

Robert T. Stibrany, Harvey J.
Schugar and Joseph A. Potenza*Department of Chemistry and Chemical Biology,
Rutgers, The State University of New Jersey, 610
Taylor Road, Piscataway, New Jersey 08854,
USACorrespondence e-mail:
potenza@rutchem.rutgers.edu

Key indicators

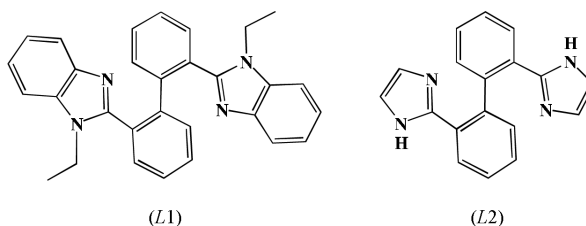
Single-crystal X-ray study
 $T = 297$ K
Mean $\sigma(\text{C}-\text{C}) = 0.006$ Å
Some non-H atoms missing
Disorder in solvent or counterion
 R factor = 0.059
 wR factor = 0.171
Data-to-parameter ratio = 14.0For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.The sterically crowded four-coordinate copper(I)
complex *rac*-bis[2,2'-bis(1-ethyl-1*H*-benzimidazol-
2-yl)biphenyl]copper(I) trifluoromethanesulfonate
toluene solvate dihydrate

The title salt, *rac*-[Cu(C₃₀H₂₆N₄)₂](CF₃SO₃)·C₇H₈·2H₂O, contains Cu(L1)₂⁺ cations, where L1 is 2,2'-bis(1-ethyl-benzimidazol-2-yl)biphenyl, separated by trifluoromethanesulfonate anions, toluene solvent molecules and two water molecules of hydration, only one of which could be defined crystallographically. Chemical and crystallographic evidence are consistent with a second, highly disordered water molecule in the asymmetric unit located in voids of 111 Å³. The ligands L1 form two nine-membered chelate rings with the Cu^I ion, resulting in a Cu[N(imine)]₄ coordination geometry which is best described as distorted 222 (*D*₂). Cu–N bond distances in the coordination sphere are long compared with those in other four-coordinate copper(I) structures containing benzimidazole ligands, possibly owing to the steric bulk associated with the ligands L1. Within each cation, the eight ring systems, consisting of four benzimidazole and four benzene fragments, are linked together by weak C–H···π and C–H···N interactions, suggesting that the cations are relatively tightly constrained sterically. The structure, when viewed along the **b** direction, may be described as a criss-crossed array of alternating cation/toluene and anion/water columns along the **b** direction arranged parallel to the (102) and (10 $\bar{2}$) planes.

Received 21 October 2004
Accepted 3 November 2004
Online 13 November 2004

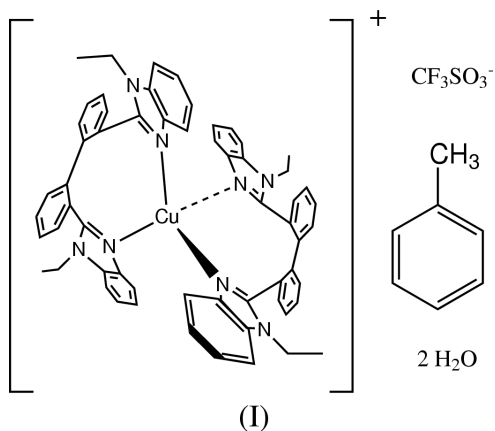
Comment

Biphenyl-based benzimidazole and imidazole ligands, such as L1 and L2, each with three torsional degrees of freedom, have been used in the study of electron self-exchange (Knapp *et al.*, 1990; Xie *et al.*, 1999) and as geometrically constraining ligands which enforce near-tetrahedral coordination in a variety of transition-metal complexes (Knapp *et al.*, 1990; Stibrany *et al.*, 2004). The copper^I ion, with a filled 3*d* subshell, is a particularly attractive vehicle for the examination of geometric constraints in a metal complex in the absence of ligand-field effects. With this in mind, the title salt, (I), was prepared and characterized structurally.



