Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Di-μ-cyanato-bis[(cyanato-κN)(tetramethylethylenediamine-κ^2N,N')copper(II)] and *catena*-poly[[μ_3-cyanato-κ^3O:N:N-bis[(cyanato-κN)(1,3-diaminopropane-κ^2N,N')copper(II)]]-μ_3-cyanato-κ^3N:N:O]

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

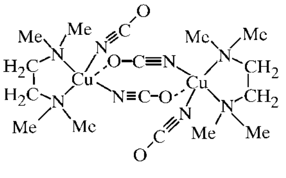
Department of Chemistry, Fudan University, Shanghai 200433, People's Republic of China
Correspondence e-mail: xgzhou@fudan.edu.cn

Received 28 August 2003
Accepted 20 October 2003
Online 8 November 2003

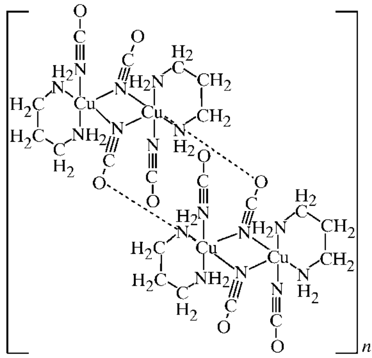
The two title Cu^{II} complexes, $[Cu_2(NCO)_4(tmeda)_2]$ (tmeda is tetramethylethylenediamine, $C_6H_{16}N_2$), (I), and $[Cu(NCO)_2(pn)]_n$ (pn is 1,3-diaminopropane, $C_3H_{10}N_2$), (II), have been synthesized and their crystal structures determined. In (I), which lies about an inversion centre, each Cu centre possesses a distorted tetragonal–pyramidal geometry with four basal N atoms from two cyanate anions [Cu—N = 1.945 (2) and 1.948 (3) Å] and one tmeda molecule [Cu—N = 2.053 (2) and 2.071 (2) Å], and one axial O atom [Cu—O = 2.737 (3) Å] from another cyanate anion. The two neighbouring Cu atoms in (I) are joined by a pair of cyanates in an end-to-end fashion, forming a dimer. In (II), each Cu centre adopts a distorted square-bipyramidal geometry, with four equatorial N atoms from two cyanates [Cu—N = 1.988 (2) and 2.007 (3) Å] and a pn ligand [Cu—N = 1.996 (3) and 2.011 (3) Å], and one apical N atom [Cu—N = 2.437 (3) Å] and an apical O atom [Cu—O = 2.900 (3) Å] from two cyanates. In contrast with (I), the two neighbouring Cu atoms in (II) are bridged by two cyanates in an end-on fashion, to form a centrosymmetric dimeric unit. These units are further crosslinked, forming a two-dimensional network structure, *via* weak interactions between the bridging cyanate O atom and a neighbouring Cu atom, plus interactions of the amine H atoms with the cyanate O atoms and the terminal cyanate N atom.

Comment

The synthesis of cyanate complexes continues to be the subject of much interest, and intensive investigations have taken place as a result of their diverse structures and potential applications in magnetic materials (Diaz *et al.*, 2001; Grove *et al.*, 2001; Hernández *et al.*, 2001). It is noteworthy that, in most dinuclear Cu–cyanate complexes for which structural and magnetic data are available, the two Cu atoms are linked together by different bridging ligands (Boillot *et al.*, 1985; Mallah *et al.*, 1986; Kahn *et al.*, 1989), while known homocyanate-bridged Cu_2 complexes with aliphatic amine co-ligands, such as substituted ethylenediamine (Mauro *et al.*, 1990; Zukerman-Schpector *et al.*, 1991), substituted diethylenetriamine (Escuer *et al.*, 1999) and azacryptate (Harding *et al.*, 1996), are scarce. To date, no two-dimensional structures linked by homocyanate-bridged Cu_2 moieties with aliphatic amine co-ligands have been reported. To gain a deeper insight into the structures and properties of homocyanate-bridged Cu_2 complexes, we report herein the syntheses and crystal structures of two new Cu–cyanate complexes with tetramethylethylenediamine (tmeda) and 1,3-diaminopropane (pn) as co-ligands, namely $[Cu(tmeda)(N_2C_2O_2)]_2$, (I), and $[Cu_2(pn)_2(N_2C_2O_2)_2]_n$, (II).



