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## Key indicators

Single-crystal X-ray study  
 $T = 93\text{ K}$   
Mean  $\sigma(\text{O}-\text{N}) = 0.004\text{ \AA}$   
 $R$  factor = 0.034  
 $wR$  factor = 0.096  
Data-to-parameter ratio = 9.0For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.Hexaaquacopper(II) dinitrate: absence of  
Jahn–Teller distortion

In the title compound,  $[\text{Cu}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ , the geometry around the  $\text{Cu}^{\text{II}}$  ion is approximately octahedral, formed by six O atoms from the coordinated water molecules. The Cu–O distances are rather similar [2.014 (2)–2.084 (2) Å] and not related by symmetry. The Jahn–Teller effect is, at best, only weakly observed in this structure, in contrast to many other structures where the hexaaquacopper(II) ion has been characterized. An extensive mesh of hydrogen-bond interactions between the coordinated water molecules and nitrate ions is a feature of the structure and may limit the degree to which the Jahn–Teller effect can be observed.

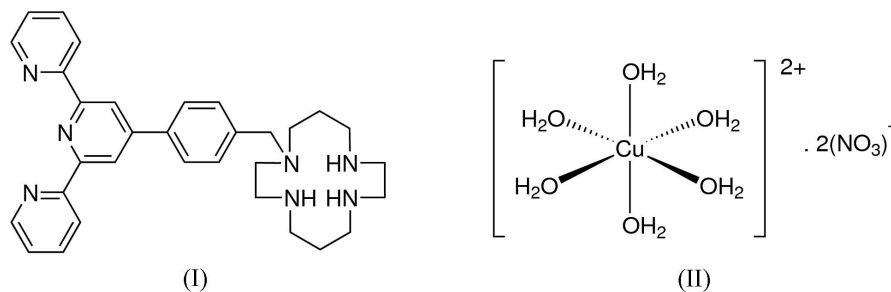
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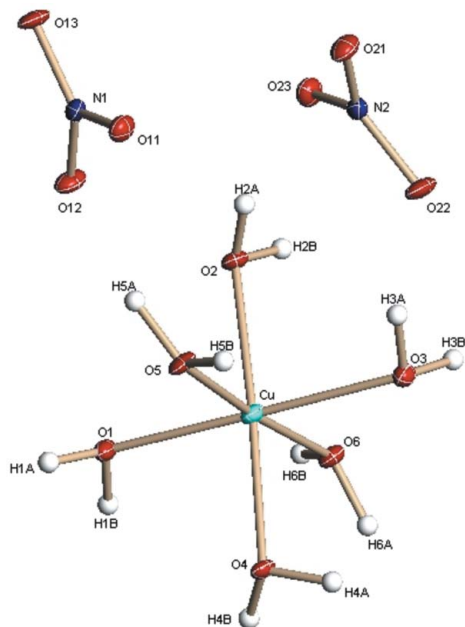
## Comment

During attempts to grow crystals of a copper complex of the ditopic ligand, 1-[4'-*p*-tolyl-(2,2':6',2''-terpyridyl)]-1,4,8,11-tetraazacyclotetradecane, (I) (Padilla-Tosta *et al.*, 2000), blue block-shaped crystals of  $[\text{Cu}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ , (II), formed instead from the reaction mixture. Attempts to grow similar crystals in the absence of the ditopic ligand proved unsuccessful, which leads us to speculate that the ditopic ligand may be influencing the crystallization process. Unfortunately, the vagaries of nucleation and crystal growth make it difficult to test this hypothesis. We report here the structure of the hexaaquacopper(II) complex as its dinitrate salt.



The asymmetric unit of (II) consists of a  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  cation and two nitrate anions. The geometry around the  $\text{Cu}^{2+}$  can be best described as octahedral, with bonds to six water molecules (Fig. 1 and Table 1). The Cu–O bond lengths are rather similar, falling in the range 2.014 (2)–2.084 (2) Å, and there is an extended hydrogen-bonding network that links the coordinated water molecules and the nitrate anions throughout the crystal structure (Fig. 2 and Table 2). Bond lengths and angles in the nitrate anions [1.233 (4)–1.272 (4) Å and 118.5 (3)–121.1 (3)°, respectively] are unremarkable, there being only small deviations from the ideal geometry.