The structure contains Cu(L1)₂⁺ cations (Fig. 1) separated by trifluoromethanesulfonate anions, and by both toluene and water molecules of solvation. Each bidentate ligand L1 forms a nine-membered chelate ring whose geometry (Fig. 2) closely

approximates the twist-boat-boat conformation, one of the 16 symmetrical forms of nine-membered rings (Evans & Boeyens, 1990). The rings exhibit axial chirality and, although not required crystallographically, each cation is coordinated by two ligands of the same type (*R,R* or *S,S*). Inversion and glide-plane symmetry operations in the space group ensure the presence of an equal number of each enantiomer in the crystal structure; hence, the title salt is a racemate.



The Cu–N(imine) bond lengths in each cation range from 2.072 (2) to 2.121 (3) Å (Table 1), all substantially longer than the Cu^I–N(imine) distances reported [range 1.91 (1)–2.03 (1) Å; Cambridge Structural Database (Version 5.25; Allen, 2002) refcodes CERQOF, FETQUQ, LOSMIP, LUYFUG, MILVIM, MILVOS, PATVUB, QORGUZ, SELPOO, SELPUV, SELRAC, VIWTEA, VUNFOZ, WATYIZ, ZOPPID, and ZUBHUZ] for 16 four-coordinate structures containing a variety of substituted benzimidazoles

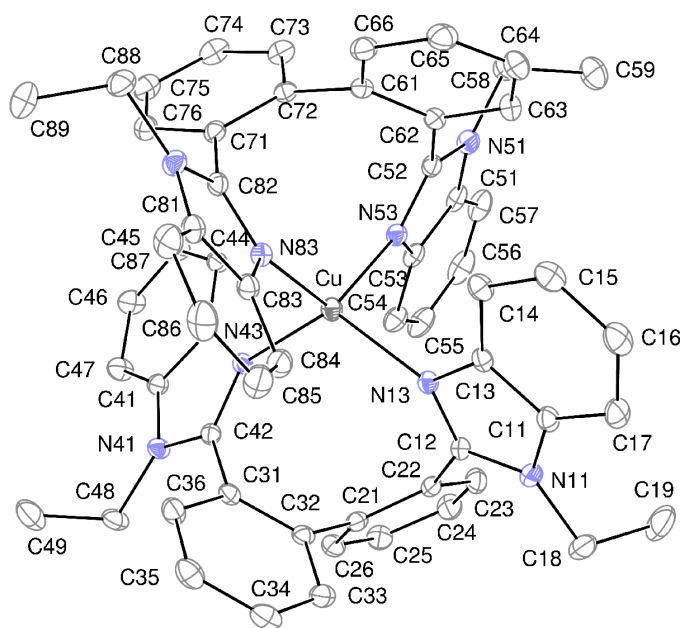


Figure 1
View of the Cu(L1)₂⁺ cation in (I), showing 15% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted.

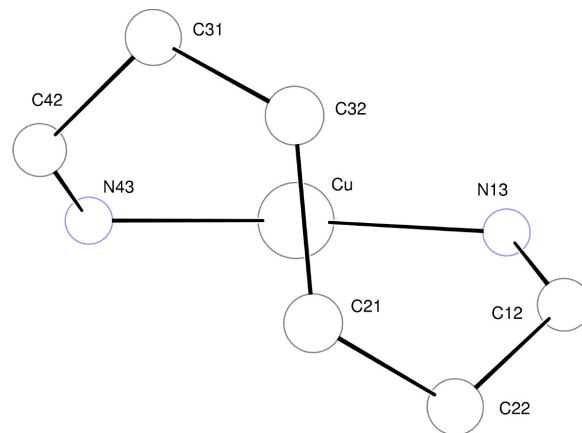


Figure 2
View of one of the nine-membered chelate rings in a Cu(L1)₂⁺ cation.

