

A compound of a novel tetraaza-macrocycle with trinuclear tetracyanonickelate-bridged cations

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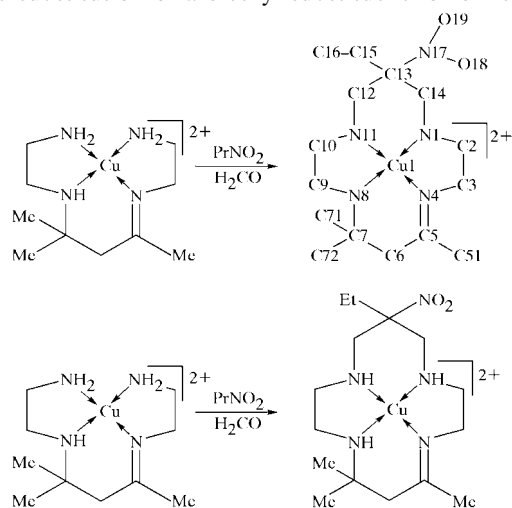
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The cation of the title compound, $[\text{Cu}(L)]^{2+}$, is formed by Michael condensation of (4,6,6-trimethyl-3,7-diazanon-3-ene-1,9-diamine)copper(II) with methanal and nitropropane. This cation forms a tetracyanonickelate(II) compound, the unit cell of which contains two centrosymmetric tetracyanonickelate(II)-bridged trinuclear cations, namely diaqua-1,3 κ^2 -O-di- μ -cyano-1:2 κ^2 C:N;1:3 κ^2 C:N-dicyano-1 κ^2 C-bis-(13-ethyl-5,7,7-trimethyl-13-nitro-1,4,8,11-tetraazacyclotetradec-4-ene)-2 κ^4 N¹,N⁴,N⁸,N¹¹;3 κ^4 N¹,N⁴,N⁸,N¹¹-dicopper(II)-nickel(II) di- μ -cyano-1:2 κ^2 C:N;1:3 κ^2 C:N-dicyano-1 κ^2 C-bis-(13-ethyl-5,7,7-trimethyl-13-nitro-1,4,8,11-tetraazacyclotetradec-4-ene)-2 κ^4 N¹,N⁴,N⁸,N¹¹;3 κ^4 N¹,N⁴,N⁸,N¹¹-dicopper(II)-nickel(II) bis[tetracyanonickelate(II)] octahydrate, $[\text{Cu}_2\text{Ni}(\text{CN})_4(\text{C}_{15}\text{H}_{31}\text{N}_5\text{O}_2)_2(\text{H}_2\text{O})_2][\text{Cu}_2\text{Ni}(\text{CN})_4(\text{C}_{15}\text{H}_{31}\text{N}_5\text{O}_2)_2] \cdot 2[\text{Ni}(\text{CN})_4] \cdot 8\text{H}_2\text{O}$. One cation, $[(L)\text{Cu}-\text{NC}-\text{Ni}(\text{CN})_2-\text{CN}-\text{Cu}(L)]^{2+}$, has an axially coordinated bridging $[\text{Ni}(\text{CN})_4]^{2-}$ ion, with a Cu–N distance of 2.226 (3) Å and a Cu–N–C angle of 168.2 (3)°. The other cation, $[(\text{H}_2\text{O})(L)\text{Cu}-\text{NC}-\text{Ni}(\text{CN})_2-\text{CN}-\text{Cu}(L)(\text{OH}_2)]^{2+}$, has water axially coordinated *trans* to a weakly bound bridging $[\text{Ni}(\text{CN})_4]^{2-}$ ion, with a Cu–O distance of 2.396 (3) Å, a Cu–N distance of 2.677 (4) Å, an O–Cu–N angle of 168.7 (1)° and a Cu–N–C angle of 137.7 (3)°. These cations, plus independent $[\text{Ni}(\text{CN})_4]^{2-}$ ions and water molecules, are linked into a hydrogen-bonded network. All $[\text{Ni}(\text{CN})_4]^{2-}$ ions are on centres of symmetry.

