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Three oxo complexes with a tetranuclear $[Cu_4(\mu_2\text{-}Cl)_6(\mu_4\text{-}O)]$ unit

Piedad Cortés,[a]* Ana María Atria,[a] María Teresa Garland[b,c] and Ricardo Baggio[d]

[a]Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Santiago, Chile, [b]CIMAT, Universidad de Chile, Santiago, Chile, [c]Departamento de Física, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Santiago, Chile, and [d]Departamento de Física, Comisión Nacional de Energía Atómica, Buenos Aires, Argentina
Correspondence e-mail: pcortes@ciq.uchile.cl

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The three title compounds, namely 4-phenyl-1*H*-imidazolium hexa-μ_2-chloro-chloro-μ_4-oxo-tris(4-phenyl-1*H*-imidazole-κN^1)tetracopper(II) monohydrate, $(C_9H_9N_2)[Cu_4Cl_7O(C_9H_8N_2)_3]\cdot H_2O$, hexa-$\mu_2$-chloro-$\mu_4$-oxo-tetrakis(pyridine *N*-oxide-κO)tetracopper(II), $[Cu_4Cl_6O(C_5H_5NO)_4]$, and hexa-μ_2-chloro-tetrakis(2-methyl-1*H*-imidazole-κN^1)-μ_4-oxo-tetracopper(II) methanol trisolvate, $[Cu_4Cl_6O(C_4H_6N_2)_4]\cdot 3CH_4O$, exhibit the same Cu_4OCl_6 framework, where the O atom at the centre of an almost regular tetrahedron bridges four copper cations at the corners. This group is in turn surrounded by a Cl_6 octahedron, leading to a rather globular species. This special arrangement of the Cu^{II} cations results in a diversity of magnetic behaviours.

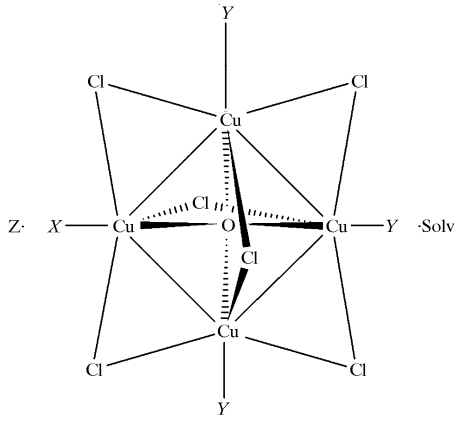
Comment

Polynuclear Cu^{II} complexes with various bridges between the metal centres have attracted much attention in the past decade, from both an experimental and a theoretical point of view, and a significant amount of research has been devoted to analysing their structural and magnetic properties.

We have for some time focused our interest on a subset of these systems, namely the $[Cu_4Cl_6OL_4]$ complexes, where *L* denotes any Lewis base ligand. They contain both a μ_4-bridging O atom and μ_2-halogen atoms in their structures, and are usually characterized by an interesting magnetic behaviour, not always easy to model. In this context, our group presented some years ago a detailed study of one such complex, *viz.* $[Cu_4Cl_6OL_4]$ (*L* is imidazole; Atria *et al.*, 1999), where the magnetic properties exhibited by the compound were successfully modelled in a rather simple and elegant fashion.

The structural complexity of these $[Cu_4Cl_6OL_4]$ systems, as well as their challenging magnetic properties, promoted sustained structural work on the subject, as disclosed by a search of the Cambridge Structural Database (CSD; Version of November 2005 and updates; Allen, 2002), which yielded 52 hits of related structures, ranging from the pioneering works performed some 40 years ago (Bertrand, 1967; Kilbourn & Dunitz, 1967) to the most recent ones (*viz*. Lyakhov *et al.*, 2004; Sun *et al.*, 2004; Skorda *et al.*, 2005).

We describe here the crystal and molecular structures of another three copper complexes sharing the same highly symmetric Cu_4OCl_6 framework and formulated as (HPhIm)·$(Cu_4Cl_6O)Cl(PhIm)_3\cdot H_2O$, (I), $(Cu_4Cl_6O)(PyNO)_4$, (II), and $(Cu_4Cl_6O)(MeIm)_4\cdot 3CH_3OH$, (III) (PhIm is 4-phenylimidazole, PyNO is pyridine *N*-oxide and MeIm is 2-methylimidazole). The present work should be considered as the introductory structural part of a comprehensive magneto-structural study, and it will be followed by magnetic studies and associated modelling, to be reported elsewhere.