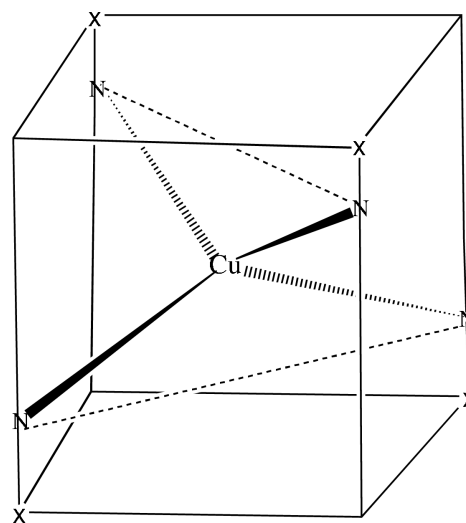


Figure 3
Idealized $\bar{4}2m$ (D_{2d}) coordination geometry for a Cu(L1)₂⁺ species. The four corners of the cube marked with x's and near the N atoms indicate the locations of ligand atoms for tetrahedral ($\bar{4}3m$, T_d) point-group symmetry. The dashed lines connect the N atoms of a given ligand.

bonded to copper(I) ions. A possible explanation for the relatively long Cu^I–N(imine) distances in the present structure is the steric bulk associated with ligand L1, which could prevent closer approach of the ligand to the metal ion. This view is consistent with the structure of the [bis(triphenylphosphine)benzimidazole]copper(I) cation which contains two bulky triphenylphosphine ligands and in which the benzimidazole ligand forms two relatively long Cu^I–N(imine) bonds [2.108 (3) and 2.133 (3) Å; de Souza Lemos *et al.*, 1998].

The N–Cu–N bond angles in Cu(L1)₂⁺ (Table 1) may be divided into three groups of two, one approximately 10° greater than, one approximately equal to, and one approximately 10° less than the tetrahedral angle. The largest are intraligand angles which correspond to the bite of the bidentate ligand L1; they are indicative of a flattening of the CuN₄ coordination geometry from tetrahedral towards $\bar{4}2m$ (D_{2d}) point-group symmetry (Fig. 3). Further reduction of the

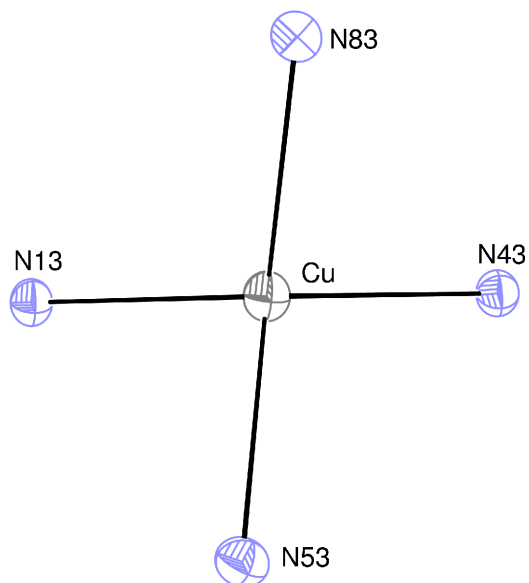


Figure 4
View of the CuN_4 unit in (I), showing the twist of the CuN_2 planes. The dihedral between the planes Cu/N13/N43 and Cu/N53/N83 is $83.12 (7)^\circ$.

