Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Bis(dicyanamido)(diethylenetriamine-κ^3N)copper(II) and (dicyanamido)(triethylenetetramine-κ^4N)copper(II) dicyanamide

Jun Luo, Xi-Geng Zhou,* Lin-Hong Weng and Xiu-Feng Hou

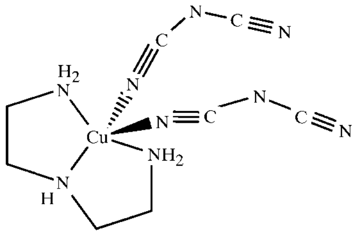
Department of Chemistry, Fudan University, Shanghai 200433, People's Republic of China
Correspondence e-mail: xgzhou@fudan.edu.cn

Received 7 July 2003
Accepted 8 August 2003
Online 16 September 2003

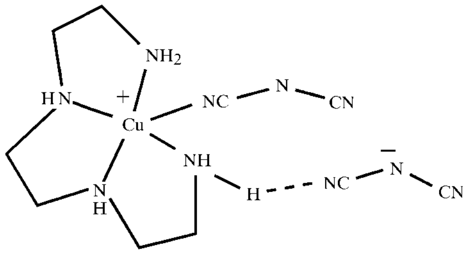
Two new complexes, [Cu(C_2N_3)$_2$(dien)] (dien is diethylenetriamine, $C_4H_{13}N_3$), (I), and [Cu(C_2N_3)(trien)](C_2N_3) (trien is triethylenetetramine, $C_6H_{18}N_4$), (II), have been characterized by single-crystal X-ray diffraction. Both complexes display a distorted tetragonal–pyramidal geometry. In (I), the Cu atom is coordinated in the basal plane by three diethylenetriamine N atoms [Cu—N = 2.000 (2), 2.004 (2) and 2.025 (2) Å] and one terminal N atom [Cu—N = 1.974 (2) Å] from one monodentate dicyanamide group, and in the apical position by one terminal N atom [Cu—N = 2.280 (2) Å] from the other monodentate dicyanamide group. In (II), the Cu atom is surrounded by four triethylenetetramine N atoms [Cu—N = 2.012 (2), 2.014 (2), 2.019 (2) and 2.031 (2) Å in the basal plane] and a terminal N atom [Cu—N = 2.130 (2) Å in the apical site] from one monodentate dicyanamide group. The other dicyanamide anion is not directly coordinated to the metal atom. In both (I) and (II), hydrogen-bond interactions between the uncoordinated terminal N atoms of two dicyanamide ions and the amine H atoms lead to the formation of three-dimensional networks.

Comment

Recently, dicyanamide (dca) complexes have attracted considerable interest because of their fascinating magnetic properties (Batten *et al.*, 1998; Jensen *et al.*, 1999; Manson *et al.*, 1999) and diverse structural types (Manson *et al.*, 1998; Batten *et al.*, 1999; Vangdal *et al.*, 2002). For example, the three-dimensional compound [Cr(C_2N_3)$_2$] is found to be magnetically ordered at temperatures as high as 47 K. It is well known that the structures and magnetic properties of complexes are related to the nature of the co-ligands (Dasna *et al.*, 2001; Jensen *et al.*, 2001, 2002; Carranza *et al.*, 2002). Although much effort has recently been focused on studies of dicyanamide complexes with amine co-ligands, including diaminopropane (Li *et al.*, 2002; Wang *et al.*, 2002; Chen *et al.*, 2003) and macrocyclic polyamines (Cho *et al.*, 2002; Gu *et al.*, 2003; Paraschiv *et al.*, 2003), very few dicyanamide complexes with diethylenetriamine (dien) or triethylenetetramine (trien) as the co-ligands have been reported (Brezina *et al.*, 1999). In order to study further how the nature of the co-ligands affects the structures and properties of dicyanamide complexes, we report here the syntheses and crystal structures of two new copper dicyanamide complexes, *viz.* [Cu(dien)(C_2N_3)$_2$], (I), and [Cu(trien)(C_2N_3)](C_2N_3), (II).



