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Diacetonitrile-1κN,3κN-bis{μ-*trans*-*N*-[3-(dimethylamino)propyl]-*N*′-(2-hydroxyethyl)oxamidato(2–)}-1:2$\kappa^5 N,N',O:O',N''$;2:3$\kappa^5 O',N'':N,N',O$-dithiocyanato-1κN,3κN-tricopper(II)

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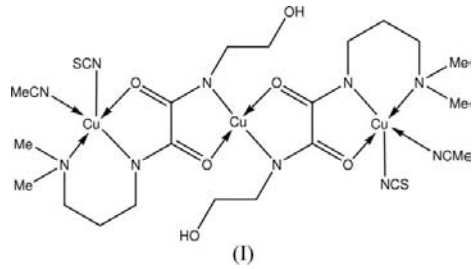
The title compound, $[Cu_3(C_9H_{17}N_3O_3)_2(NCS)_2(CH_3CN)_2]$, contains two square-pyramidal Cu^{II} units chelated by a *transoid* asymmetrical *N*-[3-(dimethylamino)propyl]-*N*′-(2-hydroxyethyl)oxamidate (dmapheoxd) dianion {H_2dmapheoxd is *N*-[3-(dimethylamino)propyl]-*N*′-(2-hydroxyethyl)oxamide}, which coordinates to another Cu^{II} ion in a square-planar environment lying on a crystallographic inversion center. Thus, the *trans*-oxamide ligand bridges two Cu^{II} ions with different coordination numbers, and this is the first instance of such a zero-dimensional oxamide-bridged complex. The activated methyl group in the coordinated acetonitrile molecule is involved in a strong nonclassical C—H···O hydrogen bond, which contributes to a one-dimensional chain extending in the *b* direction. Considering the presence of weak bonding between the Cu atom and the uncoordinated hydroxyl O atoms, a two-dimensional structure is formed parallel to the *ab* plane.

Comment

Symmetrical *N*,*N*′-disubstituted oxamides have been fully studied and are known to be versatile organic ligands which can both chelate and bridge metal ions to construct discrete and extended structures (Bencini *et al.*, 1986; Dominguez-Vera *et al.*, 1996; Real *et al.*, 1994; Sanz *et al.*, 1996). Compared with the large number of complexes bridged by symmetrical *N*,*N*′-disubstituted oxamides, only 11 complexes bridged by asymmetrical *N*,*N*′-disubstituted oxamides have been characterized to date by single-crystal X-ray diffraction (Table 3) [Cambridge Structural Database (CSD), Version 5.28; Allen, 2002]. In these complexes, all the asymmetrical ligands contain aromatic terminal groups, while no asymmetrical *N*,*N*′-bis-(aminoalkyl)oxamide has been found. Taking the above facts into account, we synthesized a novel asymmetrical ligand, *viz*. *N*-[3-(dimethylamino)propyl]-*N*′-(2-hydroxyethyl)oxamide (H_2dmapheoxd), and its tricopper complex, $[Cu_3(dmapheoxd)_2(NCS)_2(MeCN)_2]$, (I), and report the crystal structure of the complex here.



(I)

The molecular structure of complex (I) is illustrated in Fig. 1. Selected bond lengths and angles are listed in Table 1. Compound (I), a trinuclear Cu^{II} complex, is formed by two *trans*-oxamidate-chelated $[Cu(dmapheoxd)(NCS)(MeCN)]^-$ anionic units as ligands coordinating another Cu^{II} ion (Cu1) lying on a crystallographic inversion center. The central Cu^{II} atom (Cu1) is in a square-planar environment. However, considering the longer inversion-related Cu1···O1 interactions of 2.896 (7) Å to atoms O1 at ($x+1$, y, z) and ($-x-1$, $-y$, $-z$), Cu1 is in a classical [4+2] octahedral environment, and a one-dimensional chain extending in the *a* direction is formed. In the complex ligand, the outer Cu^{II} ion (Cu2) has a slightly distorted $[CuN_4O]$ square-pyramidal coordination geometry. The basal plane is defined by atom N4 of the SCN^- ligand and by three atoms (O2, N2 and N3) from the dmapheoxd ligand, with a maximum deviation of 0.013 (3) Å for atom O2 from the least-squares plane. The apical position