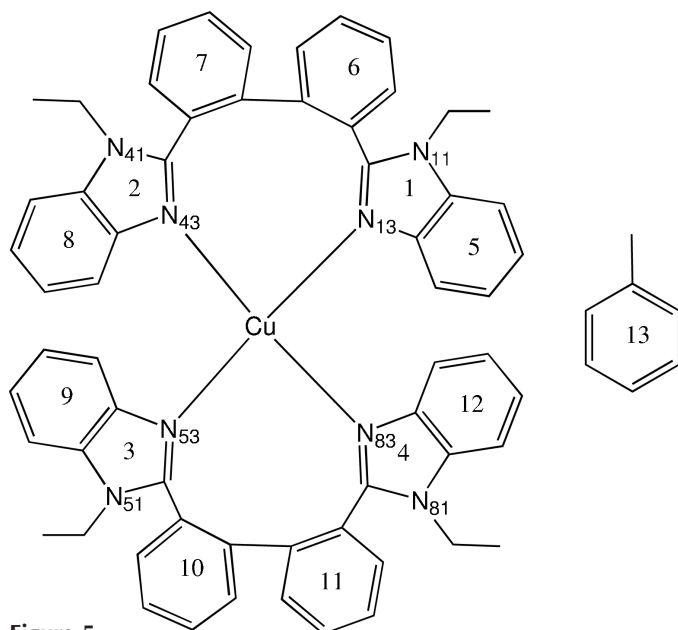


Figure 5
Sketch showing the ring-numbering scheme for the ligands $L1$ in the cation and for the toluene solvent molecule.

approximate symmetry of the CuN_4 unit to $222 (D_2)$ is effected in the main by a twisting of the two CuN_2 planes (Fig. 4), which increases two of the four interligand angles and decreases the remaining two. Similar patterns for the intra- and interligand angles have been observed for the $\text{Mn}(L3)_2^{2+}$ and $\text{Fe}(L3)_2^{2+}$ ions, where $L3$ is the *n*-propyl analog of $L1$ (Stibrany *et al.*, 2004), suggesting that the coordination geometry observed here is, in the absence of strong ligand-field effects, characteristic of this class of biphenyl-bridged bisbenzimidazole ligands.

Within each cation, the eight ring systems, consisting of four benzimidazole and four benzene fragments, are linked tog-

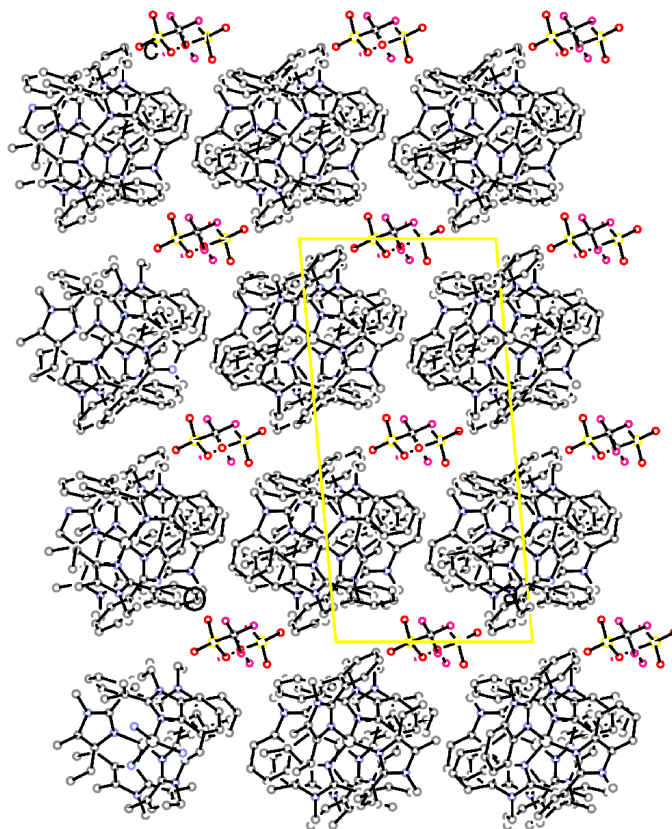


Figure 6
Projection, along the b axis, of the structure of (I). H atoms have been omitted.