(I)



(II)

In (I), the copper ion is bonded to three diethylenetriamine N atoms and two terminal N atoms from two different dicyanamide anions, thus forming a distorted tetragonal–pyramidal geometry; the basal plane comprises the three diethylenetriamine N atoms (atoms N1, N2 and N3) and one nitrile N atom (N4) of a monodentate dicyanamide group, while the apical site is occupied by one nitrile N atom (N7) of the other monodentate dicyanamide group (Fig. 1). Two different hydrogen-bonding interactions are observed in (I) (Table 2). The intramolecular hydrogen bond between one bonded dicyanamide N atom and the H atom on the nodal N atom of the dien group (N2—H2*C*···N7) results in a relatively small N7—Cu1—N2 angle of 87.31 (9)°. The intermolecular hydrogen-bonding interactions between the uncoordinated terminal N atoms of the dicyanamide groups and the terminal amino H atoms of the dien group [N···N = 3.008 (4)–3.156 (3) Å, H···N = 2.21 (4)–2.40 (3) Å and N—H···N = 145 (3)–175 (3)°] are dedicated to the construction of a three-dimensional network (Fig. 2).

In the cation of (II), the copper ion is bonded to four N atoms (atoms N4, N5, N6 and N7, in the basal plane) from the triethylenetetramine molecule and one terminal N atom (N1, in the apical site) from a dicyanamide group, while the other dicyanamide anion does not enter the inner coordination sphere (Fig. 3) but is linked to the cation *via* a hydrogen bond (Table 4). This phenomenon is also found in some other

DOI: 10.1107/S0108270103017621

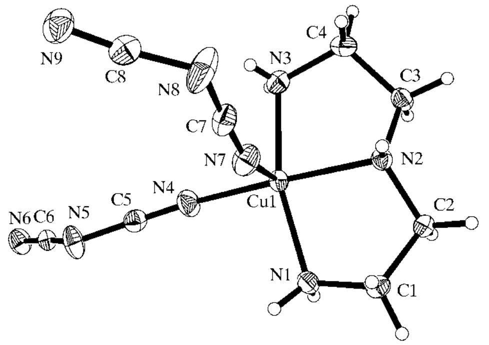


Figure 1
A view of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

dicyanamide complexes (Claramunt *et al.*, 2000; He *et al.*, 2002; Marshall *et al.*, 2002). The cations are crosslinked to form a two-dimensional network *via* intermolecular hydrogen bonds [N$\cdots$N = 3.155 (3)–3.164 (3) Å, H$\cdots$N = 2.33–2.53 Å and N—H$\cdots$N = 128–154°], and the layers are linked to one another *via* hydrogen bonds involving the uncoordinated dicyanamide anions [N$\cdots$N = 3.010 (3) and 3.213 (3) Å, H$\cdots$N = 2.14 (3) and 2.60 (2) Å, and N—H$\cdots$N = 159 and 136°], thus forming a three-dimensional structure (Fig. 4).

The Cu—N$_{\mathrm{dien}}$ distances in (I) [2.000 (2)–2.025 (2) Å; Table 1] are almost equal to the Cu—N$_{\mathrm{trien}}$ distances in (II) [2.012 (2)–2.031 (2) Å; Table 3] and are similar to the corresponding distances in aliphatic amine–copper complexes (Suenaga *et al.*, 1997; Baesjou *et al.*, 2000). The Cu—N$_{\mathrm{dca}}$ distances in (I) are quite different; the axial Cu—N$_{\mathrm{dca}}$ distance [2.280 (2) Å] is markedly longer than the basal Cu—N$_{\mathrm{dca}}$ distance [1.974 (2) Å], while the Cu—N$_{\mathrm{dca}}$ distance [2.130 (2) Å] in (II) is intermediate between the two distances in (I). The Cu—N$_{\mathrm{dca}}$ distances in (I) are comparable to the corresponding distances in [Cu(phen)(C_2N_3)$_2$] (phen is 1,10-phenanthroline; Wang *et al.*, 2000), while the axial Cu—N$_{\mathrm{dca}}$ distance in (II) is slightly shorter than that in [Cu(dmbipy)(C_2N_3)$_2$] [2.247 (2) Å; dmbipy is 5,5′-dimethyl-2,2′-bipyridine; Kooijman *et al.*, 2002]. The distortion of the tetragonal pyramid can be described by the parameter *t* (*t* indicates the relative amount of trigonality; $t = 0$ for a tetragonal pyramid