(I)



(II)

Complex (I) (Fig. 1) is a centrosymmetric dinuclear structure with two end-to-end cyanate bridges, in which each Cu^{II} ion is pentacoordinated to three cyanate anions and one tmeda ligand to give a distorted tetragonal–pyramidal geometry. For atom Cu1, the basal plane is formed by one terminal cyanate atom (N1), one bridged cyanate atom (N2) and two atoms (N3 and N4) of the tmeda ligand, the apical site being occupied by one atom ($O2^{i}$) of another bridged cyanate [symmetry code: (i) $2 - x, 2 - y, 2 - z$]. In each dimer, the Cu$\cdots$Cu distance is 5.4330 (12) Å [the closest Cu$\cdots$Cu separation is 4.9814 (14) Å].

In (II), atom Cu1 is bonded to one terminal cyanate atom (N3), one bridged cyanate atom ($N4^{ii}$) and two atoms (N1 and N2) of one pn ligand in the basal plane, along with one bridged cyanate N atom (N4) and one bridged cyanate O atom ($O2^{iii}$) in the apical sites, to form a distorted tetragonal–bipyramidal geometry [symmetry codes: (ii) $2 - x, 2 - y, -z$; (iii) $x, y - 1, z$]. Two Cu atoms are linked by two cyanates in an end-on

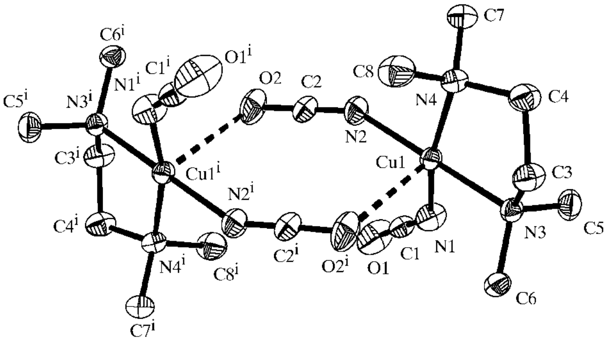


Figure 1
A view of the molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity [symmetry code: (i) $2 - x, 2 - y, 2 - z$].

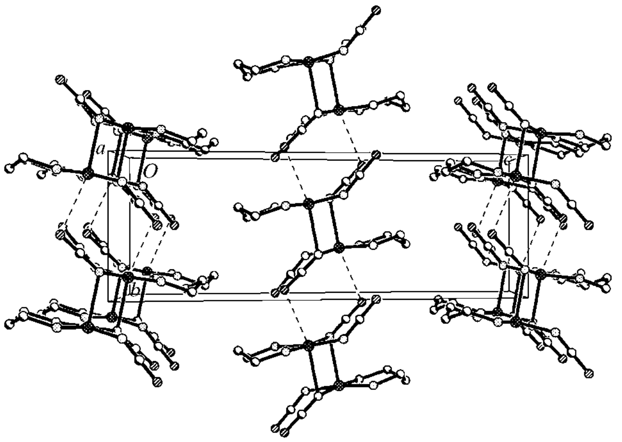


Figure 3
The one-dimensional chain structure of (II) linked *via* the weak interactions, with a view of the unit cell.

