 4,4′-Bipyridine-N,N′-dioxide, like the related 4,4′-bipy molecule, is a rigid spacer and it can act as bridging and/or terminal ligand. Its aromatic rings can be also involved in π–π stacking interactions. On the other hand, bpno has several peculiarities: (i) it can form bridges with different geometries (*cis* and *trans* coordination modes)—Scheme 1; (ii) it is a better hydrogen acceptor than 4,4′-bipy; (iii) because of the orientation of the lone pairs at the oxygen atoms, it presents a rich variety of connectivity modes through hydrogen bond interactions (Scheme 2). The convolution of coordinative, hydrogen bond, and stacking interactions leads to interesting solid-state architectures [5–7]. Moreover, the presence of the oxygen atoms makes bpno a very good ligand for the strongly oxophilic lanthanide cations [8–10].

Another interesting ligand exhibiting various coordination modes is the dicyanamido ion, $N(CN)_2^-$. The interest in the chemistry generated by this ligand is mainly justified by the search for new magnetic materials [11]. The versatility of the dicyanamido ligand also

---

* Corresponding author. Tel.: +40-744-870656; fax: +40-21-3159249.
E-mail address: marius.andruh@dnt.ro (M. Andruh).

0277-5387/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0277-5387(02)01411-0



Scheme 1.

prompted the chemists to use it as a tecton in the crystal engineering of coordination polymers [12]. Interesting extended structures have been obtained by combining the bridging ability of the $N(CN)_2^-$ ligand with other bridging ligands, for example pyrazine [11d], bipyrimidine [12d], 4,4′-Bipyridine [13], 1,2-bis(4-pyridyl)ethylene [12a,14].

In this paper we report on new frameworks constructed from 4,4′-bipyridine-N,N′-dioxide and the dicyanamido tectons, focusing on the role of the hydrogen bond interactions in sustaining the solid-state supramolecular architectures.

2. Experimental

2.1. Synthesis

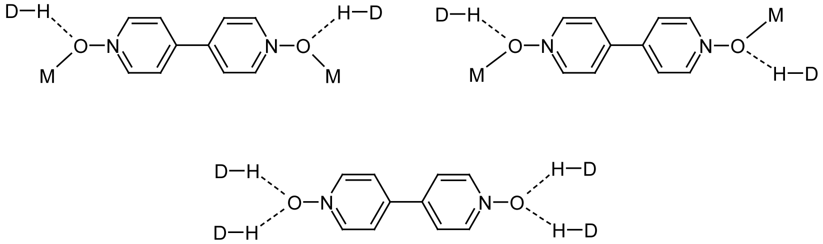
The three compounds have been obtained following the same general procedure: to the ethanolic solution (15 ml) containing $M(ClO_4)_2 \cdot 6H_2O$ (0.2 mmol) and $NaN(CN)_2$ (0.4 mmol) was added an ethanolic solution (10 ml) of 4,4-bipyridine-N,N′-dioxide (0.4 mmol). Slow evaporation of the resulting mixtures led to highly crystalline materials. $[Co(bpno)_2\{N(CN)_2\}_2(H_2O)_2]$ **1**, orange crystals. *Anal.*: Found: C, 47.5; H, 3.2; N, 23.7%. Calc.: C, 47.76; H, 3.31; N, 23.22%. IR bands (KBr, cm^{-1}): 3110m, 2301m, 2247m, 2187vs, 1470s, 1355s, 1174s, 1004s, 1029w, 834s, 530m. $[Mn(bpno)_2\{N(CN)_2\}_2(H_2O)_2]$ **2**, orange crystals. *Anal.*: Found: C, 47.9; H, 3.1; N, 23.6%. Calc.: C, 48.08; H, 3.39; N, 23.37%. IR bands (KBr, cm^{-1}): 3110m 3044m, 2282m, 2223m, 2162vs, 1676m, 1471s, 1431m, 1364m, 1244s, 1225s, 1181s, 1023m, 866m, 836s, 708w, 645w, 546s. $[Cu(bpno)\{N(CN)_2\}_2(H_2O)]$ **3**, brown crystals. *Anal.*: Found: C, 41.7; H, 2.6; N, 27.7%. Calc.: C, 41.79; H, 2.49; N, 27.86%. IR bands (KBr, cm^{-1}): 3397s, 3110m, 2309vs, 2250vs, 2180vs, 1657w, 1473s, 1426w, 1371s, 1209vs, 1176s, 1031w, 927w, 839s, 520m.