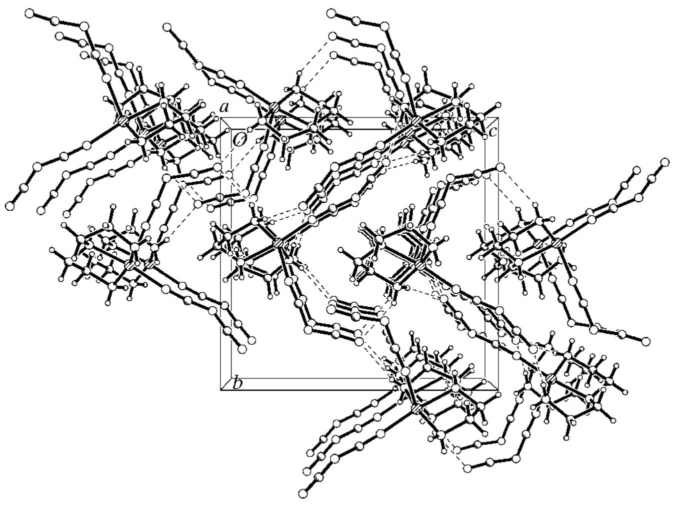


Figure 2
The three-dimensional network of (I) formed by hydrogen-bonding interactions (dashed lines).

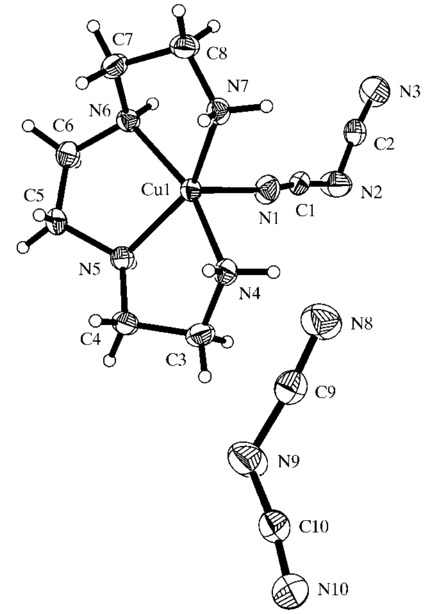


Figure 3
A view of the molecule of (II) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

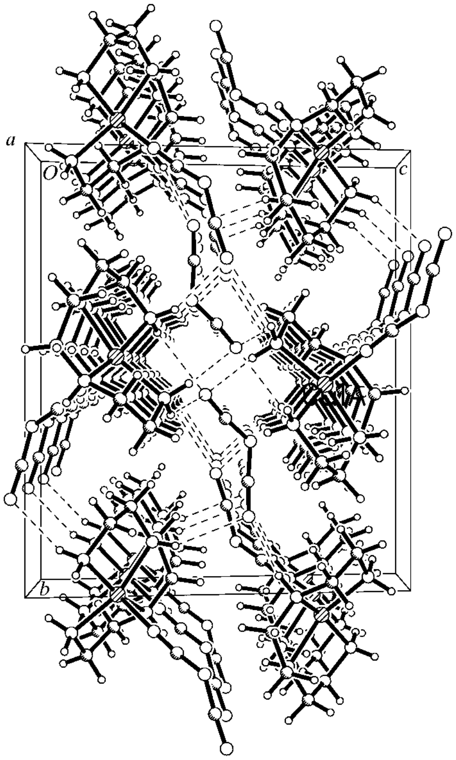


Figure 4
The three-dimensional network of (II) formed by hydrogen-bonding interactions (dashed lines).

and $t = 1$ for a trigonal bipyramid; Addison *et al.*, 1984), which is 0.18 and 0.16 for (I) and (II), respectively. In (I), the $N_{basal}—Cu—N_{basal}$ (for two neighbouring basal N atoms) and $N_{apical}—Cu—N_{basal}$ angles are in the ranges 84.02 (9)–94.98 (10) and 87.31 (9)–101.00 (9)°, respectively. The corresponding values in (II) are 84.03 (8)–97.74 (8) and 98.25 (9)–104.63 (9)°, respectively, indicating that the distortion of the tetragonal pyramid in (I) and (II) is not serious.