Comment

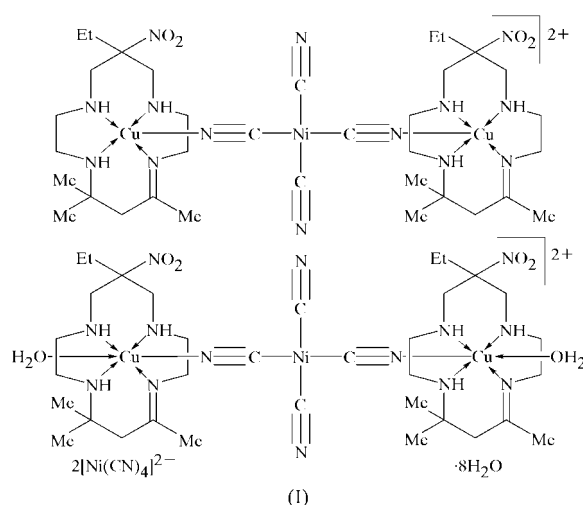
Michael condensations of (polyamine)metal complexes with methanal and nitroalkanes form nitroalkyl-substituted cyclic amine complexes (Lawrance, Lye *et al.*, 1993; Lawrance, Maeder *et al.*, 1993; Comba *et al.*, 1986), such as 6-methyl-6-nitro-1,4,8,11-tetraazacyclotetradecane)copper(II), which is formed from (3,7-diazanonane-1,9-diamine)metal compounds, methanal and nitroethane (Comba *et al.*, 1988*a,b*). The (tetraaza-macrocycle)copper(II) cation, $[\text{Cu}(L)]^{2+}$, present in the title compound, formed by an analogous reaction of (4,6,6-

trimethyl-3,7-diazanon-3-ene-1,9-diamine)copper(II) with methanal and nitropropane, differs by the presence of the imine function, the introduction of the 5,7,7-trimethyl substituents and the substitution of a 6-ethyl substituent for 6-methyl.



Structures of a number of methyl/nitro-substituted azamacrocycle compounds obtained by reaction of (amine)metal compounds with nitroethane and methanal have been reported, but this is the first for an ethyl/nitro-substituted analogue derived from nitropropane.

The structures of many compounds of (amine)metal cations with cyanometallate anions have been reported, often with oligo- or polymeric structures with bridging cyanometallate ions (Cernak *et al.*, 2002).



The title compound, (I), which crystallizes from aqueous solutions containing $[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{Cu}(L)]^{2+}$, has the formal composition $[\text{Cu}(L)][\text{Ni}(\text{CN})_4] \cdot 2.5\text{H}_2\text{O}$, but has two structurally distinct centrosymmetric tetracyanonickelate(II)-bridged (aza-macrocycle)copper(II) trinuclear cations, two independent tetracyanonickelate(II) anions, and one coordinated and four uncoordinated water molecules (see Fig. 1 and Table 1).

Atom Cu1A is in a square-planar coordination environment formed by the three secondary amine atoms, *viz.* N1A, N8A and N11A, and imine atom N4A of macrocycle L^a , with atom

N55 of the $[\text{Ni}5(\text{CN})_4]^{2-}$ tetracyanonickelate(II) ion coordinated axially; the result is a centrosymmetric trinuclear cation, $[(L^a)\text{Cu}-\text{NC}-\text{Ni}(\text{CN})_2-\text{CN}-\text{Cu}(L^a)]^{2+}$, with a $\text{Cu}\cdots\text{Cu}$ separation of 10.426 (5) Å (see Fig. 2).

Atom Cu1B is in a square-planar coordination environment formed by the four N atoms, *viz.* N1B, N4B, N8B and N11B, of macrocycle L^b , with weaker axial interactions with water atom O10 and atom N65 of the $[\text{Ni}6(\text{CN})_4]^{2-}$ ion forming a weakly bound centrosymmetric trinuclear cation, $[(\text{H}_2\text{O})(L^b)\text{Cu}-\text{NC}-\text{Ni}(\text{CN})_2-\text{CN}-\text{Cu}(L^b)(\text{OH}_2)]^{2+}$, with a $\text{Cu}\cdots\text{Cu}$ separation of 10.599 (5) Å (see Fig. 3).