The similarity of the Cu–O bond lengths is rather unusual in that Jahn–Teller distortion often leads to two of the copper-ligand bonds that lie along one axis being much longer than

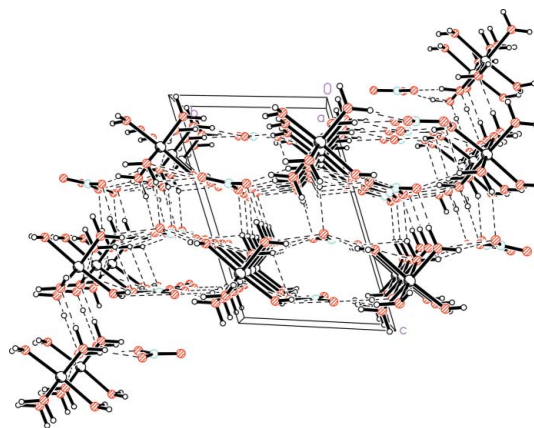


**Figure 1**

A perspective view of the title  $\text{Cu}^{\text{II}}$  complexes, (II), showing the atom-labelling scheme with 50% probability displacement ellipsoids. H atoms are drawn as small spheres of arbitrary radii.

the remaining four copper–ligand bonds. A number of Jahn–Teller-distorted hexaaquacopper(II) complexes have been characterized by X-ray crystallography, *viz.*  $X-3(\text{C}_2\text{H}_{10}\text{N}_2^{2+})-2(\text{O}_{12}\text{P}_4^{4-})$  (Averbuch-Pouchot & Durif, 1989),  $X-2(\text{ClO}_4^-)-2(\text{C}_6\text{H}_{10}\text{N}_2\text{O}_2)$  (Benedetti *et al.*, 1986),  $X-2(\text{C}_6\text{H}_4\text{Cl}-\text{O}_3\text{S}^-)$  (Bernardinelli *et al.*, 1991),  $X-2(\text{C}_7\text{H}_7\text{O}_3\text{S}^-)$  (Couldwell *et al.*, 1978),  $X-2(\text{C}_9\text{H}_9\text{O}_9\text{S}_3^{3-}-1.3(\text{H}_2\text{O}))$  (Dalrymple *et al.*, 2002),  $X-2(\text{C}_2\text{H}_{10}\text{N}_2^{2+})-\text{O}_{18}\text{P}_6^{6-}$  (Durif & Averbuch-Pouchot, 1989),  $X-\text{C}_6\text{H}_8\text{CuO}_{10}^{2-}$  (Filippova, 2000),  $X-2(\text{C}_{12}\text{H}_{10}\text{O}_4\text{P}^-)-2(\text{C}_2\text{H}_5\text{NO}_2)$  (Głowiak & Podgorska, 1986),  $X-\text{C}_{16}\text{H}_{16}-\text{CuO}_{10}^{2-}$  (Honghui *et al.*, 1988),  $X-\text{C}_{16}\text{H}_{16}\text{CuO}_{10}^{2-}$  (Kennard & Smith, 1989),  $X-2(\text{Cl}_4^-), 2(\text{H}_2\text{O})$  (Li *et al.*, 2004),  $X-2\text{Cl}^- - 2(\text{C}_{10}\text{H}_8\text{N}_2\text{O}_2)-2(\text{H}_2\text{O})$  (Ma *et al.*, 2001),  $X-2(\text{C}_7\text{H}_5\text{O}_6\text{S}^-)-2(\text{H}_2\text{O})$  (Ma *et al.*, 2003),  $X-2(\text{NH}_4^+)-2(\text{SO}_4^{2-})$  (Maslen *et al.*, 1988),  $X-2(\text{C}_{24}\text{H}_{44}\text{H}_{16}\text{O}_4\text{Pt}_4^{4+})-10(\text{ClO}_4^-)-9(\text{H}_2\text{O})$  (Navarro *et al.*, 2000),  $X-(\text{C}_6\text{H}_8\text{CuO}_{10}^{2+})$  (Rodríguez-Martin *et al.*, 2002),  $X-2(\text{C}_8\text{H}_{11}\text{N}_4\text{O}^+)-2(\text{SO}_4^{2-})-2(\text{H}_2\text{O})$  (Shamuratov *et al.*, 1993) and  $(X)_n-2n(\text{C}_5\text{H}_8\text{O}_4^-)-4n(\text{H}_2\text{O})$  (Zviedre *et al.*, 1985), where  $X$  is  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ . In these cases, the axial Cu–O bond lengths fall in the range 2.202–2.423 Å, in comparison with the equatorial bond lengths (1.945–2.084 Å). The mean axial bond length is between 8.7 and 24% longer than the mean equatorial bond length in these structures (the mean value of these percentage differences is 18.6% over 20 structures). In our structure, the mean bond length along the longest axis (O2–Cu–O4) is only 1.6% longer than that along the remaining axes.