(I) X=Cl^-; Y=Phlm; Z=$HPhlm^+$; Solv=H_2O
(II) X=Y=PyNO; Solv: $0.2H_2O$
(III) X=Y=Melm; Solv: 3MeOH
Phlm: 4-phenylimidazole;
PyNO: pyridine *N*-oxide;
Melm: 2-methylimidazole

Figs. 1–3 show individual ellipsoid plots of the three compounds [Fig. 2, in particular, shows only one of the two very similar independent molecules in (II), hereafter referred to as (II) and (II′)], while Tables 1, 3 and 4 provide selected bond distances and angles of the central cores. Tables 2 and 5 present some hydrogen-bonding interactions for (I) and (III). In all three structures, the four Cu atoms bound to O1 define an almost perfect tetrahedron with the O atom at its centre, while each chloride anion coordinates to two different Cu*i*/Cu*j* cations and lies at the bisector of the corresponding Cu*i*—O1—Cu*j* angles. The Cl_6 array defines a nearly perfect octahedron, centred at, though beyond bonding distance to, atom O1 and interpenetrating the copper tetrahedron. The major differences found in the complexes are due to the external ligands attached to copper, *viz.* three PhIm groups and one chloride ion in (I), four PyNO groups in (II), and four MeIm groups in (III). This situation makes (I) unique in the sense that, since the fourth ligand is an anion, the complete globular core becomes an anion itself, requiring a charged $HPhIm^+$ cation as a counter-ion to achieve charge balance. The other two cores, instead, are neutral.

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Each metal centre is five-coordinate, with τ parameters (Addison *et al.*, 1984) showing coordination geometries biased towards an irregular trigonal bipyramid (ideal τ = 1) rather than to a square pyramid (ideal τ = 0). The observed τ ranges are 0.74–0.87 for (I), 0.62–0.84 for (II) and 0.64–0.82 for (III).

In all cases, the trigonal base is defined by three chloride ions [mean Cu—Cl = 2.41 (6), 2.41 (8), 2.42 (11) and 2.42 (4) Å for (I), (II), (II′) and (III), respectively], the O atom occupying one of the apical positions [mean Cu—O = 1.909 (9), 1.90 (3), 1.90 (2) and 1.913 (5) Å]. The remaining apex is, in turn, filled either by an aromatic N atom [from PhIm in (I), except for Cu4, where the site is occupied by Cl7, or from MeIm in (III)] or by an O atom [from PyNO in (II)] [mean Cu—N = 1.921 (7) and 1.947 (11) Å for (I) and (III); mean Cu—O = 1.910 (19) and 1.904 (16) Å for (II) and (II′)].

The cage structure is such that all Cu^{II} cations are at similar distances from each other, *viz*. the shortest diagonal of the six rhomboidal Cu—O—Cu—Cl loops in the Cu_4OCl_6 cage. The intermetallic distances span the ranges 3.0658 (10)–3.1563 (10), 3.0778 (15)–3.1316 (14), 3.0358 (16)–3.1673 (17) and 3.0945 (9)–3.1436 (9) Å. These differences are among the largest reported in similar structures [the maximum being 3.061–3.197 Å for the 7-azaindole analogue to the compounds reported here (Poitras & Beauchamp, 1992)].

Table 6 compares the mean values of the Cu—O and Cu—Cl core bond distances in all reported cases in the CSD with those in the structures presented here. The similarity is apparent, confirming the rigidity of the Cu_4OCl_6 nucleus.

The external ligands do not exhibit any non-standard features worth mentioning.

The crystal structures of (I) and (III) are stabilized by different solvents molecules and counter-ions, *viz*. an $HPhIm^+$ ion and a (disordered) water molecule in (I), and three methanol molecules (one of them disordered) in (III). Owing to their different capabilities for hydrogen bonding and π contacts, these species interact with neighbouring molecules in quite a diverse way, leading to different non-bonding interaction schemes. Structure (I) contains a number of medium strength N—H$\cdots X$ bonds (X = Cl and O; Table 2), which organize the molecules into broad two-dimensional structures parallel to $(\bar{1}10)$. A similar situation is found in (III), with the difference that here the strongest N—H$\cdots X$ bonds (Table 5) determine by themselves the three-dimensional structure. Finally, in structure (II), there are no significant intermolecular interactions.

In spite of the fact that measurement of the magnetic susceptibility as a function of temperature showed that all three compounds follow the Curie–Weiss law, they have dissimilar magnetic properties. Evaluation of these behaviours, as well as a search for adequate fitting models, is in progress.