2.2. Crystal structure determination

The data collection for compounds **1**–**3** has been made on a KUMA KM-4 CCD area detector equipped with a graphite monochromatized Mo Kα radiation source ($\lambda = 0.71073$ Å). The data were corrected for absorption effect using psi-scan, and the structures were solved by direct methods and refined for all data using SHELXL-97 [15]. Non-hydrogen atoms were refined anisotropically, hydrogen atoms were inserted in calculated positions, except H-atoms of water molecules, which positions were found in electron densities maps, and refined on an assumption of a ‘ride-on model’. The crystal data for compound **1** and **3** and other pertinent information are summarized in Table 1. Compound **2** is isomorphous with compound **1**: $a = 8.117(1)$ Å; $b = 8.790(1)$ Å; $c = 9.571(1)$ Å; $\alpha = 70.89(1)°$; $\beta = 79.40(1)°$; $\gamma = 73.46(1)°$; $V = 615.42$ Å^3.

Table 1
Crystal data and details of the structure determination for compound **1** and **3**

Compound	**1**	**3**
Formula sum	$C_{12}H_{10}Co_{0.50}N_5O_3$	$C_{14}H_{10}CuN_8O_3$
Formula weight	301.71	401.84
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions		
a (Å)	8.100(1)	8.359(1)
b (Å)	8.728(1)	8.905(1)
c (Å)	9.440(1)	12.006(1)
α (°)	71.19(1)	69.44(1)
β (°)	79.05(1)	70.15(1)
γ (°)	72.96(1)	78.20(1)
Cell volume (Å^3)	600.63(12)	783.35(14)
Z	2	2
Density, calculated (g cm^{-3})	1.657	1.703
$F(0\ 0\ 0)$	309	406
μ (mm^{-1})	0.78	1.43
Collected	4660	6105
Independent reflections	2551	3336
Observed reflections [$I > 2\sigma(I)$]	2305	3095
R_1	0.0287	0.0240
R_{all}	0.0328	0.0268
Largest difference peak and hole (e Å^{-3})	0.31/−0.48	0.39/−0.51



Scheme 2.

2.3. Other physical measurements

The IR spectra (KBr pellets) was measured on a BIO-RAD FTS 135 spectrometer. UV–Vis spectra (diffuse reflectance technique) have been recorded with a VSU2 spectrophotometer by using MgO as a standard.

3. Results and discussion

The reactions between three transition metal perchlorates, $M(ClO_4)_2\cdot 6H_2O$ (M = Co, Mn, Cu), with 4,4′-bipyridine-N,N′-dioxide and sodium dicyanamide, in a 1:2:2 molar ratio, lead to the following complexes: $[Co(bpno)_2\{N(CN)_2\}_2(H_2O)_2]$ **1**, $[Mn(bpno)_2\{N(CN)_2\}_2(H_2O)_2]$ **2**, and $[Cu(bpno)\{N(CN)_2\}_2(H_2O)]$ **3**. The infrared spectra of the three complexes indicate, apart from the characteristic bands of the organic ligand, the absence of the perchlorate anions and the presence of the dicyanamido ions. The characteristic bands of the dicyanamido ligand are due to the following vibration modes: $\nu_s + \nu_{as}(NC)$ and $\nu(C{\equiv}N)$ [16]. The $\nu_s + \nu_{as}(NC)$ vibrations are located in the IR spectra of the three complexes as follows: **1**: 2301 cm^{-1}; **2**: 2283 cm^{-1}; **3**: 2309 cm^{-1}. There are two $\nu(C{\equiv}N)$ bands for each compound: **1**: 2247 and 2187 cm^{-1}; **2**: 2223 and 2162 cm^{-1}; **3**: 2250 and 2180 cm^{-1}. The solid-state electronic spectrum of compound **1** displays the characteristic band of a hexacoordinated cobalt(II) ion (536 nm) which is assigned to the $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transition. The electronic spectrum of the copper(II) complex, **3**, shows two bands located at 414 and 485 nm, and a large unsymmetrical band with maximum around 900 nm and a tail on its low-energy side.

The crystal structures of the three compounds have been solved. Since the manganese derivative, **2**, is isomorphous with compound **1**, only the structure of the cobalt derivative will be described here.