We are aware of only six crystallographic studies of copper(II) complexes where static Jahn–Teller distortions are not observed in complexes where all six donors are otherwise identical, *viz.* in  $X-(\text{BrO}_3)_2$  (Blackburn *et al.*, 1991),  $\text{Cu}(\text{en})_3^{2+}-\text{SO}_4^{2-}$  (Cullen & Lingafelter, 1970),  $2\text{K}^+-\text{Pb}^{2+}-$

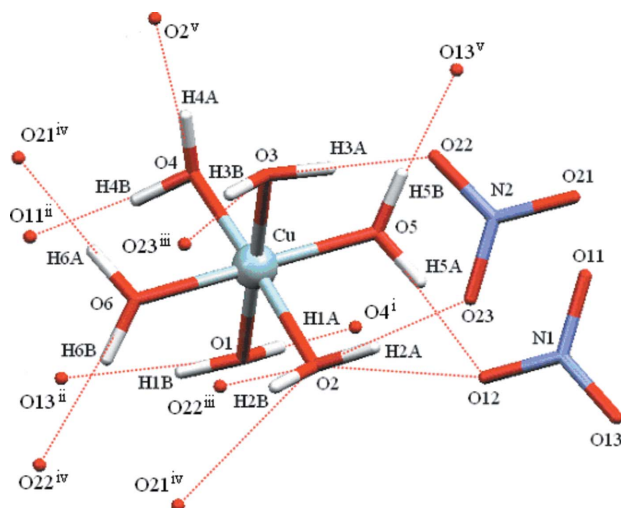


**Figure 2**

A packing diagram, showing hydrogen-bonding interactions (dashed lines) within the crystal structure of the complex. Key: Cu, N, O, and H atoms are shown with light blue (large), purple, red, and light blue (small) circles, respectively.

$\text{Cu}(\text{NO}_2)_6^{4-}$  (Cullen & Lingafelter, 1971),  $\text{Cu}[\{(\text{CH}_3)_2\text{N}\}_2\text{P}(\text{O})\text{OP}(\text{O})[\text{N}(\text{CH}_3)_2]_2]_3(\text{Cl}_4)_2$  (Joesten *et al.*, 1970),  $X-(\text{SiF}_6)^{2-}-6(\text{H}_2\text{O})$  (Ray *et al.*, 1973) and  $2\text{Tl}^+-\text{Pb}^{2+}-\text{Cu}(\text{NO}_2)_6^{2-}$  (Takagi *et al.*, 1976), where  $X$  is  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ . The structure we report further stands out from these other six because, in this case, the Cu atom lies on a general position, with all Cu–O bond lengths being independently refined. In the other six cases, the Cu atoms are located on special positions in higher symmetry space groups ( $P\bar{a}3$ ,  $P\bar{3}1c$ ,  $Fm\bar{3}$ ,  $P\bar{3}c1$ ,  $R\bar{3}$  and  $Fm\bar{3}$ , respectively).