In (I) and (II), each dicyanamide group is almost planar, with C≡N triple-bond distances in the range 1.133 (3)–1.145 (3) Å, C—N single-bond distances in the range 1.288 (3)–1.306 (3) Å, and C—N—C and N—C—N angles of 120.5 (3)–123.4 (3) and 172.0 (3)–176.4 (3)°, respectively. These values are in good agreement with those in other dicyanamide-containing compounds (Kurmoo & Kepert, 1998; Batten *et al.*, 1999; Carranza *et al.*, 2002; Vangdal *et al.*, 2002).

Experimental

A solution of diethylenetriamine (0.60 mmol, 61.90 mg) in ethanol (4 ml) and a solution of copper acetate (0.60 mmol, 119.79 mg) in ethanol (4 ml) were mixed and stirring for 5 min. To the resulting deep-blue mixture was added an aqueous solution (2 ml) of sodium dicyanamide (0.60 mmol, 53.42 mg). After stirring for another 5 min, the solution was filtered and the filtrate evaporated slowly in air. After one week, deep-blue block-shaped crystals of (I) were isolated in 35% yield. Analysis calculated for $C_8H_{13}CuN_9$: C 32.16, H 4.39, N 42.19%; found: C 31.84, H 4.43, N 42.30%. Complex (II) was prepared in a similar manner using triethylenetetramine as the starting material (yield 27%). Analysis calculated for $C_{10}H_{18}CuN_{10}$: C 35.13, H 5.31, N 40.97%; found: C 34.83, H 5.17, N 41.29%.

Compound (I)

Crystal data

$[Cu(C_2N_3)_2(C_4H_{13}N_3)]$
$M_r = 298.81$
Orthorhombic, $P2_12_12_1$
$a = 7.0284$ (10) Å
$b = 12.935$ (2) Å
$c = 13.197$ (2) Å
$V = 1199.8$ (3) Å^3
$Z = 4$
$D_x = 1.654$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 3569 reflections
$\theta = 2.2$–27.0°
$\mu = 1.82$ mm^{-1}
$T = 293$ (2) K
Block, blue
0.30 × 0.20 × 0.10 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.611$, $T_{max} = 0.839$
5547 measured reflections

2367 independent reflections
2249 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$
$\theta_{max} = 26.0°$
$h = -8 \rightarrow 4$
$k = -15 \rightarrow 15$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.059$
$S = 1.05$
2367 reflections
183 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0287P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.44$ e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = 0.020 (14)

Table 1
Selected geometric parameters (Å, °) for (I).

Cu1—N4	1.974 (2)	Cu1—N2	2.025 (2)
Cu1—N1	2.000 (2)	Cu1—N7	2.280 (2)
Cu1—N3	2.004 (2)		
N4—Cu1—N1	94.46 (10)	N3—Cu1—N2	84.02 (9)
N4—Cu1—N3	94.98 (10)	N4—Cu1—N7	101.00 (9)
N1—Cu1—N3	160.88 (11)	N1—Cu1—N7	96.57 (11)
N4—Cu1—N2	171.68 (10)	N3—Cu1—N7	97.89 (11)
N1—Cu1—N2	84.24 (9)	N2—Cu1—N7	87.31 (9)

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*C*···N9^{i}	0.83 (3)	2.40 (3)	3.113 (4)	145 (3)
N1—H1*D*···N6^{ii}	0.89 (3)	2.31 (3)	3.156 (3)	159 (2)
N2—H2*C*···N7	0.80 (3)	2.60 (3)	2.977 (3)	111 (2)
N3—H3*C*···N6^{iii}	0.90 (4)	2.21 (4)	3.108 (4)	175 (3)
N3—H3*D*···N9^{iv}	0.71 (3)	2.32 (3)	3.008 (4)	164 (3)

Symmetry codes: (i) $\frac{3}{2}-x, 2-y, \frac{1}{2}+z$; (ii) $x-\frac{1}{2}, \frac{3}{2}-y, -z$; (iii) $\frac{1}{2}+x, \frac{3}{2}-y, -z$; (iv) $\frac{1}{2}+x, \frac{5}{2}-y, -z$.