The structure of **1** consists of centrosymmetric, mononuclear $[Co(bpno)_2\{N(CN)_2\}_2(H_2O)_2]$ entities. Both bpno and dicyanamido groups act as terminal ligands (Fig. 1). Selected bond distances and angles are collected in Table 2. The dicyanamido ligand is co-ordinated to the metal ion through the nitrogen atom arising from one of the nitrile groups. The two Co–N distances are 2.081(4) Å. The Co–O bond lengths are slightly different: Co–O(bpno) = 2.096(11) Å; Co–O(aqua) = 2.122(11) Å. The cobalt(II) ion exhibits a *trans–trans–trans*-octahedral stereochemistry. The C–N–C angle of the dicyanamide is 122.86(15)°.

Table 2
Selected bond distances and angles for compounds **1** and **3**

1		**3**	
Bond distances			
Co–N(2)	2.081(14)	Cu–N(12)	1.934(14)
Co–O(11)	2.096(11)	Cu–N(13)	1.946(16)
Co–O(1)	2.122(11)	Cu–O(21)^a	1.987(12)
		Cu–O11	1.994(12)
		Cu–O	2.249(12)c
Bond angles			
N(2)^b–Co–N(2)	180	N(12)–Cu–N(13)	175.29(7)
N(2)^b–Co–O(11)	87.63(5)	N(12)–Cu–O(21)^a	93.27(5)
N(2)–Co–O(11)	92.37(5)	N(13)–Cu–O(21)^a	85.56(6)
N(2)–Co–O(11)^b	87.63(5)	N(12)–Cu–O(11)	88.66(6)
O(11)–Co–O(11)^b	180	N(13)–Cu–O(11)	91.30(6)
N(2)^b–Co–O(1)^b	92.34(5)	O(21)^a–Cu–O(11)	164.93(5)
N(2)–Co–O(1)^b	87.66(5)	N(12)–Cu–O	93.16(6)
O(11)–Co–O(1)^b	92.31(4)	N(13)–Cu–O	91.52(6)
O(11)^b–Co–O(1)^b	87.69(4)		
N(2)–Co–O(1)	92.34(5)		

[a] Symmetry codes $x, y, -1+z$.
[b] Symmetry code $-x, -y, -z$.

The most intriguing features of the crystal structure of **1** arise from the interactions at supramolecular level. Both bpno and dicyanamido ligands act as hydrogen bond acceptors, being involved in hydrogen bonds with the aqua ligands. The structure is composed of layers, which are parallel to the (1 1 0) plane (Fig. 2). Two systems of H-bonds are present, H(1)···N(1) = 2.10 Å (O(1)–N(1) = 2.93(2) Å) (Fig. 3(a)), and H(2)···O(21) = 1.81 Å (O(1)–O(21) = 2.71(2) Å) (Fig. 3(b)), which are extended throughout the whole layer. Each mononuclear entity is involved in both systems of hydrogen bonds, which results in a quite complex supramolecular architecture as shown in Fig. 2. The third dimension of the crystal results from the superposition of the layers, which interact through weak π–π stacking of the bpno aromatic rings (Fig. 4). The distance associated to these π–π interactions is 3.6 Å.

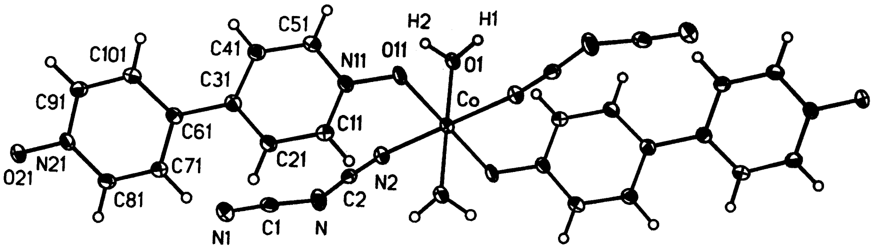


Fig. 1. Perspective view of $[Co(bpno)_2\{N(CN)_2\}_2(H_2O)_2]$ **1**, along with the atom numbering scheme.