Jahn–Teller distortion may not be observed in a crystallographic study if either there is disorder in the structure (so that a defined long axis is randomly distributed over the three orientations relative to the unit cell axes), or there is sufficient thermal motion to allow the long and short bonds in a structure to exchange over time (sometimes referred to as the dynamic Jahn–Teller effect). In these cases, the averaging inherent in the X-ray experiment (over spatial location in the crystal in the first case or time in the second) might be expected to manifest itself in the crystallographic modelling process as larger than expected anisotropic displacement parameters for the donor atoms along the direction of the copper–ligand bond. This effect has been discussed (Cullen *et al.*, 1970) and may be significant in a number of the literature cases (Blackburn *et al.*, 1991; Cullen *et al.*, 1971; Takagi *et al.*, 1976). Table 3 presents the anisotropic displacement parameters of Cu and the water O atoms in the structure of (II). The largest principal axes of the ellipsoids are not directed along the Cu–O bonds (Fig. 1). Taken together, these data strongly suggest the lack of Jahn–Teller distortion (static or dynamic) in the structure of (II). Here, three marginally longer Cu–O bonds (Cu–O2, Cu–O3 and Cu–O4) are meridionally distributed around the Cu atom, as are the Cu–O shorter bonds. The variation in the Cu–O bond lengths of the structure, and the absence of any significant Jahn–Teller effect, may be explained by the influence of the hydrogen-bonding network in the crystal structure of the complex (Fig. 3



**Figure 3**  
A perspective view of the Cu<sup>II</sup> complex, (II), showing the hydrogen-bonding interactions (dashed lines) involving the dication. [Symmetry codes: (i)  $-x, -y, -z$ ; (ii)  $x - 1, y - 1, z$ ; (iii)  $-x + 1, -y + 1, -z + 1$ ; (iv)  $x, y - 1, z$ ; (v)  $x - 1, y, z$ .]

and Table 2). All of the coordinated water molecules are involved in several hydrogen bonds, which means that, while the copper centre may not be in its lowest energy Jahn–Teller distorted state, this could be made up for by the large number of weak interactions that may each be marginally stronger in the less distorted structure.

## Experimental

A solution of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (50 mg) in ethanol (5 ml) was added to a cooled filtered solution of ligand *L*, (I) (0.15 g), in ethanol (5 ml). The reaction mixture was heated at reflux for 1 h, and, upon cooling to room temperature, afforded a blue–green insoluble precipitate (0.11 g). The precipitate was suspended in ethanol–water (1:1, 5 ml), then the mixture was filtered after it was heated to reflux for 1 h. The solution was allowed to cool to room temperature overnight. The solution was kept in a refrigerator for about two months during which time blue crystals of (II) suitable for X-ray analysis were produced. No crystals of (I) or its copper complex were produced in this way.

### Crystal data

$[\text{Cu}(\text{H}_2\text{O})_6](\text{NO}_3)_2$	$Z = 2$
$M_r = 295.67$	$D_x = 2.126 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 5.7404 (8) \text{ \AA}$	Cell parameters from 2722 reflections
$b = 7.6452 (10) \text{ \AA}$	$\theta = 2.9\text{--}26.4^\circ$
$c = 11.4655 (15) \text{ \AA}$	$\mu = 2.43 \text{ mm}^{-1}$
$\alpha = 106.428 (2)^\circ$	$T = 93 (2) \text{ K}$
$\beta = 98.399 (2)^\circ$	Block, blue
$\gamma = 101.504 (2)^\circ$	$0.55 \times 0.34 \times 0.12 \text{ mm}$
$V = 461.84 (11) \text{ \AA}^3$	

### Data collection

Bruker SMART CCD diffractometer	1556 independent reflections
$\varphi$ and $\omega$ scans	1494 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 1999)	$R_{\text{int}} = 0.020$
$T_{\text{min}} = 0.341, T_{\text{max}} = 0.744$	$\theta_{\text{max}} = 25.1^\circ$
2917 measured reflections	$h = -6 \rightarrow 6$
	$k = -8 \rightarrow 8$
	$l = -13 \rightarrow 13$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.034$   
 $wR(F^2) = 0.096$   
 $S = 0.91$   
 1556 reflections  
 172 parameters  
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0546P)^2 + 2.7318P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.60 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -1.14 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters ( $\text{\AA}, ^\circ$ ).