Compound (II)

Crystal data

$[Cu(C_2N_3)(C_6H_{18}N_4)](C_2N_3)$
$M_r = 341.88$
Monoclinic, $P2_1/n$
$a = 7.4132$ (11) Å
$b = 15.170$ (2) Å
$c = 13.312$ (2) Å
$\beta = 101.881$ (2)°
$V = 1465.0$ (4) Å^3
$Z = 4$
$D_x = 1.550$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 3137 reflections
$\theta = 2.7$–26.3°
$\mu = 1.50$ mm^{-1}
$T = 298$ (2) K
Block, blue
0.30 × 0.20 × 0.10 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.661$, $T_{max} = 0.864$
7199 measured reflections
3185 independent reflections

2668 reflections with $I > 2\sigma(I)$
$R_{int} = 0.026$
$\theta_{max} = 27.0°$
$h = -9 \rightarrow 6$
$k = -17 \rightarrow 19$
$l = -17 \rightarrow 15$

Table 3
Selected geometric parameters (Å, °) for (II).

Cu1—N7	2.012 (2)	Cu1—N5	2.031 (2)
Cu1—N4	2.014 (2)	Cu1—N1	2.130 (2)
Cu1—N6	2.019 (2)		
N7—Cu1—N4	97.74 (8)	N6—Cu1—N5	84.03 (8)
N7—Cu1—N6	85.24 (8)	N7—Cu1—N1	104.63 (9)
N4—Cu1—N6	161.06 (9)	N4—Cu1—N1	99.05 (9)
N7—Cu1—N5	151.29 (9)	N6—Cu1—N1	98.25 (9)
N4—Cu1—N5	84.57 (8)	N5—Cu1—N1	103.23 (9)

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N6—H6···N8^{v}	0.91 (3)	2.14 (3)	3.010 (3)	159 (2)
N5—H5···N8^{vi}	0.79 (2)	2.60 (2)	3.213 (3)	136 (2)
N7—H7B···N3^{vii}	0.90	2.53	3.155 (3)	128
N7—H7B···N10^{viii}	0.90	2.49	3.142 (3)	130
N7—H7A···N10^{ix}	0.90	2.23	3.088 (3)	160
N4—H4B···N3^{x}	0.90	2.33	3.164 (3)	154
N4—H4A···N10^{viii}	0.90	2.52	3.188 (3)	131

Symmetry codes: (v) $-x, 1-y, 1-z$; (vi) $x, y, 1+z$; (vii) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$; (viii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (ix) $x-\frac{1}{2}, \frac{3}{2}-y, \frac{1}{2}+z$; (x) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.087$
$S = 1.03$
3185 reflections
198 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0432P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.54$ e Å^{-3}
$\Delta\rho_{\min} = -0.44$ e Å^{-3}

In (I), the positions of the amine H atoms were found in a difference Fourier map and refined freely, along with their isotropic displacement parameters. The other H atoms were constrained to an ideal geometry, with C—H distances of 0.97 Å. In (II), atoms H5 and H6 were located in a difference Fourier map. All other H atoms were placed in idealized positions and constrained to ride on their parent atoms, with C—H distances of 0.97 Å and N—H distances of 0.90 Å.

For both compounds, data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2000); software used to prepare material for publication: *SHELXTL*.

This project was supported by the National Natural Science Foundation of the People's Republic of China.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1027). Services for accessing these data are described at the back of the journal.

References

Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.

Baesjou, P. J., Driessen, W. L., Reedijk, J. & Spek, A. L. (2000). *Inorg. Chim. Acta*, **306**, 237–240.

Batten, S. R., Jensen, P., Kepert, C. J., Kurmoo, M., Moubaraki, B., Murray, K. S. & Price, D. J. (1999). *J. Chem. Soc. Dalton Trans.* pp. 2987–2997.