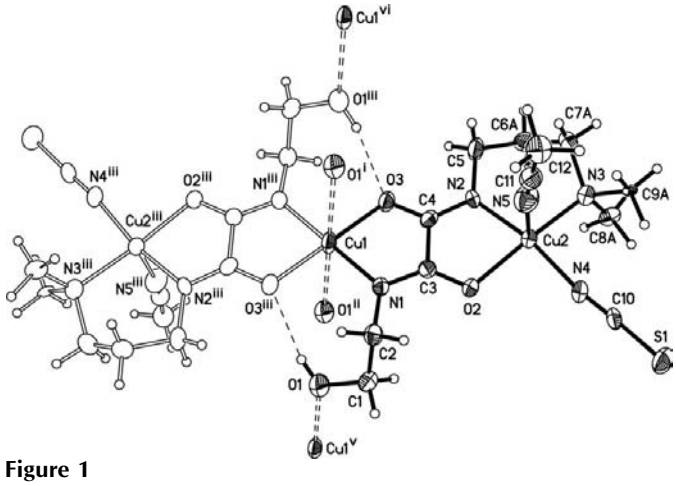


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen bonds and weak Cu—O bonds are shown as dotted and double-dotted lines, respectively. Disordered atoms C6*B*–C9*B* and C6B^{iii}–C9B^{iii} have been omitted for clarity. [Symmetry codes: (i) $x+1$, y, z; (ii) $-x-1$, $-y$, $-z$; (iii) $-x$, $-y$, $-z$; (v) $x-1$, y, z; (vi) $-x+1$, $-y$, $-z$.]

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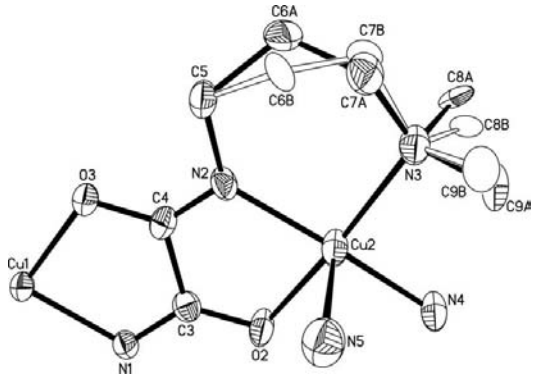

Figure 2
The positional disorder of the dimethylaminopropyl group in the dmapheoxd ligand. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

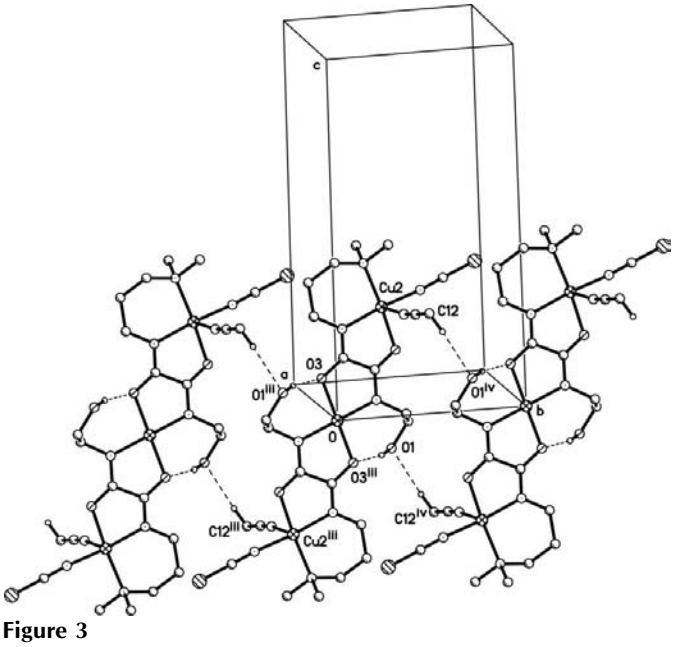

Figure 3
The one-dimensional chain extending in the *b* direction. H atoms not involved in hydrogen bonding have been omitted for clarity. [Symmetry codes: (iii) $-x, -y, -z$; (iv) $-x, -y+1, -z$.]