ether by weak inter- and intraligand $\text{C}-\text{H}\cdots\text{N}$ interactions and by $\text{C}-\text{H}\cdots\pi$ interactions (Table 3 and Fig. 5). Four of the five $\text{C}-\text{H}\cdots\text{N}$ interactions are of the interligand type and link the ligating imine N atoms of one ligand to the H atoms at the 4-positions of a benzimidazole fragment on the second ligand. They are all relatively near the center of gravity of the cation. A fifth $\text{C}-\text{H}\cdots\text{N}$ interaction is of the intraligand type and links a benzene H atom to the amine N atom of a benzimidazole fragment. The present data are insufficient to determine whether these contacts are stabilizing or destabilizing. Indeed, Desiraju & Steiner (1999) 'caution readers from classifying all short intramolecular $\text{C}-\text{H}\cdots\text{O}$ contacts as hydrogen bonds just because they are short.' The same would appear to apply to $\text{C}-\text{H}\cdots\text{N}$ contacts, as in the present structure. Three of the four H atoms involved in the interligand $\text{C}-\text{H}\cdots\text{N}$ interactions also exhibit short distances to the centroids of the four benzene rings, which are consistent with $\text{C}-\text{H}\cdots\pi$ interactions. These latter contacts, which of necessity cannot be present in comparable structures containing ligand $L2$, suggest that the cations in the present structure are relatively tightly constrained sterically compared with their imidazole counterparts.

In the crystal structure, the cations and the toluene solvent molecules are arranged in columns parallel to the b axis (Figs. 6 and 7), with cations in a given column related to each other by 2_1 symmetry operations of the space group. The trifluoromethanesulfonate anions occupy sites between the cations

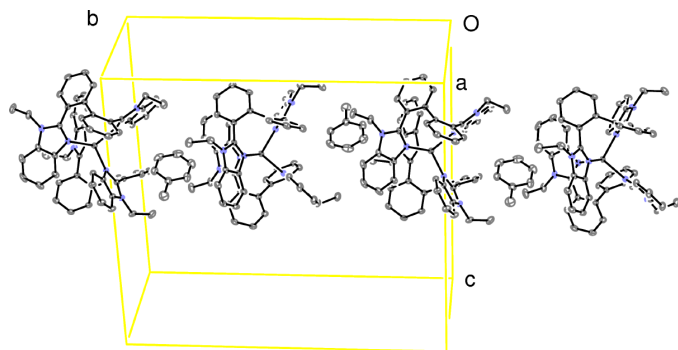


Figure 7
View, in profile, of a cation/toluene column.

and, along with the water molecules of solvation, form a second type of column parallel to the *b* axis and centered about inversion centers having coordinates $x = \frac{1}{2}$ ($2b$ and $2d$ sites). These latter columns contain alternating anion and water solvent species; they also encompass the centroids of two sizeable voids in the structure which are thought to contain additional water molecules (see below). Additionally, the water molecule which was located crystallographically forms an O—H...O hydrogen bond to one of the O atoms of the trifluoromethanesulfonate anion (Table 2). The toluene molecules of solvation occupy sites between cations (Fig. 7); they are linked to adjacent cations by several C—H... π interactions between the toluene C—H atoms and the ring centroids of the cation, some of which are quantified in Table 3. Overall, the structure is perhaps best viewed as a criss-crossed array of alternating cation/toluene and anion/water columns along the *b* direction arranged parallel to the (102) and (10 $\bar{2}$) planes (Fig. 6).

Experimental

To a 10 ml mixture of 1:1 *v/v* acetonitrile/toluene containing 50 mg (0.12 mmol) of $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{CF}_3\text{SO}_3)\cdot\text{CH}_3\text{CN}$, 106 mg (0.24 mmol) of *L1* was added. A clear pale-yellow solution resulted, which was sealed in a jar containing diethyl ether to allow vapor diffusion. No steps were taken to exclude adventitious water from the system. Crystals of the title salt precipitated over a period of 3 d. IR (KBr pellet, cm^{-1}): 3660 (*s*), 3474 (*br*), 3059 (*m*), 2976 (*m*), 2935 (*m*), 1613 (*m*), 1466 (*s*), 1407 (*s*), 1276 (*s*), 1150 (*s*), 1031 (*s*), 751 (*s*), 638 (*s*). ^1H NMR (400 MHz, CDCl_3): δ 7.38 (*s*, $J = 8.1$ Hz, 4H), 7.28 (*m*, 6H), 7.11 (*m*, 11H), 6.91 (*d*, $J = 7.6$ Hz, 4H), 6.76 (*d*, $J = 7.6$ Hz, 4H), 6.52 (*t*, $J = 7.6$ Hz, 4H), 5.87 (*d*, $J = 8.1$ Hz, 4H), 4.27 (*d*, sextet, $J = 54.5$ Hz, $J = 7.2$ Hz, 8H), 2.37 (*s*, 3H), 1.85 (*s*, 2H, water), 1.53 (*t*, $J = 7.1$ Hz, 12H).