Batten, S. R., Jensen, P., Moubaraki, B., Murray, K. S. & Robson, R. (1998). *Chem. Commun.* pp. 439–440.

Brezina, F., Travnicek, Z., Sindelar, Z., Pastorek, R. & Marek, J. (1999). *Transition Met. Chem.* **24**, 459–462.

Bruker (2000). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Carranza, J., Brennan, C., Sletten, J., Lioret, F. & Julve, M. (2002). *J. Chem. Soc. Dalton Trans.* pp. 3164–3170.

Chen, X.-Y., Cheng, P., Zhao, B., Yan, S.-P., Liao, D.-Z. & Jiang, Z.-H. (2003). *J. Mol. Struct.* **655**, 179–184.

Cho, J.-H., Lee, U. & Kim, J.-C. (2002). *Transition Met. Chem.* **27**, 429–432.

Claramunt, A., Escuer, A., Mautner, F.-A., Sanz, N. & Vicente, R. (2000). *J. Chem. Soc. Dalton Trans.* pp. 2627–2630.

Dasna, I., Golhen, S., Ouahab, L., Daro, N. & Sutter, J.-P. (2001). *New J. Chem.* **25**, 1572–1576.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Gu, W., Bian, H.-D., Xu, J.-Y., Liu, Z.-Q., Cheng, P., Yan, S.-P., Liao, D.-Z. & Jiang, Z.-H. (2003). *Inorg. Chem. Commun.* **6**, 966–970.

He, Y., Kou, H.-Z., Zhou, B.-C., Xiong, M., Wang, R.-J. & Li, Y. (2002). *Acta Cryst.* E**58**, m389–m391.

Jensen, P., Batten, S. R., Fallon, G. D., Moubaraki, B., Murray, K. S. & Price, D. J. (1999). *Chem. Commun.* pp. 177–178.

Jensen, P., Batten, S. R., Moubaraki, B. & Murray, K. S. (2001). *J. Solid State Chem.* **159**, 352–361.

Jensen, P., Batten, S. R., Moubaraki, B. & Murray, K. S. (2002). *J. Chem. Soc. Dalton Trans.* pp. 3712–3722.

Kooijman, H., Spek, A. L., van Albada, G. A. & Reedijk, J. (2002). *Acta Cryst.* C**58**, m124–m126.

Kurmoo, M. & Kepert, C. J. (1998). *New J. Chem.* **12**, 1515–1524.

Li, B.-L., Ding, J.-G., Lang, J.-P., Xu, Z. & Chen, J.-T. (2002). *J. Mol. Struct.* **616**, 175–179.

Manson, J. L., Kmety, C. R., Epstein, A. J. & Miller, J. S. (1999). *Inorg. Chem.* **38**, 2552–2553.

Manson, J. L., Lee, D. W., Rheingold, A. L. & Miller, J. S. (1998). *Inorg. Chem.* **37**, 5966–5967.

Marshall, S. R., Rheingold, A. L., Dawe, L. N., Shum, W. W., Kitamura, C. & Miller, J. S. (2002). *Inorg. Chem.* **41**, 3599–3601.

Paraschiv, C., Sutter, J.-P., Schmidtmann, M., Müller, A. & Andruh, M. (2003). *Polyhedron*, **22**, 1611–1615.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Sheldrick, G. M. (2000). *SHELXTL*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Suenaga, Y., Wu, L. P., Kuroda-Sowa, T., Munakata, M. & Maekawa, M. (1997). *Polyhedron*, **16**, 67–70.

Vangdal, B., Carranza, J., Lioret, F., Julve, M. & Sletten, J. (2002). *J. Chem. Soc. Dalton Trans.* pp. 566–574.

Wang, Z.-M., Luo, J., Sun, B.-W., Yan, C.-H., Gao, S. & Liao, C.-S. (2000). *Acta Cryst.* C**56**, 786–788.

Wang, Z.-M., Sun, B.-W., Luo, J., Gao, S., Liao, C.-S., Yan, C.-H. & Li, Y. (2002). *Inorg. Chim. Acta*, **332**, 127–134.