is occupied by atom N5 of a coordinated acetonitrile molecule. In the basal plane, the Cu2—N2(amide) bond [1.972 (6) Å] is shorter than the Cu2—N3(amine) bond [2.052 (9) Å], which is consistent with the stronger donor ability of the deprotonated amide N atom compared with the amine N atom (Jubert *et al.*, 2002). The axial Cu—N bond length [Cu2—N5 = 2.390 (9) Å] is significantly longer than those in the basal plane, from which atom Cu2 is displaced by 0.177 (3) Å towards the apex. The Cu1···Cu2 distance is 5.248 (3) Å.

Although several examples have been observed of *cis*-oxamide bridging ligands chelating two metal ions with different coordination numbers (Cronin *et al.*, 1999; Sun *et al.*, 2007; Tao, Zang, Cheng *et al.*, 2003), for *transoid* ligands the metal ions usually have equal ligancy, such as both five or both four (denoted [5+5] and [4+4], respectively). Among the reported crystal structures of *trans*-oxamide bridging complexes, only two two-dimensional complexes have the coordination modes [4+5] (Chen *et al.*, 1998) and [5+6] (Chen *et al.*, 1994). The title compound also has the coordination mode [4+5], and it is the first instance of a zero-dimensional complex with different ligancies. The hydroxyl group in the dmapheoxd ligand acts as a donor of the intramolecular hydrogen bond [O1—H1···O3^{iii}; symmetry code: (iii) $-x, -y, -z$; Table 2] and a seven-membered hydrogen-bonding circuit is formed (Fig. 1), folding at C2···O3^{iii} with a dihedral angle of 59.2 (3)°.

The distances C3—N1 [1.307 (9) Å] and C4—N2 [1.275 (9) Å] have typical C═N values. Whereas the bond lengths of C3—O2 [1.262 (9) Å] and C4—O3 [1.291 (8) Å] are in accordance with those of (O═)C—O$^-$ fragments in many complexes (Berg *et al.*, 2002; Delgado *et al.*, 2006; Nash & Schaefer, 1969), the oxamide fragment is best described as N═C—O$^-$ rather than delocalized.

The dimethylaminopropyl group in the dmapheoxd ligand is disordered over two positions (C6*A*–C9*A* and C6*B*–C9*B*), with occupancy factors of 0.55 and 0.45, respectively (Fig. 2). The puckering parameters (Cremer & Pople, 1975) of the corresponding six-membered chelating rings around Cu2 are Q = 0.575 (19) Å, θ = 142.7 (14)° and φ = 26 (2)°, and Q = 0.698 (15) Å, θ = 68.5 (10)° and φ = 196.5 (11)°, respectively.

In the crystal structure, only one classical hydrogen bond is observed, as noted above (Table 2). Nevertheless, due to the activation of the methyl group by the cyano group of the acetonitrile ligand, the methyl group interacts with the O atom of the hydroxyl group of a neighboring molecule, forming a nonclassical C—H···O hydrogen bond (Fig. 3), *via* which a one-dimensional chain extending in the *b* direction is formed. On the other hand, considering the presence of weak bonding between atom Cu1 and the uncoordinated hydroxyl O atoms, a two-dimensional structure is formed parallel to the *ab* plane.

Experimental

All reagents were of AR grade and were used without further purification. For the synthesis of the H_2dmapheoxd ligand, an ethanol solution (10 ml) of 3-dimethylamino-1-propylamine (1.26 ml, 10 mmol) was added very slowly, *via* a dropping funnel, to an ethanol solution (10 ml) of diethyl oxalate (1.36 ml, 10 mmol) with continuous stirring. The mixture was stirred quickly for 30 min, and then an ethanol solution (10 ml) containing enthanolamine (0.60 ml) was added dropwise. The reaction solution was stirred at room temperature for 3 h. The resulting solution was concentrated under vacuum and H_2dmapheoxd precipitated as a white powder (yield 78%).