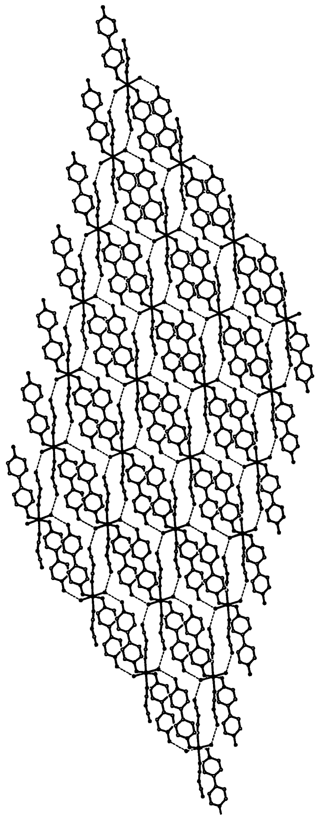
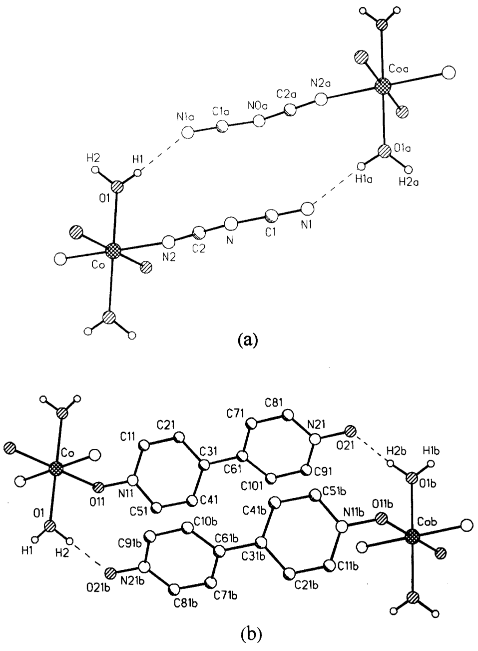


Fig. 2. View of a layer in compound **1**.



(a)

(b)

Fig. 3. Hydrogen bonding in crystal **1:** (a) hydrogen bond interactions between the dicyanamido and aqua ligands; (b) hydrogen bond interactions involving the bpno ligand.

The crystallographic investigation of compound **3** reveals infinite chains, $^{1}_{\infty}$[Cu(bpno)$\{$N(CN)$_2\}_2$(H$_2$O)], which result by connecting the copper(II) ions with the bpno bridges (Fig. 5). The 1-D coordination polymers run along the crystallographic *c* axis. The distance between the copper atoms within the chain is 12.00 Å. Each copper atom exhibits a distorted square-pyramidal stereochemistry. The basal plane is formed by two oxygen atoms of the bpno bridges, and two nitrogen atoms of the terminal dicyanamido ligands. The fifth coordination site is occupied by the aqua ligand. Selected bond distances and angles are given in Table 2. The percentage of trigonal distortion from square-pyramidal geometry is described by the parameter τ, defined as $[(\theta-\varphi)/60]\times 100$, where θ and φ are the angles between the donor atoms forming the plane in a square-pyramidal geometry [17]. The value of the τ parameter for the coordination polyhedron of copper(II) in **3** is 17.1%. The C–N–C angles of the dicyanamide ions are practically identical: C(22)–N(2)–C(12) = 121.84(1)°, and C(23)–N(3)–C(13) = 121.66(1)°.

The supramolecular order on nanometric scale in the crystalline state of [Cu(bpno)$\{$N(CN)$_2\}_2$(H$_2$O)] is created by the interplay of coordinative and hydrogen bond interactions. The chains are arranged in parallel planes related by the center of symmetry, thus forming double-layers parallel to (0 1 0), with the aqua ligands directed in between. Due to hydrogen bonds interactions, H(2)··· N(22) = 2.06 Å (O–N(22) = 2.845(2) Å) and H(1)··· N(23) = 2.00 Å (O–N(23) = 2.840(2) Å) (Fig. 6), the chains in the double-layers are joined into an infinite two-dimensional arrangement (Fig. 7). The three-dimensional structure is then achieved by the stacking of these double-layers, which are held together only by weak intermolecular forces. Since the bpno ligands are oriented more or less perpendicularly to the double-layers, there are no apparent π–π interactions between double-layers.