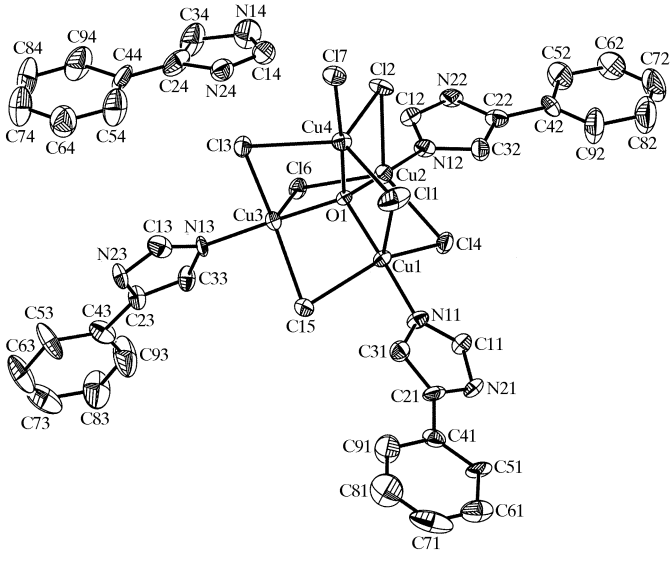

Figure 1
A displacement ellipsoid plot of (I) (30% probability level).

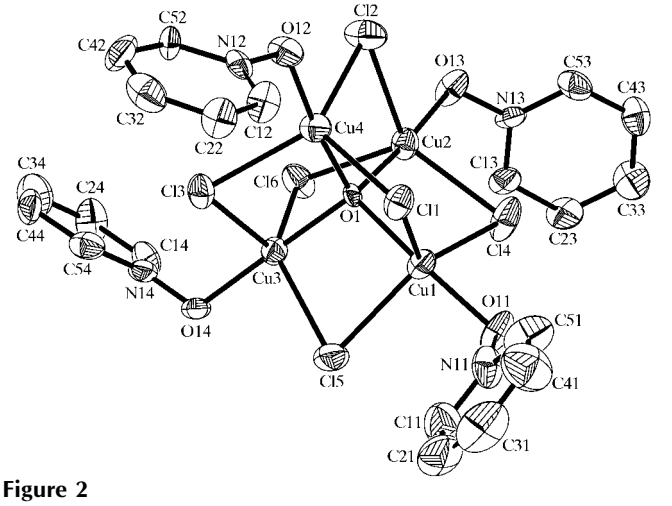

Figure 2
A displacement ellipsoid plot of one of the (very similar) independent moieties in (II), as representative of both (30% probability level).

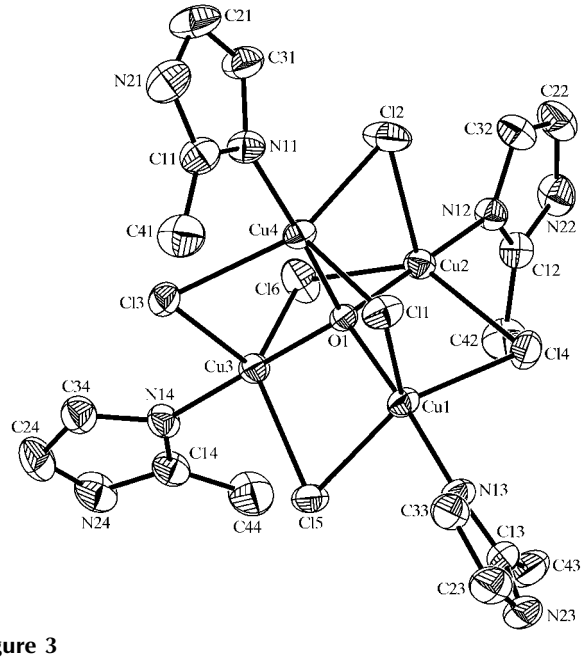

Figure 3
A displacement ellipsoid plot of (III) (30% probability level).

Experimental

All chemicals and reagents are commercially available and were used as received without further purification. The three copper(II) complexes were synthesized according to a previously reported method (Atria *et al.*, 1999). A methanol solution of the organic ligand (1 mmol) was added with constant stirring to a solution containing copper chloride (1 mmol) in the same solvent. The resulting solution was refluxed for 45 min. Single crystals suitable for X-ray analysis were obtained by slow evaporation of a solution of the complex in methanol. Analysis calculated for (I): C 38.95, H 2.82, N 10.09%; found C 38.70, H 2.78, N 9.89%; calculated for (II): C 27.71, H 2.37, N 6.46%; found C 27.69, H 2.11, N 6.25%; calculated for (III): C 25.15, H 4.00, N 12.34%; found: C 24.99, H 3.87, N 12.07%.