For the preparation of the title compound, (I), piperidine (0.2 mmol) and a solution of $CuCl_2{\cdot}2H_2O$ (0.0256 g, 0.15 mmol) in acetonitrile (5 ml) were added successively to a solution of H_2dmapheoxd (0.0217 g, 0.1 mmol) in acetonitrile (5 ml). The mixture was stirred quickly for 30 min and then an acetonitrile solution (5 ml) containing KSCN (0.0098 g, 0.1 mmol) was added dropwise. The reaction solution was stirred continuously at 333 K for a further 5 h. Green crystals of the title complex suitable for X-ray analysis were obtained from the solution after slow evaporation at room temperature for 7 d (yield 70%). Elemental analysis calculated

for $C_{24}H_{40}Cu_3N_{10}O_6S_2$: C 35.18, H 4.92, N 17.09%; found: C 35.28, H 4.99, N 17.04%.

Crystal data

$[Cu_3(C_9H_{17}N_3O_3)_2(NCS)_2(C_2H_3N)_2]$
M_r = 819.45
Triclinic, $P\overline{1}$
a = 6.040 (5) Å
b = 8.262 (6) Å
c = 17.256 (13) Å
α = 91.999 (10)°
β = 97.831 (10)°
γ = 96.185 (10)°
V = 847.1 (11) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 2.04 mm^{-1}
T = 298 (2) K
0.19 × 0.12 × 0.08 mm

Data collection

Bruker APEX area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.698, T_{max} = 0.854
4458 measured reflections
2987 independent reflections
1649 reflections with $I > 2\sigma(I)$
R_{int} = 0.048

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	1.954 (6)	Cu2—N4	1.948 (7)
Cu1—O3	1.964 (5)	Cu2—N5	2.390 (9)
Cu2—N2	1.972 (6)	Cu2—O2	2.015 (6)
Cu2—N3	2.052 (7)	Cu1···O1^{i}	2.896 (7)
N1^{iii}—Cu1—O3	95.2 (2)	N4—Cu2—N5	92.1 (3)
N1—Cu1—O3	84.8 (2)	N4—Cu2—O2	89.1 (2)
O2—Cu2—N3	169.2 (2)	N4—Cu2—N3	91.5 (3)
O2—Cu2—N5	91.4 (3)	C2—N1—Cu1	128.6 (5)
N2—Cu2—N3	95.0 (3)	C3—N1—C2	118.6 (6)
N2—Cu2—N5	97.0 (3)	C3—N1—Cu1	112.7 (5)
N2—Cu2—O2	82.7 (2)	C4—N2—C5	118.0 (6)
N3—Cu2—N5	99.3 (3)	C4—N2—Cu2	113.6 (5)
N4—Cu2—N2	167.9 (3)	C5—N2—Cu2	127.9 (5)
N4—Cu2—N3	91.5 (3)		

Symmetry code: (i) $x+1, y, z$; (iii) $-x, -y, -z$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O3^{iii}	0.85	2.15	2.985 (8)	168
C12—H12C···O1^{iv}	0.96	2.39	3.320 (11)	163

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

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.063
$wR(F^2)$ = 0.175
S = 1.00
2987 reflections
247 parameters
19 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.63 e Å^{-3}
$\Delta\rho_{min}$ = −0.49 e Å^{-3}

The hydroxyl H atom was located in a difference Fourier map and treated as riding, with O—H = 0.85 Å and U_{iso}(H) = 0.08 Å^2. The remaining H atoms were placed in calculated positions, with C—H = 0.96 (methyl) or 0.97 Å (methylene), and refined in riding mode, with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(methyl C). The CH_3 groups were allowed to rotate freely. Atoms C6, C7, C8 and C9 of the *N*-[3-(dimethylamino)propyl] group appeared to be disordered and were refined as two parts (occupancy factors = 0.55 and 0.45).