bonding mode to define a dimer (Fig. 2). These dimeric units are linked together to form a one-dimensional chain (Fig. 3) *via* weak interactions [Cu$\cdots$O = 2.900 (3) Å]. These chains are then crosslinked *via* hydrogen bonds (Table 3) involving the terminal cyanate N atom [N$\cdots$N = 3.188 (4) Å], the bridging cyanate O atom [N$\cdots$O = 3.034 (4) Å] and the terminal cyanate O atoms [N$\cdots$O = 3.120 (4) and 3.162 (4) Å], thus forming a two-dimensional network (Fig. 4). To our knowledge, such two-dimensional networks are rare in Cu–cyanate complexes. In (II), the cyanates exhibit two types of coordination mode, one of which is end-on within the dimer, while the second cyanate is end-to-end between dimers. The Cu$\cdots$Cu distance within the dimers in (II) is 3.2137 (9) Å and that between neighbouring units is 5.375 (2) Å.

Interestingly, by replacing tmeda with pn as the co-ligand, the title Cu complexes change from a simple dimer to a two-dimensional structure, and the bonding model of the bridging cyanate also changes. This may be attributed to the steric difference between the two aliphatic amine ligands. As tmeda is more sterically crowded than pn, in (I), the bridging cyanates adopt an end-to-end bonding fashion to reduce the steric repulsion between two tmeda ligands. In contrast with (I), the metal ion should be sterically unsaturated if (II) has a similar structure to (I). As a result, the smaller pn ligand allows the bonding model of the bridged cyanate to change from end-to-end to end-on and forces the Cu atom to coordinate further to the neighbouring O atom, thus forming a one-dimensional infinite chain with a higher coordination number.

In (I), the Cu—N(tmeda) bond lengths [2.053 (2)–2.071 (2) Å] are longer than the Cu—N(cyanate) distances [1.945 (2)–1.948 (3) Å; Table 1]. These data are similar to the corresponding distances in $\{[\mathrm{Cu}L(\mathrm{NCO})_n](\mathrm{ClO_4})\}_n$ (L is *N*,*N*,*N*′,*N*″,*N*″-pentamethyl-3-azapentane-1,5-diamine; Vicente *et al.*, 1994). In contrast with (I), the Cu—N bond lengths in the basal plane of (II) [1.988 (2)–2.011 (3) Å; Table 2] show no distinct differences and are comparable with the corre-

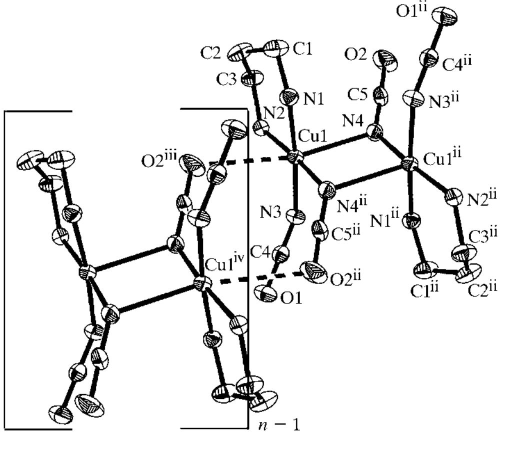


Figure 2
A view of the Cu^{II} coordination environment of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity [symmetry codes: (ii) $2 - x, 2 - y, -z$; (iii) $x, y - 1, z$; (iv) $1 - x, 2 - y, -z$].

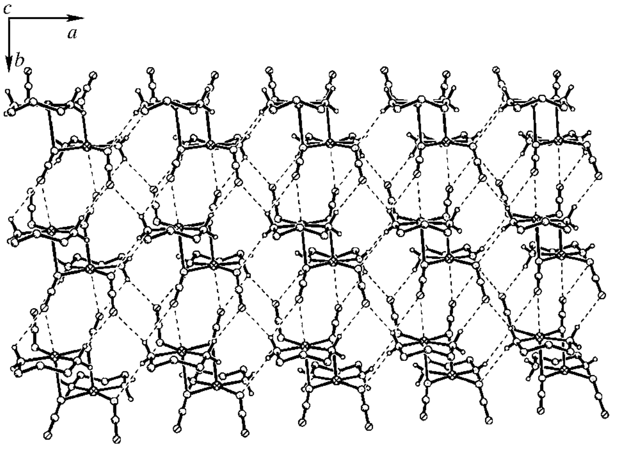


Figure 4
The two-dimensional network of (II) crosslinked *via* hydrogen-bond interactions, viewed along the *c* axis.