For the two (aza-macrocycle)copper(II) cations, the $\text{Cu}-\text{N}_{\text{ring}}$ distances are similar (with the $\text{Cu}-\text{N}_{\text{imine}}$ distance *ca* 0.03 Å shorter than the mean $\text{Cu}-\text{N}_{\text{amine}}$ distance), the configuration is the same (1*S*,8*R*,11*R*; Spek, 2002) and the conformations are similar. The nitro group and the C72 methyl component of the gem-dimethyl group are axially oriented on the same side of the N_4 macrocycle coordination plane as the N1–H1 and N11–H11 groups, with the N8–H8 group and the axial ligand (N55 for Cu1A and O10 for Cu1B) on the other side. The N_4 plane is less tetrahedrally twisted and the Cu atom is further displaced from this plane for the $[\text{Cu}1\text{A}(L^a)]^{2+}$ ion [± 0.017 (2) and 0.246 (2) Å] than for the $[\text{Cu}1\text{B}(L^b)]^{2+}$ ion [± 0.067 (2) and 0.088 (2) Å]; these planes are inclined at 30.9 (2)°. The C15 methylene substituents of both macrocycles are equatorially oriented, with the terminal methyl group, C16A, of the $[\text{Cu}(L^a)]^{2+}$ ion further equatorially extended and closer to atom O18A, while the C16B group is axially oriented on the same side as axial water ligand O10.

The coordinated isocyano atom N55 is close to the square-pyramidal axis of the $[\text{Cu}1\text{A}(L^a)]^{2+}$ ion, with $\text{N}_{\text{ring}}-\text{Cu}1\text{A}-\text{N}55$ angles of between 95.1 (1) and 99.3 (1)°. The non-bridging N56–C56–Ni5 group is approximately aligned with the C7A \cdots C14A axis [$\text{N}56\cdots\text{Ni}5\cdots\text{Cu}1\text{A}-\text{C}7\text{A} = -1.4$ (2)°].

The ion is tilted with respect to the N_4 coordination plane so that the $\text{N}8\text{A}\cdots\text{N}56$ distance [6.250 (5) Å] is longer than the $\text{N}1\text{A}\cdots\text{N}56(-x, 2-y, -z)$ distance [4.998 (5) Å].

For $[\text{Cu}1\text{B}(L^b)]^{2+}$, the coordinated water O and isocyano N atoms are displaced from the square-bipyramidal axis, with $\text{N}_{\text{ring}}-\text{Cu}1\text{B}-\text{O}10$ angles of 87.1 (1)–101.8 (1)° and $\text{N}_{\text{ring}}-\text{Cu}1\text{B}-\text{N}65$ angles of 81.9 (1)–96.8 (1)°.

The dimensions of the coordinated and non-coordinated $[\text{Ni}(\text{CN})_4]^{2-}$ ions, all centrosymmetric, do not differ significantly. The two tetracyanonickelate(II) anions including atoms Ni7 and Ni8, and the water molecules including atoms O11, O12, O13 and O14 have no direct interaction with the copper(II) cations, though all are linked into a hydrogen-bonding network (see Table 2).

Chain polymeric structures are present for bis(ethane-1,2-diamine)copper(II) tetracyanonickelate(II), $[-\text{Cu}(\text{en})_2-\text{NC}-\text{Ni}(\text{CN})_2-\text{CN}-\text{Cu}(\text{en})_2-]$ (Luo *et al.*, 2000; Lokaj *et al.*, 1991),