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3136). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Bencini, A., Benelli, C., Fabretti, A. C., Frachini, G. & Gatteschi, D. (1986). *Inorg. Chem.* **25**, 1063–1066.
Berg, K. E., Pellegrin, Y., Blondin, G., Ottenwaelder, X., Journaux, Y., Canovas, M. M., Mallah, T., Parsons, S. & Aukauloo, A. (2002). *Eur. J. Inorg. Chem.* **2**, 323–325.
Bruker (2002). *SAINT* (Version 6.02) and *SMART* (Version 5.62). Bruker AXS Inc., Madison, Wisconsin, USA.
Chen, Z.-N., Liu, S.-X., Qiu, J., Wang, Z.-M., Huang, J.-L. & Tang, W.-X. (1994). *J. Chem. Soc. Dalton Trans.* pp. 2989–2993.
Chen, Z.-N., Zhang, H.-X., Su, C.-Y., Zhou, Z.-Y., Zheng, K.-C. & Kang, B.-S. (1998). *Inorg. Chem.* **37**, 3877–3880.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Cronin, L., Mount, A. R., Parsons, S. & Robertson, N. (1999). *J. Chem. Soc. Dalton Trans.* pp. 1925–1927.

Table 3
The 11 previously reported complexes bridged by asymmetrical *N*,*N*′-disubstituted oxamides.

Complex	CSD refcode	Substituent 1 of the oxamide ligand	Substituent 2 of the oxamide ligand
$[MnCu(obzp)(H_2O)_3]_n\cdot nH_2O$[a]	JASNOG	Benzoate	Propionate
$[MnCu(obze)(H_2O)_4]\cdot 2H_2O$[b]	KOCYUW	Benzoate	Ethanoate
$[CoCu(obze)(H_2O)_4]\cdot 2H_2O$[c]	PIWZOK	Benzoate	Ethanoate
$\{[Cu_2(oxbe)_2(DMF)]Mn(H_2O)\}_n\cdot nDMF\cdot nH_2O$[d]	TUSWOT	Benzoate	2-Aminoethyl
$\{[Cu(oxbe)]_2Co(H_2O)_2\}\cdot 2DMF\cdot$DMA[e]	BAZDIQ	Benzoate	2-Aminoethyl
$\{[Ni(oxbe)]_2Ni(H_2O)_2\}\cdot 2.5$DMF[f]	ULOQIV	Benzoate	2-Aminoethyl
$\{[Cu(oxbe)(py)]_2Ni(py)_2\}\cdot 2$DMF[g]	ABOCAW	Benzoate	2-Aminoethyl
$\{[Ni(oxbe)]_2Cu(H_2O)_2\}\cdot 2.5$DMF[h]	OBUCIY	Benzoate	2-Aminoethyl
$\{[Cu(oxbp)]_2Co(H_2O)_2\}\cdot 1.5DMF\cdot 0.5H_2O$[i]	IYEWIS	Benzoate	3-Aminopropyl
$\{Na_2[Cu(oxbp)]_2(H_2O)\}_n\cdot nH_2O$[j]	NAQWAE	Benzoate	3-Aminopropyl
$[Sn_2(oxhh)(phenyl)_4]$[k]	QEHNIB	2-Hydroxyphenyl	2-Hydroxy-1-methyl-2-phenylethyl

Notes: (*a*) Pei *et al.* (1989) (obzp is oxamido-*N*-benzoato-*N*′-propionate); (*b*) Pei *et al.* (1991) (obze is oxamido-*N*-benzoato-*N*′-ethanoate); (*c*) Larionova *et al.* (1997); (*d*) Zang *et al.* (2003) [oxbe is *N*-benzoato-*N*′-(2-aminoethyl)oxamide; DMF is dimethylformamide]; (*e*) Tao, Zang, Hu *et al.* (2003) (DMA is dimethylamine); (*f*) Tao, Zang, Cheng *et al.* (2003); (*g*) Tao, Zang *et al.* (2004) (py is pyridine); (*h*) Tao, Mei *et al.* (2004); (*i*) Tao, Zang, Mei *et al.* (2003) [oxbp is *N*-benzoato-*N*′-(3-aminopropyl)oxamide]; (*j*) Matović *et al.* (2005); (*k*) Jiménez-Pérez *et al.* (2006) [H_4oxhh is (1*S*,2*R*)-(−)-*N*-(2-hydroxy-1-methyl-2-phenylethyl)-*N*′-(2-hydroxyphenyl)oxamide].