Crystal data

$[\text{Cu}(\text{C}_{30}\text{H}_{26}\text{N}_4)_2](\text{CF}_3\text{SO}_3)\cdot\text{C}_7\text{H}_8\cdot 2\text{H}_2\text{O}$
 $M_r = 1225.08$

Monoclinic, $P2_1/c$
 $a = 11.1715$ (7) Å
 $b = 24.1173$ (10) Å
 $c = 23.0286$ (9) Å
 $\beta = 95.190$ (4)°
 $V = 6179.1$ (5) Å³
 $Z = 4$
 $D_x = 1.298$ Mg m⁻³
 $D_m = 1.33$ (1) Mg m⁻³

D_m measured by flotation in *n*-heptane/2-iodo-2-methylpropane/2-bromopropane

Mo $K\alpha$ radiation
Cell parameters from 956 reflections
 $\theta = 3.2$ – 20.8 °
 $\mu = 0.45$ mm⁻¹
 $T = 297$ (1) K
Wedge, pale yellow
 $0.52 \times 0.32 \times 0.14$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 φ and ω scans
Absorption correction: multi-scan (SADABS; Blessing, 1995)
 $T_{\min} = 0.731$, $T_{\max} = 0.939$
44390 measured reflections

10883 independent reflections
7598 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.044$
 $\theta_{\max} = 25.1$ °
 $h = -13 \rightarrow 8$
 $k = -26 \rightarrow 28$
 $l = -27 \rightarrow 27$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.059$
 $wR(F^2) = 0.171$
 $S = 1.00$
10883 reflections
777 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1023P)^2 + 2.3428P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.58$ e Å⁻³
 $\Delta\rho_{\min} = -0.39$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu—N13	2.088 (3)	Cu—N53	2.121 (3)
Cu—N43	2.072 (2)	Cu—N83	2.119 (2)
N83—Cu—N53	119.01 (9)	N43—Cu—N53	109.51 (10)
N43—Cu—N13	118.16 (9)	N43—Cu—N83	100.48 (10)
N13—Cu—N83	111.57 (10)	N13—Cu—N53	99.15 (10)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O4—H41O...O3	0.96 (8)	2.22 (9)	3.000 (9)	137 (10)

Table 3

Selected intra- and interspecies C—H...N and C—H... π interactions.

C—H	N or <i>Cg</i> (<i>J</i>)	H...N, <i>Cg</i> (<i>J</i>)	C—H...N, <i>Cg</i> (<i>J</i>)
C14—H14	N83	2.88	135
C44—H44	N53	2.82	133
C54—H54	N43	2.89	133
C84—H84	N13	2.90	135
C66—H66	N81	2.98	117
C14—H14	<i>Cg</i> (10)	2.87	131
C44—H44	<i>Cg</i> (11)	2.89	128
C54—H54	<i>Cg</i> (6)	2.91	132
C17—H17	<i>Cg</i> (9) ⁱⁱ	3.01	140
C45—H45	<i>Cg</i> (5) ⁱⁱⁱ	2.82	148
C65—H65	<i>Cg</i> (11) ^{iv}	2.96	123
C88—H88A	<i>Cg</i> (10) ^{iv}	3.05	144
C91—H91	<i>Cg</i> (5)	2.85	154
C92—H92	<i>Cg</i> (3)	2.79	141
C94—H94	<i>Cg</i> (4) ^v	2.98	153
C95—H95	<i>Cg</i> (8) ^v	3.04	159

Notes: *Cg*(*J*) corresponds to the center of gravity of the *J*th ring, as defined in Fig. 5. Interactions with H...*Cg* distances shorter than 3.10 Å are reported. Symmetry codes: (ii) $x - 1, y, z$; (iii) $x + 1, y, z$; (iv) $2 - x, -y, -z$; (v) $2 - x, \frac{1}{2} + y, \frac{1}{2} - z$.