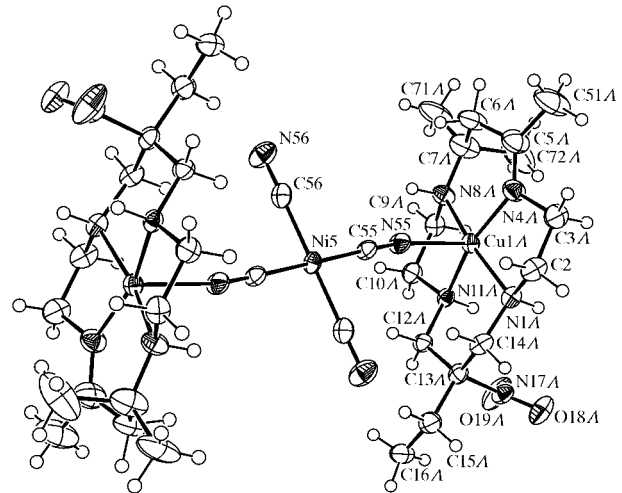


Figure 2

The $[(L^a)\text{Cu}-\text{NC}-\text{Ni}(\text{CN})_2-\text{CN}-\text{Cu}(L^a)]^{2+}$ cation, drawn with displacement ellipsoids at the 50% probability level.

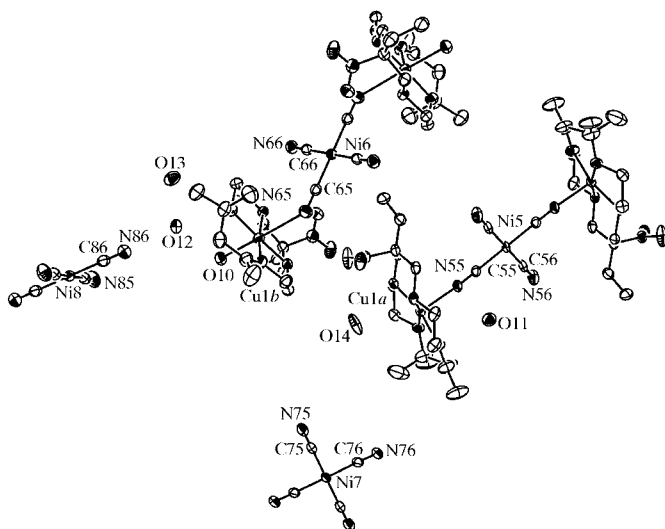


Figure 1

The structure of the title compound, drawn with displacement ellipsoids at the 50% probability level for non-H atoms, showing the asymmetric unit (labelled atoms and atoms of associated macrocycles), with additional atoms generated by symmetry operations to complete the tetracyanonickelate(II) anions and trinuclear cations.

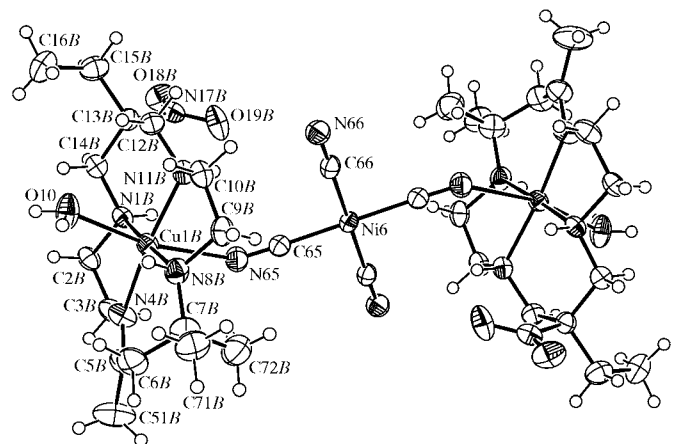


Figure 3

The $[(\text{H}_2\text{O})(L^a)\text{Cu}-\text{NC}-\text{Ni}(\text{CN})_2-\text{CN}-\text{Cu}(L^b)(\text{OH}_2)]^{2+}$ cation, drawn with displacement ellipsoids at the 50% probability level.

and for analogous cyanometallate compounds of other (tetraamino)copper(II) cations, including the *meso*-(5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)-copper(II), $[\text{Cu}(L^1)]^{2+}$, compounds with $[\text{Fe}(\text{CN})_6]^{3-}$ (Zou *et al.*, 1998) and $[\text{Cr}(\text{CN})_6]^{3-}$ (El Fallah *et al.*, 2001). The $[\text{Ni}(\text{CN})_4]^{2-}$ compounds formed by $[\text{Ni}(L^1)]^{2+}$ (Gainsford & Curtis, 1984) and (3,10-diethyl-1,3,5,8,10,12-hexaazacyclotetradecane)nickel(II) (Kou *et al.*, 2000) have similar structures, but with the Ni–N_{cyno} distances longer than Cu–N_{cyno}. The two faces of these (aza-macrocycle)metal(II) cations are equivalent, favouring the symmetrical structures observed. The two faces of the $[\text{Cu}(L)]^{2+}$ cation are inherently different, the configuration observed having the axial nitro and methyl groups on the same side, which minimizes the interaction with an axial substituent coordinated on the other side. For the $[\text{Cu}(L^a)]^{2+}$ ion, the isocyano N atom is coordinated on this less congested side, while for the $[\text{Cu}(L^b)]^{2+}$ ion, water is bound on this side and the isocyano group is bound more weakly on the other side.