Compound (I)

Crystal data

$(C_9H_9N_2)[Cu_4Cl_7O(C_9H_8N_2)_3]\cdot H_2O$
M_r = 1114.03
Triclinic, $P\overline{1}$
a = 12.394 (3) Å
b = 14.823 (3) Å
c = 14.924 (3) Å
α = 97.707 (6)°
β = 113.562 (5)°
γ = 112.860 (5)°
V = 2175.6 (8) Å^3
Z = 2
D_x = 1.701 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 2.40 mm^{-1}
T = 297 (2) K
Block, blue
0.25 × 0.19 × 0.17 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
T_{min} = 0.57, T_{max} = 0.66
22917 measured reflections
9092 independent reflections
5466 reflections with $I > 2\sigma(I)$
R_{int} = 0.057
θ_{max} = 28.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.067
S = 0.98
9092 reflections
517 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0156P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.44 e Å^{-3}

Table 1
Selected bond lengths (Å) for (I).

Cu1—O1	1.921 (3)	Cu1—Cu3	3.0923 (9)
Cu2—O1	1.899 (3)	Cu1—Cu4	3.1272 (10)
Cu3—O1	1.903 (3)	Cu2—Cu3	3.1563 (10)
Cu4—O1	1.913 (3)	Cu2—Cu4	3.1179 (11)
Cu1—Cu2	3.0658 (10)	Cu3—Cu4	3.1394 (9)

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

D—H···A	D—H	H···A	D···A	D—H···A
N21—H21···Cl6^{i}	0.86	2.44	3.213 (4)	150
N22—H22···Cl7^{ii}	0.86	2.54	3.373 (4)	164
N23—H23···Cl7^{iii}	0.86	2.50	3.351 (4)	169
N14—H14···O1*WA*	0.86	1.99	2.782 (10)	154
N14—H14···O1*WB*	0.86	1.97	2.734 (13)	147
N14—H14···O1*WC*	0.86	2.06	2.82 (3)	146
N24—H24···Cl3	0.86	2.52	3.351 (5)	162

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

Compound (II)

Crystal data

$[Cu_4Cl_6O(C_5H_5NO)_4]\cdot 0.2H_2O$
M_r = 863.30
Triclinic, $P\overline{1}$
a = 11.638 (3) Å
b = 16.237 (4) Å
c = 17.139 (4) Å
α = 106.249 (5)°
β = 102.401 (6)°
γ = 94.255 (5)°
V = 3005.7 (13) Å^3
Z = 4
D_x = 1.908 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 3.36 mm^{-1}
T = 297 (2) K
Block, blue
0.15 × 0.05 × 0.03 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
T_{min} = 0.64, T_{max} = 0.91
24860 measured reflections
10510 independent reflections
5765 reflections with $I > 2\sigma(I)$
R_{int} = 0.076
θ_{max} = 25.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.068
$wR(F^2)$ = 0.095
S = 1.04
10510 reflections
703 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0142P)^2 + 7.7343P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.85 e Å^{-3}
$\Delta\rho_{min}$ = −0.61 e Å^{-3}

Table 3
Selected bond lengths (Å) for (II).

Cu1—O1	1.923 (4)	Cu1′—O1′	1.926 (5)
Cu2—O1	1.909 (4)	Cu2′—O1′	1.879 (5)
Cu3—O1	1.917 (4)	Cu3′—O1′	1.907 (4)
Cu4—O1	1.853 (4)	Cu4′—O1′	1.871 (4)
Cu1—Cu2	3.0778 (15)	Cu1′—Cu2′	3.0697 (15)
Cu1—Cu3	3.1085 (15)	Cu1′—Cu3′	3.0358 (16)
Cu1—Cu4	3.1316 (14)	Cu1′—Cu4′	3.1067 (15)
Cu2—Cu3	3.1014 (14)	Cu2′—Cu3′	3.1673 (17)
Cu2—Cu4	3.0820 (14)	Cu2′—Cu4′	3.0873 (14)
Cu3—Cu4	3.1117 (15)	Cu3′—Cu4′	3.0962 (15)

Compound (III)