The structures described in this paper illustrate the formation of interesting solid-state architectures by means of hydrogen bond interactions established only between the ligands coordinated to the metallic centers. There are no uncoordinated molecules in crystals **1**–**3**.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. **1**: 188169; **3**: 188170. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

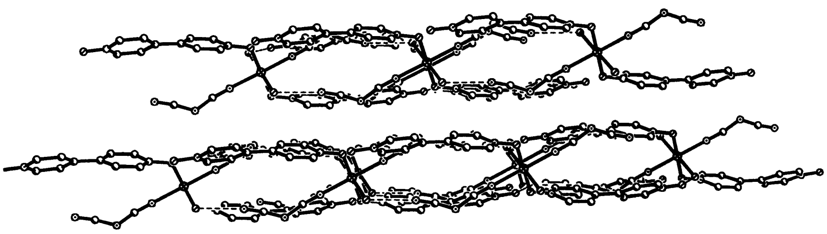


Fig. 4. Packing diagram in crystal **1** showing the superposition of two layers.

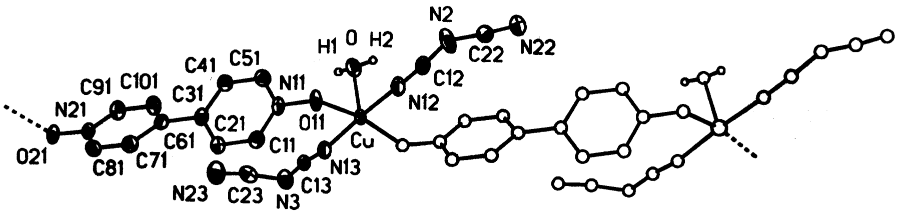


Fig. 5. View of a polymeric chain in compound **3**.

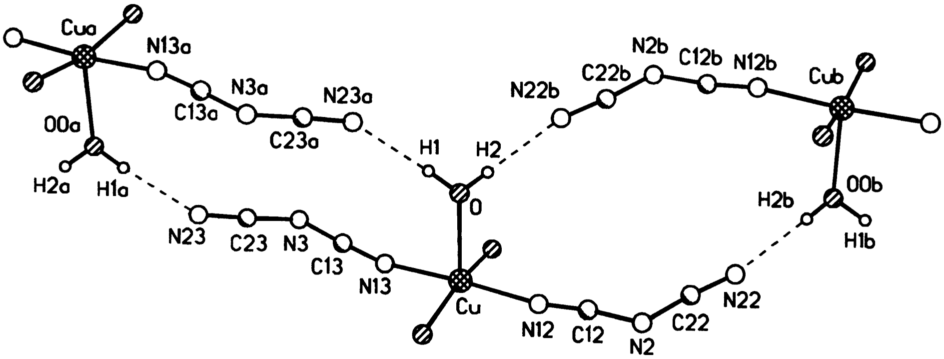
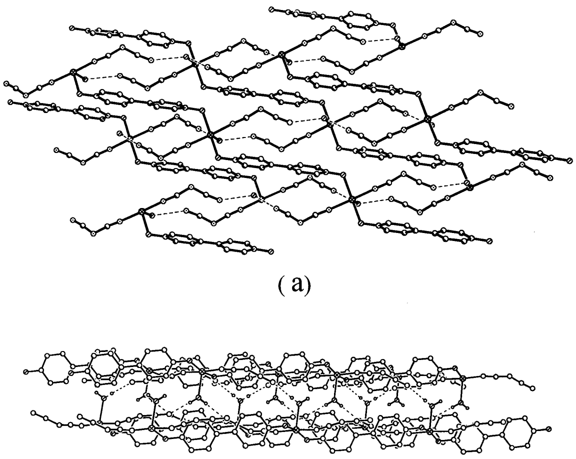


Fig. 6. H-bond system in a layer of compound **3**.



(a)

(b)

Fig. 7. Perspective views of a double layer in compound **3**: (a) view along the crystallographic *b* axis; (b) view along the crystallographic *a* axis.

Acknowledgements

This work was supported by the Romanian Ministry of Education, Grants 1-D and 30-C (CNCSIS).