The structure, originally containing a cation, an anion, a toluene molecule and one water molecule (near the $2d$ site in $P2_1/c$) in the asymmetric unit, was solved and refined, but the O atom of the water molecule could not be refined to convergence. Examination of the

structure at this point using *PLATON* (Spek, 2003), revealed two voids of 111 Å³, encompassing the centers of symmetry at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ and $\frac{1}{2}, 0, 0$, the *2b* sites in *P2₁/c*; these voids were considered to be possible locations for additional solvent species, most likely water. The measured density [1.33 (1) Mg m⁻³] compares poorly with the value calculated for one water molecule per asymmetric unit [1.298 Mg m⁻³]; the agreement is improved considerably with two (1.317 Mg m⁻³) or three (1.337 Mg m⁻³) water molecules in the asymmetric unit. IR spectroscopic analysis confirms the presence of water in the crystal structure, but does not indicate the amount. The integrated proton NMR spectrum is consistent with one cation, one toluene molecule, and at least one water molecule in the asymmetric unit; it is also consistent with the absence of either acetonitrile or diethyl ether. We note, however, that the water content may be underestimated by the NMR technique, owing to the possibility of proton exchange. Attempts to place additional water molecules at peaks near the centers of the voids led to divergence. At this point, a data set corresponding to omission of the missing solvent was generated by using the *SQUEEZE* algorithm (Spek, 2003; van der Sluis & Spek, 1990) and the structure was refined to convergence. *PLATON* estimated an electron count of 9 for each of the two voids above, but this may be an underestimation, particularly if some low-angle reflections are absent from the data set, as was the case in a different structure containing large solvent voids (Linden *et al.*, 2002). Based on the observed and calculated densities, the IR and NMR spectroscopic data, and the electron counts obtained using the *SQUEEZE* algorithm, our best estimate of the total water content in the present structure is approximately two molecules per asymmetric unit.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT-Plus* (Bruker, 2000); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to

refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *ORTEP-32* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Bruker, 2000).

We thank the referee, Dr Alan Lough, for helpful comments.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
 Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
 Bruker (2000). *SHELXTL* (Version 6.10), *SAINT-Plus* (Version 6.02) and *SMART-WNT/2000* (Version 5.622). Bruker AXS Inc., Madison, Wisconsin, USA.
 Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
 Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond*, IUCr Monographs on Crystallography, No. 9, pp. 115–116. Oxford University Press.
 Evans, D. G. & Boeyens, J. C. A. (1990). *Acta Cryst.* **B46**, 524–532.
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
 Knapp, S., Keenan, T. P., Zhang, X., Fikar, R., Potenza, J. A. & Schugar, H. J. (1990). *J. Am. Chem. Soc.* **112**, 3452–3464.
 Linden, A., Awad, E. M., Elwan, N. M., Hassaneen, H. M. & Heimgartner, H. (2002). *Acta Cryst.* **C58**, o122–o124.
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
 Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
 Sluis, P. van der & Spek, A. L. (1990). *Acta Cryst.* **A46**, 194–201.
 Souza Lemos, S. de, Bessler, K. E. & Lang E. S. (1998). *Z. Anorg. Allg. Chem.* **624**, 701–707.
 Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
 Stibrany, R. T., Lobanov, M. V., Schugar, H. J. & Potenza, J. A. (2004). *Inorg. Chem.* **43**, 1472–1480.
 Xie, B., Elder, T., Wilson, L. J. & Stanbury, D. M. (1999). *Inorg. Chem.* **38**, 12–19.