Delgado, F. S., Kerbellec, N., Ruiz-Peres, C., Cano, J., Lloret, F. & Julve, M. (2006). *Inorg. Chem.* **45**, 1012–1020.
Dominguez-Vera, J. M., Gulvez, N., Colacio, E., Cuesta, R., Costes, J. P. & Laurent, J. P. (1996). *J. Chem. Soc. Dalton Trans.* pp. 861–865.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Jiménez-Pérez, V. M., Nöth, H., Ariza-Castolo, A., Flores-Parra, A. & Contreras, R. (2006). *J. Organomet. Chem.* **691**, 1584–1589.
Jubert, C., Mohamadou, A., Gërard, C., Brandes, S., Tabard, A. & Barbier, J. P. (2002). *J. Chem. Soc. Dalton Trans.* pp. 2660–2669.
Larionova, J., Chavan, S. A., Yakhmi, J. V., Frøystein, A. G., Sletten, J., Sourisseau, C. & Kahn, O. (1997). *Inorg. Chem.* **36**, 6374–6381.
Matović, Z. D., Miletić, V. D., Samardžić, G., Pelosi, G., Ianelli, S. & Trifunović, S. (2005). *Inorg. Chim. Acta*, **358**, 3135–3144.
Nash, C. P. & Schaefer, W. P. (1969). *J. Am. Chem. Soc.* **91**, 1319–1324.
Pei, Y., Kahn, O., Nakatani, K., Codjovi, E., Mathonière, C. & Slettent, J. (1991). *J. Am. Chem. Soc.* **113**, 6558–6564.
Pei, Y., Nakatani, K., Kahn, O., Sletten, J. & Renard, J. P. (1989). *Inorg. Chem.* **28**, 3170–3175.
Real, J. A., Ruiz, R., Faus, J., Lloret, F., Julve, M., Journaux, Y., Philochelevisalles, M. & Bois, C. (1994). *J. Chem. Soc. Dalton Trans.* pp. 3769–3773.
Sanz, J. L., Cervera, B., Ruiz, R., Bois, C., Faus, J., Lloret, F. & Julve, M. (1996). *J. Chem. Soc. Dalton Trans.* pp. 1359–1366.
Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Siemens (1994). *XP*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sun, W., Li, Y.-T., Wu, Z.-Y. & Xiao, N.-Y. (2007). *Acta Cryst.* C**63**, m111–m113.
Tao, R.-J., Mei, C.-Z., Zang, S.-Q. & Niu, J.-Y. (2004). *Chin. J. Struct. Chem. (Jiegou Huaxue)*, **23**, 936–939.
Tao, R.-J., Zang, S.-Q., Cheng, Y.-X., Wang, Q.-L., Hu, N.-H., Niu, J.-Y. & Liao, D.-Z. (2003). *Polyhedron*, **22**, 2911–2916.
Tao, R.-J., Zang, S.-Q., Hu, N.-H., Wang, Q.-L., Cheng, Y.-X., Niu, J.-Y. & Liao, D.-Z. (2003). *Inorg. Chim. Acta*, **353**, 325–331.
Tao, R.-J., Zang, S.-Q., Mei, C.-Z., Wang, Q.-L., Lou, B.-Y., Niu, J.-Y., Cheng, Y.-X. & Liao, D.-Z. (2003). *J. Cluster Sci.* **14**, 459–469.
Tao, R.-J., Zang, S.-Q., Wang, Q.-L., Cheng, Y.-X., Niu, J.-Y. & Liao, D.-Z. (2004). *J. Coord. Chem.* **57**, 947–953.
Zang, S.-Q., Tao, R.-J., Wang, Q.-L., Hu, N.-H., Cheng, Y.-X., Niu, J.-Y. & Liao, D.-Z. (2003). *Inorg. Chem.* **42**, 761–766.