Cu—O5	2.014 (2)	N1—O11	1.241 (4)
Cu—O1	2.034 (2)	N1—O12	1.245 (4)
Cu—O6	2.041 (2)	N1—O13	1.268 (4)
Cu—O4	2.064 (2)	N2—O21	1.233 (4)
Cu—O3	2.074 (2)	N2—O23	1.252 (4)
Cu—O2	2.084 (2)	N2—O22	1.272 (4)
O5—Cu—O1	89.49 (10)	O6—Cu—O3	85.17 (10)
O5—Cu—O6	175.94 (10)	O4—Cu—O3	92.35 (10)
O1—Cu—O6	93.58 (10)	O5—Cu—O2	89.50 (10)
O5—Cu—O4	91.38 (10)	O1—Cu—O2	87.93 (10)
O1—Cu—O4	88.81 (10)	O6—Cu—O2	87.96 (10)
O6—Cu—O4	91.34 (10)	O4—Cu—O2	176.61 (9)
O5—Cu—O3	91.72 (10)	O3—Cu—O2	90.89 (10)
O1—Cu—O3	178.31 (10)		

**Table 2**

Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ ).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
O1—H1A...O4 <sup>i</sup>	0.98 (2)	1.91 (2)	2.894 (3)	179 (3)
O1—H1B...O13 <sup>ii</sup>	0.97 (2)	1.79 (2)	2.741 (4)	168 (4)
O2—H2B...O22 <sup>iii</sup>	0.98 (2)	2.12 (2)	3.038 (4)	156 (3)
O2—H2A...O23	0.98 (2)	2.00 (2)	2.940 (4)	162 (3)
O2—H2B...O21 <sup>iv</sup>	0.98 (2)	2.38 (3)	2.912 (4)	113 (3)
O3—H3A...O22	0.98 (2)	1.83 (2)	2.779 (4)	162 (3)
O3—H3B...O23 <sup>iii</sup>	0.97 (2)	1.88 (2)	2.827 (4)	167 (3)
O4—H4A...O2 <sup>v</sup>	0.97 (2)	1.99 (2)	2.942 (4)	167 (4)
O4—H4A...O1 <sup>v</sup>	0.97 (2)	2.60 (4)	3.070 (3)	110 (3)
O4—H4B...O11 <sup>ii</sup>	0.97 (2)	1.79 (2)	2.763 (4)	175 (3)
O5—H5A...O12	0.97 (2)	1.78 (2)	2.735 (3)	166 (4)
O5—H5A...N1	0.97 (2)	2.50 (3)	3.417 (4)	156 (3)
O5—H5A...O11	0.97 (2)	2.58 (3)	3.285 (3)	130 (3)
O5—H5B...O13 <sup>v</sup>	0.96 (2)	1.78 (2)	2.740 (4)	172 (4)
O5—H5B...N1 <sup>v</sup>	0.96 (2)	2.47 (2)	3.365 (4)	155 (3)
O5—H5B...O12 <sup>v</sup>	0.96 (2)	2.45 (3)	3.123 (3)	126 (3)
O6—H6B...O21 <sup>iv</sup>	0.98 (2)	2.44 (3)	3.154 (3)	130 (3)
O6—H6B...O22 <sup>iv</sup>	0.98 (2)	1.91 (2)	2.860 (4)	162 (4)
O6—H6B...N2 <sup>iv</sup>	0.98 (2)	2.51 (2)	3.436 (4)	157 (3)

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

**Table 3**

Selected anisotropic displacement parameters ( $\text{\AA}^2$ ).

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Cu	0.0058 (3)	0.0106 (3)	0.0126 (3)	0.00344 (18)	0.00374 (17)	0.00079 (17)
O1	0.0078 (12)	0.0084 (13)	0.0119 (12)	0.0020 (10)	0.0045 (10)	0.0012 (9)
O2	0.0050 (11)	0.0102 (13)	0.0130 (12)	0.0047 (10)	0.0024 (9)	0.0003 (9)
O3	0.0091 (12)	0.0099 (13)	0.0123 (12)	0.0032 (10)	0.0053 (10)	0.0027 (10)
O4	0.0052 (11)	0.0079 (13)	0.0134 (12)	0.0031 (10)	0.0035 (9)	0.0013 (9)
O5	0.0067 (12)	0.0120 (13)	0.0160 (13)	0.0076 (10)	0.0064 (10)	0.0021 (10)
O6	0.0058 (12)	0.0114 (13)	0.0137 (12)	0.0063 (10)	0.0046 (10)	0.0014 (9)

H atoms were located in a difference Fourier map. The O—H distances were restrained to 1.00 (2) Å, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$ . In the final difference map the deepest hole is located 0.89 Å from the Cu atom.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *MERCURY* (Version 1.4; Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXTL*.