Crystal data

$[Cu_4Cl_6O(C_4H_6N_2)_4]\cdot 3CH_4O$
M_r = 907.42
Monoclinic, $P2_1/n$
a = 10.2454 (13) Å
b = 17.826 (2) Å
c = 19.557 (2) Å
β = 94.877 (2)°
V = 3558.9 (7) Å^3
Z = 4
D_x = 1.694 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 2.85 mm^{-1}
T = 297 (2) K
Block, blue
0.23 × 0.19 × 0.05 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
T_{min} = 0.56, T_{max} = 0.87
17557 measured reflections
7783 independent reflections
5314 reflections with $I > 2\sigma(I)$
R_{int} = 0.054
θ_{max} = 27.5°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.107
S = 1.08
7783 reflections
390 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0443P)^2 + 0.1035P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.026
$\Delta\rho_{max}$ = 0.78 e Å^{-3}
$\Delta\rho_{min}$ = −0.92 e Å^{-3}

Table 4
Selected bond lengths (Å) for (III).

Cu1—O1	1.913 (3)	Cu1—Cu3	3.1375 (9)
Cu2—O1	1.907 (3)	Cu1—Cu4	3.1354 (9)
Cu3—O1	1.916 (3)	Cu2—Cu3	3.1146 (9)
Cu4—O1	1.914 (3)	Cu2—Cu4	3.0945 (9)
Cu1—Cu2	3.1144 (9)	Cu3—Cu4	3.1436 (9)

Table 5
Hydrogen-bond geometry (Å, °) for (III).

D—H···A	D—H	H···A	D···A	D—H···A
N21—H21···Cl3^{i}	0.86	2.36	3.220 (5)	174
N22—H22···Cl5^{ii}	0.86	2.49	3.304 (5)	159
N23—H23···O1*A*	0.86	1.97	2.813 (10)	167
N23—H23···O2*A*	0.86	2.15	2.935 (10)	152
N24—H24···O1*B*	0.86	1.87	2.727 (7)	175
O1*B*—H1*B*···O1*C*^{iii}	0.82	2.19	2.655 (9)	116
O1*C*—H1*C*···Cl4^{iv}	0.82	2.56	3.274 (7)	146
O1*A*—H1*A*···Cl6^{v}	0.82	2.47	3.223 (9)	153
O2*A*—H2*A*···Cl2^{vi}	0.82	2.74	3.416 (9)	141

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

Table 6
Comparison of mean bond distances in the Cu_4OCl_6 cores (Å).

	⟨Cu—O⟩	⟨Cu—Cl⟩
Literature*	1.909 (17)	2.41 (5)
(I)	1.909 (17)	2.41 (5)
(II)	1.90 (3)	2.41 (8)
(II′)	1.90 (2)	2.42 (11)
(III)	1.913 (5)	2.42 (4)

*Average of 52 structures in the 2005 version of the CSD.

H atoms attached to C and N atoms were placed at calculated positions (N—H = 0.86 Å, aromatic C—H = 0.93 Å and methyl C—H = 0.96 Å) and allowed to ride. Even though located in a rather shallow electron-density plateau, H atoms from the methyl groups were also included (AFIX 137 in *SHELXL97*; Sheldrick, 1997) because of their incidence in the refinement. The alcohol OH groups were treated by use of the AFIX 147 instruction in *SHELXL97*, subject to orientational restraint. H atoms bound to the disordered water molecule in (I) were not included in the model. All H atoms were assigned a U_{iso}(H) value of xU_{eq}(carrier), with x = 1.2 for aromatic H atoms, and x = 1.5 for methyl and hydroxy H atoms. In spite of the heavy atoms present, the crystals used for data collection were poorly diffracting, and only with measurement times of 20, 20 and 15 s per frame for (I), (II) and (III), respectively, was it possible to account for an observed/unique ratio of reflections of *ca* 0.5. A residual effect of this was the uncertainty with which some solvent molecules could be determined; thus, in (I), a full hydration water molecule was treated as split into three partially occupied sites, and was refined with an overall isotropic displacement parameter and occupations restrained to sum to unity, and in (III), one of the three methanol solvent molecules was treated as split over two sites, refined with occupation factors summing to unity. In addition, a *PLATON* (Spek, 2003) run detected in this latter structure (void) solvent-accessible regions of 35 Å^3, in which the electron density was hardly distinguishable from background. A *PLATON* SQUEEZE refinement, however, did not significantly improve the refinement. The rather high R indices obtained are probably the result of poor data quality. However, the large number of parameters might also have played a non-negligible role [see Krebs (2000) for a detailed analysis].

For all compounds, data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3008). Services for accessing these data are described at the back of the journal.

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