Experimental

Aqua(13-ethyl-5,7,7-trimethyl-13-nitro-1,4,8,11-tetraazacyclotetradec-4-ene)copper(II) bis(perchlorate), $[\text{Cu}(L)(\text{H}_2\text{O})](\text{ClO}_4)_2$, was prepared by condensation of (4,6,6-trimethyl-3,7-diazanon-3-ene-1,9-diamine)copper(II) perchlorate (Blight & Curtis, 1962; Curtis, 1972; Curtis *et al.*, 2003), methanal and nitropropane in water, with NaHCO_3 as base. The mauve-coloured tetracyanonickelate(II) compound precipitated when aqueous solutions containing $[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{Cu}(L)]^{2+}$ were mixed. The sparingly soluble compound was recrystallized by evaporation of an aqueous solution.

Crystal data

$[\text{Cu}_2\text{Ni}(\text{CN})_4(\text{C}_{15}\text{H}_{31}\text{N}_5\text{O}_2)_2 \cdot (\text{H}_2\text{O})_2][\text{Cu}_2\text{Ni}(\text{CN})_4(\text{C}_{15}\text{H}_{31}\text{N}_5\text{O}_2)_2][\text{Ni}(\text{CN})_4]_2 \cdot 8\text{H}_2\text{O}$	$V = 2710.6 (1) \text{ \AA}^3$
$M_r = 2339.23$	$Z = 1$
Triclinic, $P\bar{1}$	$D_x = 1.431 \text{ Mg m}^{-3}$
$a = 11.7497 (2) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 14.0540 (3) \text{ \AA}$	Cell parameters from 7862 reflections
$c = 17.9014 (4) \text{ \AA}$	$\theta = 2.3\text{--}29.3^\circ$
$\alpha = 70.154 (1)^\circ$	$\mu = 1.52 \text{ mm}^{-1}$
$\beta = 78.165 (1)^\circ$	$T = 120 (2) \text{ K}$
$\gamma = 81.290 (1)^\circ$	Plate, purple
	$0.35 \times 0.35 \times 0.08 \text{ mm}$

Data collection

Bruker SMART 1K CCD area detector diffractometer	14 372 independent reflections
ω scans	9857 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2001)	$R_{\text{int}} = 0.034$
$T_{\text{min}} = 0.538$, $T_{\text{max}} = 0.885$	$\theta_{\text{max}} = 29.1^\circ$
$R_{\text{int}} = 0.047$ before correction	$h = -15 \rightarrow 15$
22 241 measured reflections	$k = -19 \rightarrow 19$
	$l = -24 \rightarrow 23$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0668P)^2 + 5.1175P]$
$R[F^2 > 2\sigma(F^2)] = 0.063$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.162$	$(\Delta/\sigma)_{\text{max}} = 0.006$
$S = 1.05$	$\Delta\rho_{\text{max}} = 1.41 \text{ e \AA}^{-3}$
14 372 reflections	$\Delta\rho_{\text{min}} = -0.73 \text{ e \AA}^{-3}$
666 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