sponding distances in $[Cu_2(N_2C_2O_2)(medien)_2](ClO_4)_2$ (medien is 4-methyldiethylenetriamine; Escuer *et al.*, 1999). The apical Cu—N(cyanate) [2.437 (3) Å] or Cu—O(cyanate) distances [2.900 (3) Å] in (II) are longer than the Cu—N distances in the basal plane. A similar situation is also seen in (I). The N—Cu—N angles (two neighbouring N atoms) are in the range 85.35 (8)–94.16 (12)° for (I) and 84.56 (11)–97.19 (11)° for (II). Both ranges deviate from the ideal value of 90°, but the N(basal)—Cu—O(apical) angles in (I) [87.20 (8)–98.81 (10)°] deviate less than those in (II) [74.01 (10)–100.84 (9)°], indicating that the geometry of (II) is more distorted than that of (I).

In (I) and (II), the geometric parameters for the tmeda [1.480 (4)–1.505 (4) Å and 107.9 (2)–111.6 (2)°] and pn [1.460 (5)–1.466 (4) Å and 113.9 (3)–119.2 (3)°] ligands are normal for aliphatic amine-containing complexes (Kovbasyuk *et al.*, 1997; Zukerman-Schpector *et al.*, 1991). The cyanates are almost linear, with N—C and C—O bond lengths in the ranges 1.146 (3)–1.169 (4) and 1.188 (3)–1.211 (3) Å, respectively. The N—C—O angles [177.8 (3)–178.8 (3)°] are similar to those in other cyanate complexes (Rojo *et al.*, 1989; Real *et al.*, 1993; Otieno *et al.*, 1993).

Experimental

To a solution of copper acetate (0.60 mmol, 119.79 mg) in ethanol (4 ml) was added tmeda (0.60 mmol, 69.73 mg) in ethanol (4 ml). After stirring for 5 min, an aqueous solution of sodium cyanate (2 ml; 0.60 mmol, 39.01 mg) was added and the mixture stirred for a further 5 min. The solution was filtered and the filtrate left to evaporate slowly in air. After one week, blue block-shaped crystals of (I) were isolated in 67% yield. Analysis calculated for $C_{16}H_{32}Cu_2N_8O_4$: C 36.43, H 6.11, N 21.24%; found: C 36.02, H 5.82, N 21.38%. Crystals of (II) were prepared in a similar manner, using the pn ligand as a starting material, resulting in an 11% yield. Analysis calculated for $C_{10}H_{20}Cu_2N_8O_4$: C 27.09, H 4.55, N 25.27%; found: C 26.32, H 4.61, N 24.73%.

Compound (I)

Crystal data

$[Cu_2(NCO)_4(C_6H_{16}N_2)_2]$
$M_r = 527.58$
Triclinic, $P\overline{1}$
$a = 7.656$ (2) Å
$b = 8.613$ (2) Å
$c = 9.671$ (2) Å
$\alpha = 78.893$ (3)°
$\beta = 71.433$ (3)°
$\gamma = 77.984$ (3)°
$V = 585.8$ (2) Å^3
$Z = 1$
$D_x = 1.496$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2262 reflections
$\theta = 2.4$–27.0°
$\mu = 1.85$ mm^{-1}
$T = 293$ (2) K
Block, blue
0.50 × 0.45 × 0.45 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.406$, $T_{\max} = 0.434$
2462 measured reflections
2033 independent reflections
1883 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.016$
$\theta_{\max} = 25.0°$
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 9$
$l = -11 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.082$
$S = 1.06$
2033 reflections
141 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0519P)^2 + 0.0912P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.53$ e Å^{-3}
$\Delta\rho_{\min} = -0.37$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.066 (5)