References

[1] (a) O.M. Yaghi, H. Li, C. Davis, D. Richardson, T.L. Groy, Acc. Chem. Res. 31 (1998) 474;
(b) S. Kitagawa, M. Kondo, Bull. Chem. Soc. Jpn. 71 (1998) 1739;
(c) S.R. Batten, R. Robson, Angew. Chem., Int. Ed. 37 (1998) 1460;
(d) P.J. Hagram, D. Hagram, J. Zubieta. Angew. Chem., Int. Ed. 38 (1999) 2638;
(e) M.J. Zaworotko, Chem. Commun. (2001) 1;
(f) R. Robson, J. Chem. Soc., Dalton Trans. (2000) 3735;
(g) A.N. Khlobystov, A.J. Blake, N.R. Champness, D.A. Lemenovskii, A.G. Majouga, N.V. Zyk, M. Schröder, Coord. Chem. Rev. 222 (2001) 155.

[2] D.L. Long, A.J. Blake, N.R. Champness, M. Schröder, Chem. Commun. (2001) 2273.

[3] M.J. Plater, M.R.St.J. Foreman, A.M.Z. Slawin, Inorg. Chim. Acta 303 (2000) 132.

[4] S. Bruda, M. Andruh, H.W. Roesky, Y. Journaux, M. Noltemeyer, E. Rivière, Inorg. Chem. Commun. 4 (2001) 111.

[5] B.Q. Ma, S. Gao, H.L. Sun, G.X. Xu, J. Chem. Soc., Dalton Trans. (2001) 130.

[6] B.Q. Ma, H.L. Sun, S. Gao, G.X. Xu, Inorg. Chem. 40 (2001) 6247.

[7] D. Visinescu, G.I. Pascu, M. Andruh, J. Magull, H.W. Roesky, Inorg. Chim. Acta 340 (2002) 201.

[8] D.L. Long, A.J. Blake, N.R. Champness, M. Schröder, Chem. Commun. (2000) 1369.

[9] S. Tanase, M. Andruh, A. Müller, M. Schmidtmann, C. Mathonière, G. Rombaut, Chem. Commun. (2001) 1084.

[10] D.L. Long, A.J. Blake, N.R. Champness, C. Wilson, M. Schröder, J. Am. Chem. Soc. 123 (2001) 3401.

[11] (a) J.L. Manson, D.W. Lee, A.L. Rheingold, J.S. Miller, Inorg. Chem. 37 (1998) 5966;
(b) S.R. Batten, P. Jensen, K.S. Murray, R. Robson, Chem. Commun. (1998) 439;
(c) P. Jensen, S.R. Batten, G.D. Fallon, B. Moubaraki, K.S. Murray, D.J. Price, Chem. Commun. (1999) 177;
(d) J.L. Manson, Q.-Z. Huang, J.W. Lynn, H.J. Koo, M.H. Whangbo, R. Bateman, T. Otsuka, N. Wada, D.N. Argyriou, J.S. Miller, J. Am. Chem. Soc. 123 (2001) 162.

[12] (a) S.R. Batten, A.R. Harris, P. Jensen, K.S. Murray, A. Ziebell, J. Chem. Soc., Dalton Trans. (2000) 3829;
(b) P.M. van der Werff, S.R. Batten, P. Jensen, B. Moubaraki, K.S. Murray, Inorg. Chem. 40 (2001) 1718;
(c) J.W. Raebiger, J.L. Manson, R.D. Sommer, U. Geiser, A.L. Rheingold, J.S. Miller, Inorg. Chem. 40 (2001) 2579;
(d) S. Martín, M.G. Barandika, J.I. Ruiz de Larramendi, R. Cortés, M. Font-Bardia, L. Lezama, Z.E. Serna, X. Solans, T. Rojo, Inorg. Chem. 40 (2001) 3687;
(e) A.M. Kutasi, S.R. Batten, B. Moubaraki, K.S. Murray, J. Chem. Soc., Dalton Trans. (2002) 819;
(f) J. Luo, M. Hong, J. Weng, Y. Zhao, R. Cao, Inorg. Chim. Acta 329 (2002) 59.

[13] (a) B.W. Sun, S. Gao, Z.M. Wang, Chem. Lett. (2001) 2;
(b) B.W. Sun, B.Q. Ma, Z.M. Wang, New J. Chem. 24 (2000) 853.

[14] S.R. Batten, B.F. Hoskins, R. Robson, Chem. Eur. J. 6 (2000) 156.

[15] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.

[16] H. Köhler, A. Kolbe, G. Lux, Z. Anorg. Allg. Chem. 428 (1977) 103.

[17] B.J. Hathaway, in: G. Wilkinson, R.D. Gillard, J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, vol. 5, Pergamon, Oxford, 1987, p. 607.