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

Cu1A–N4A	1.999 (4)	Cu1B–N8B	2.018 (4)
Cu1A–N11A	2.013 (3)	Cu1B–N1B	2.020 (3)
Cu1A–N8A	2.031 (3)	Cu1B–N11B	2.026 (4)
Cu1A–N1A	2.041 (3)	Cu1B–O10	2.396 (3)
Cu1A–N55	2.226 (3)	Cu1B–N65	2.677 (4)
N4A–C5A	1.304 (6)	N4B–C5B	1.304 (6)
Cu1B–N4B	1.986 (4)		
N4A–Cu1A–N11A	164.6 (2)	N4B–Cu1B–N11B	170.7 (2)
N4A–Cu1A–N8A	95.6 (2)	N8B–Cu1B–N11B	86.9 (2)
N11A–Cu1A–N8A	85.9 (1)	N1B–Cu1B–N11B	91.0 (2)
N4A–Cu1A–N1A	85.4 (2)	N4B–Cu1B–O10	101.6 (2)
N11A–Cu1A–N1A	89.7 (1)	N8B–Cu1B–O10	87.0 (2)
N8A–Cu1A–N1A	166.8 (2)	N1B–Cu1B–O10	93.9 (1)
N4A–Cu1A–N55	99.9 (2)	N11B–Cu1B–O10	87.3 (2)
N11A–Cu1A–N55	95.1 (1)	N4B–Cu1B–N65	88.6 (2)
N8A–Cu1A–N55	96.7 (2)	N8B–Cu1B–N65	96.8 (2)
N1A–Cu1A–N55	96.1 (1)	N1B–Cu1B–N65	81.9 (1)
C55–N55–Cu1A	168.2 (3)	N11B–Cu1B–N65	82.2 (1)
N4B–Cu1B–N8B	95.9 (2)	O10–Cu1B–N65	168.7 (1)
N4B–Cu1B–N1B	86.0 (2)	C65–Ni6–C66	89.1 (2)
N8B–Cu1B–N1B	177.7 (2)	C65–N65–Cu1B	137.7 (3)

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
N1A–H1A \cdots N85 ⁱ	0.91	2.26	3.124 (5)	159
N11A–H11A \cdots O14	0.91	2.11	2.869 (5)	140
N11A–H11A \cdots O19A	0.91	2.41	2.978 (5)	121
N1B–H1B \cdots O19A	0.91	2.12	2.937 (5)	149
N8B–H8B \cdots O12	0.91	2.13	3.041 (5)	174
N8B–H8B \cdots O10	0.91	2.58	3.052 (5)	113
N11B–H11B \cdots O19B	0.91	2.29	2.874 (5)	122
O10–H10E \cdots N75 ⁱⁱ	0.84 (5)	1.92 (5)	2.745 (6)	168 (5)
O10–H10F \cdots O12	0.85 (5)	1.93 (5)	2.702 (5)	151 (5)
O11–H11E \cdots N66 ⁱⁱⁱ	0.84 (3)	2.04 (4)	2.870 (5)	170 (6)
O11–H11F \cdots N56	0.83 (5)	2.28 (5)	3.106 (5)	172 (5)
O12–H12F \cdots N86	0.83 (4)	1.97 (4)	2.788 (5)	168 (6)
O12–H12E \cdots O13	0.84 (4)	1.88 (3)	2.702 (5)	171 (6)
O13–H13E \cdots O11 ^{iv}	0.84 (4)	1.94 (4)	2.733 (5)	158 (6)
O13–H13F \cdots N56 ⁱⁱⁱ	0.83 (4)	2.15 (4)	2.973 (6)	170 (5)
O14–H14E \cdots N76 ⁱⁱ	0.82 (4)	2.03 (4)	2.847 (5)	174 (7)
O14–H14F \cdots N85 ⁱ	0.82 (5)	2.10 (5)	2.872 (6)	159 (6)

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

C- and N-bound H atoms were placed in calculated positions and treated as riding. Water H atoms were located from difference syntheses, and their positions were refined with restrained O–H distances [0.82 (2) \AA] and H–O–H angles [$\text{H}\cdots\text{H} = 1.35 (2) \text{ \AA}$].

Data collection: SMART (Bruker, 1997); cell refinement: SMART; data reduction: SAINT (Bruker, 2001); program(s) used to solve structure: SHELXTL (Bruker, 1997); program(s) used to refine structure: SHELXTL; molecular graphics: ORTEP-3.2 (Farrugia, 1997); software used to prepare material for publication: SHELXTL.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1674). Services for accessing these data are described at the back of the journal.

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