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

Cu1—N2	1.945 (2)	Cu1—N4	2.071 (2)
Cu1—N1	1.948 (3)	Cu1—O2^{i}	2.737 (3)
Cu1—N3	2.053 (2)	Cu1—Cu1^{i}	5.4330 (12)
N2—Cu1—N1	94.16 (12)	N3—Cu1—N4	85.35 (8)
N2—Cu1—N3	174.55 (10)	N2—Cu1—O2^{i}	89.48 (9)
N1—Cu1—N3	90.61 (10)	N1—Cu1—O2^{i}	98.81 (10)
N2—Cu1—N4	90.68 (10)	N3—Cu1—O2^{i}	87.20 (8)
N1—Cu1—N4	164.90 (11)	N4—Cu1—O2^{i}	95.52 (8)

Symmetry code: (i) $2 - x, 2 - y, 2 - z$.

Compound (II)

Crystal data

$[Cu(NCO)_2(C_3H_{10}N_2)]$
$M_r = 221.72$
Monoclinic, $P2_1/n$
$a = 6.711$ (2) Å
$b = 6.636$ (2) Å
$c = 19.230$ (6) Å
$\beta = 100.049$ (3)°
$V = 843.3$ (4) Å^3
$Z = 4$
$D_x = 1.746$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2190 reflections
$\theta = 3.1$–26.8°
$\mu = 2.56$ mm^{-1}
$T = 298$ (2) K
Block, blue
0.20 × 0.10 × 0.10 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.629$, $T_{\max} = 0.784$
4002 measured reflections
1859 independent reflections
1517 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.033$
$\theta_{\max} = 27.2°$
$h = -8 \rightarrow 8$
$k = -8 \rightarrow 7$
$l = -17 \rightarrow 24$

Table 2
Selected geometric parameters (Å, °) for (II).

Cu1—N1	2.011 (3)	Cu1—N4	2.437 (3)
Cu1—N2	1.996 (3)	Cu1—O2^{iii}	2.900 (3)
Cu1—N3	1.988 (2)	Cu1—Cu1^{ii}	3.2137 (9)
Cu1—N4^{ii}	2.007 (3)	Cu1—Cu1^{iv}	5.375 (2)
N3—Cu1—N2	88.59 (11)	N4^{ii}—Cu1—N4	87.89 (10)
N3—Cu1—N4^{ii}	91.74 (11)	N1—Cu1—N4	91.02 (11)
N2—Cu1—N4^{ii}	174.85 (12)	N3—Cu1—O2^{iii}	93.13 (10)
N3—Cu1—N1	172.23 (12)	N2—Cu1—O2^{iii}	74.01 (10)
N2—Cu1—N1	94.50 (12)	N4^{ii}—Cu1—O2^{iii}	100.84 (9)
N4^{ii}—Cu1—N1	84.56 (11)	N1—Cu1—O2^{iii}	80.90 (10)
N3—Cu1—N4	95.68 (11)	N4—Cu1—O2^{iii}	167.40 (8)
N2—Cu1—N4	97.19 (11)		

Symmetry codes: (ii) $2 - x, 2 - y, -z$; (iii) $x, y - 1, z$; (iv) $1 - x, 2 - y, -z$.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.090$
$S = 1.04$
1859 reflections
125 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0497P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.58$ e Å^{-3}
$\Delta\rho_{\min} = -0.38$ e Å^{-3}

Table 3
Hydrogen-bonding and contact geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O1$^{\mathrm{v}}$	0.86 (3)	2.28 (3)	3.120 (4)	163 (3)
N2—H2*A*···N3$^{\mathrm{iv}}$	0.70 (3)	2.55 (3)	3.188 (4)	153 (3)
N2—H2*B*···O1$^{\mathrm{vi}}$	0.81 (4)	2.42 (4)	3.162 (4)	153 (3)
N2—H2*B*···O2$^{\mathrm{iii}}$	0.81 (4)	2.56 (3)	3.034 (4)	119 (3)
N1—H1*B*···N3$^{\mathrm{ii}}$	0.84 (4)	2.53 (4)	3.318 (4)	156 (4)