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## References

- Averbuch-Pouchot, M. T. & Durif, A. (1989). *Acta Cryst.* **C45**, 46–49.
- Benedetti, E., Bavoso, A., Di Blasio, B., Pavone, V. & Pedone, C. (1986). *Inorg. Chim. Acta*, **123**, 155–159.
- Bernardinelli, G., Lucken, E. A. C. & Costines, M. (1991). *Z. Kristallogr.* **195**, 141–142.
- Blackburn, A. C., Gallucci, J. C. & Gerkin, R. E. (1991). *Acta Cryst.* **C47**, 1786–1789.
- Bruker (1999). *SADABS*, *SAINT-Plus* (Version 6.22) and *SMART* (Version 5.045), Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* **B58**, 389–397.
- Couldwell, C., Prout, K., Robey, D., Taylor, R. & Rossotti, F. J. C. (1978). *Acta Cryst.* **B34**, 1491–1499.
- Cullen, D. L. & Lingafelter, E. C. (1970). *Inorg. Chem.* **9**, 1858–1864.
- Cullen, D. L. & Lingafelter, E. C. (1971). *Inorg. Chem.* **10**, 1264–1268.
- Dalrymple, S. A., Parvez, M. & Shimizu, G. K. H. (2002). *Inorg. Chem.* **41**, 6986–6996.
- Durif, A. & Averbuch-Pouchot, M. T. (1989). *Acta Cryst.* **C45**, 1884–1887.
- Filippova, I. G. (2000). *Russ. J. Coord. Chem.* **26**, 276–280; translation of *Koord. Khim.* **26**, 295.
- Glowiak, T. & Podgorska, I. (1986). *Inorg. Chim. Acta*, **125**, 83–88.
- Honghui, W., Naijue, Z., Heng, F., Ronncchang, L. & Kui, W. (1988). *Sci. Sin. Ser. B: Chem. Biol. Agri. Med. Earth Sci. (Engl. Ed.)*, **31**, 20–27.
- Joesten, M. D., Hussain, M. S. & Lenhert, P. G. (1970). *Inorg. Chem.* **9**, 151–161.
- Kennard, C. H. L. & Smith, G. (1989). *Z. Kristallogr.* **188**, 63–68.
- Li, X. H., Xia, F. Y., Xiao, H. P. & Hu, M. L. (2004). *Acta Cryst.* **E60**, i31–i32.
- Ma, B.-Q., Sun, H.-L., Gao, S. & Xu, G.-X. (2001). *Inorg. Chem.* **40**, 6247–6253.
- Ma, J. F., Yang, J. & Liu, J. F. (2003). *Acta Cryst.* **E59**, m485–m486.
- Maslen, E. N., Watson, K. J. & Moore, F. H. (1988). *Acta Cryst.* **B44**, 102–107.
- Navarro, J. A., Freisinger, E. & Lippert, B. (2000). *Inorg. Chem.* **39**, 2301–2305.
- Padilla-Tosta, M. E., Lloris, J. M., Martinez-Manez, R., Benito, A., Soto, J., Pardo, T., Miranda, M. A. & Marcos, M. D. (2000). *Eur. J. Inorg. Chem.* 741–748.
- Ray, S., Zalkin, A. & Templeton, D. H. (1973). *Acta Cryst.* **B29**, 2748–2751.
- Rodriguez-Martin, Y., Sanchiz, J., Ruiz-Perez, C., Lloret, F. & Julve, M. (2002). *Cryst. Eng. Commun.* pp. 631–637.
- Shamuratov, E. B., Sharipov, K. T., Batsanov, A. S., Struchkov, Yu. T., Khudoyarov, A. B. & Mirdzhalalov, F. F. (1993). *Koord. Khim.* **19**, 155–159. (In Russian.)
- Sheldrick, G. M. (2001). *SHELXTL*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Takagi, S., Joesten, M. D. & Lenhert, P. G. (1976). *Acta Cryst.* **B32**, 326–328.
- Zviedre, I., Bel'skii, V. K. & Shvarts, E. M. (1985). *Latv. PSR Zinat. Akad. Vestis Kim. Ser.* pp. 672–677. (In Russian.)