Symmetry codes: (ii) $2-x, 2-y, -z$; (iii) $x, y-1, z$; (iv) $1-x, 2-y, -z$; (v) $2-x, 1-y, -z$; (vi) $1-x, 1-y, -z$.

In (I), all the H atoms were constrained to an ideal geometry, with C3—H and C4—H distances of 0.97 Å and all other C—H distances 0.96 Å. In (II), the amine H atoms were found from a difference Fourier map and refined freely, with all other H atoms placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances of 0.97 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 China.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1183). Services for accessing these data are described at the back of the journal.

References

Boillot, M.-L., Kahn, O., O'Connor, C. J., Gouteron, J., Jeannin, S. & Jeannin, Y. (1985). *J. Chem. Soc. Chem. Commun.* pp. 178–180.
Bruker (2000). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Diaz, C., Ribas, J., Fallah, M. S. E., Solans, X. & Font-Bardiá, M. (2001). *Inorg. Chim. Acta*, **312**, 1–6.
Escuer, A., Font-Bardiá, M., Peñalba, E., Solans, X. & Vicente, R. (1999). *Inorg. Chim. Acta*, **286**, 189–196.
Grove, H., Julve, M., Lloret, F., Kruger, P. E., Törnroos, K. W. & Sletten, J. (2001). *Inorg. Chim. Acta*, **325**, 115–124.
Harding, C. J., Mabbs, F. E., MacInnes, E. J. L., McKee, V. & Nelson, J. (1996). *J. Chem. Soc. Dalton Trans.* pp. 3227–3230.
Hernández, M. L., Urtiaga, M. K., Barandika, M. G., Cortés, R., Lezama, L., Pinta, N. D. L., Arriortua, M. I. & Rojo, T. (2001). *J. Chem. Soc. Dalton Trans.* pp. 3010–3014.
Kahn, O., Mallah, T., Gouteron, J., Jeannin, S. & Jeannin, Y. (1989). *J. Chem. Soc. Dalton Trans.* pp. 1117–1126.
Kovbasyuk, L. A., Fritsky, I. O., Kokozay, V. N. & Iskenderov, T. S. (1997). *Polyhedron*, **16**, 1723–1729.
Mallah, T., Boillot, M.-L., Kahn, O., Gouteron, J., Jeannin, S. & Jeannin, Y. (1986). *Inorg. Chem.* **25**, 3058–3065.
Mauro, A. E., Klein, S. I., Saldaña, J. S., Simone, C. A. D., Zukerman-Schpector, J. & Castellano, E. E. (1990). *Polyhedron*, **9**, 2937–2939.
Otieno, T., Rettig, S. J., Thompson, R. C. & Trotter, J. (1993). *Inorg. Chem.* **32**, 4384–4390.
Real, J. A., Mollar, M., Ruiz, R., Faus, J., Lloret, F., Julve, M. & Philoche-Levisalles, M. (1993). *J. Chem. Soc. Dalton Trans.* pp. 1483–1488.
Rojo, T., Cortés, R., Lezama, L., Mesa, J. L., Via, J. & Arriortua, M. I. (1989). *Inorg. Chim. Acta*, **165**, 91–98.
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.
Vicente, R., Escuer, A., Peñalba, E., Solans, X. & Font-Bardiá, M. (1994). *J. Chem. Soc. Dalton Trans.* pp. 3005–3008.
Zukerman-Schpector, J., Castellano, E. E., De Simone, C. A., Oliva, G. & Mauro, A. E. (1991). *Acta Cryst.* C**47**, 957–959.