Absorption correction:
empirical
T_{min} = 0.005, T_{max} = 0.107
2627 measured reflections
2072 independent reflections
1846 observed reflections
$[I > 2\sigma(I)]$

$h = -10 \rightarrow 9$
$k = -10 \rightarrow 11$
$l = -15 \rightarrow 16$
3 standard reflections
frequency: 60 min
intensity variation: 5%

Refinement

Refinement on F^2
$R(F) = 0.0800$ $[F^2 > 2\sigma(F^2)]$
$wR(F^2) = 0.2260$
$S = 1.12$
2071 reflections
124 parameters
Calculated weights
$w = 1/[\sigma^2(F_o^2) + (0.1455P)^2 + 0.7706P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.490$ e Å^{-3}
$\Delta\rho_{min} = -0.704$ e Å^{-3}
Extinction correction: none
Atomic scattering factors
from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8, 6.1.1.4)

H atoms were constrained to give C—H = 0.97 Å, H—C—H = 109.5°, staggered conformations and U(H) = $1.5U_{eq}$(C). Data collection: *DIF*4 (Stoe & Cie, 1988). Cell refinement: *DIF*4. Data reduction: local programs. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick,1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1992). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL*93 and local programs.

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ti	0	$\tfrac{1}{2}$	$\tfrac{1}{2}$	0.0544 (4)
P	0.26521 (12)	0.74208 (10)	0.55322 (7)	0.0502 (4)
Cl1	0.1591 (2)	0.32056 (12)	0.54216 (10)	0.0770 (5)
Cl2	−0.0921 (2)	0.49041 (13)	0.64936 (8)	0.0711 (5)
O	0.1628 (3)	0.6213 (3)	0.5485 (2)	0.0526 (7)
N1	0.1918 (5)	0.8505 (4)	0.6222 (3)	0.0597 (9)
N2	0.4386 (4)	0.6924 (4)	0.5898 (3)	0.0622 (10)
N3	0.2807 (5)	0.8222 (4)	0.4542 (3)	0.0604 (9)
C11	0.1087 (8)	0.8063 (5)	0.6997 (4)	0.080 (2)
C12	0.2559 (7)	0.9829 (5)	0.6354 (4)	0.0717 (14)
C21	0.5628 (7)	0.7893 (7)	0.6130 (5)	0.087 (2)
C22	0.4735 (9)	0.5646 (8)	0.6242 (7)	0.129 (3)
C31	0.1538 (7)	0.8986 (6)	0.4084 (4)	0.0791 (15)
C32	0.3861 (7)	0.7784 (6)	0.3867 (3)	0.0731 (14)

Table 2. *Geometric parameters* (Å, °)

Ti—O	1.945 (3)	N1—C11	1.445 (7)
Ti—Cl1	2.3224 (14)	N1—C12	1.454 (6)
Ti—Cl2	2.333 (2)	N2—C22	1.400 (7)
P—O	1.510 (3)	N2—C21	1.472 (7)
P—N2	1.627 (4)	N3—C31	1.446 (7)
P—N3	1.631 (4)	N3—C32	1.460 (7)
P—N1	1.639 (4)		
O—Ti—Cl1	90.31 (10)	C11—N1—C12	113.9 (4)
O—Ti—Cl2	91.04 (9)	C11—N1—P	120.1 (3)
Cl1—Ti—Cl2	89.48 (6)	C12—N1—P	121.3 (4)
O—P—N2	107.0 (2)	C22—N2—C21	114.0 (5)
O—P—N3	117.7 (2)	C22—N2—P	123.7 (4)
N2—P—N3	105.4 (2)	C21—N2—P	120.4 (4)
O—P—N1	107.4 (2)	C31—N3—C32	112.2 (4)
N2—P—N1	115.3 (2)	C31—N3—P	121.1 (3)
N3—P—N1	104.4 (2)	C32—N3—P	121.5 (4)
P—O—Ti	158.7 (2)		

The title compound was prepared by the addition of excess hmpa (40 mmol) to a solution of TiCl$_4$ (10 mmol) in toluene. A sparingly soluble solid was deposited and removed by filtration. Good quality orange crystals were grown from the remaining dilute mother liquor. As a result of the air- and moisture-sensitive nature of this work, Schlenk and vacuum techniques were employed and the crystals were sealed inside Lindemann capillary tubes in an argon-filled glove box prior to data collection.

References

Bränden, C.-I. & Lindqvist, l. (1960). *Acta Chem. Scand.* 14, 726-732.
Gregory, K., Schleyer, P. von R. & Snaith, R. (1991). *Adv. Inorg. Chem.* 37, 47-141.
Mimoun, R., Postel, M., Casabianca, F., Fischer, J. & Mitschler, A. (1982). *Inorg. Chem.* 21, 1303-1306.
Mulvey, R. E. (1991). *Chem. Soc. Rev.* 26, 167-209.
Postel, M., Casabianca, F., Gauffreteau, Y. & Fischer, J. (1986). *Inorg. Chim. Acta,* 113, 173-180.
Sheldrick, G. M. (1990). *SHELXTL/PC User's Manual.* Siemens Analytical X-ray Instruments Inc., Madison, USA.
Sheldrick, G. M. (1992). *SHELXL*93. Beta test version. Univ. of Göttingen, Germany.
Stoe & Cie (1988). *DIF*4. *Diffractometer Control Program.* Version 7.04. Stoe & Cie, Darmstadt, Germany.
Thorn, D. L. & Harlow, R. L. (1992). *Inorg. Chem.* 31, 3917-3923.
Wakefield, B. J. (1990). In *Organolithium Methods.* London: Academic Press.

Dilithium Zinc Crotonate, a Mixed-Metal Sheet Polymeric Structure

WILLIAM CLEGG, PAUL A. HUNT AND
BRIAN P. STRAUGHAN

Department of Chemistry, University of Newcastle, Newcastle upon Tyne NE1 7RU, England

Abstract

The structure of dilithium zinc tetra-*trans*-2-butenoate, [Li$_2$Zn(C$_4$H$_5$O$_2$)$_4$], is made up of polymeric sheets. Each crotonate anion bridges three metal ions, with one O atom

attached to one metal atom and the other O atom attached to two metal atoms. All the zinc and lithium cations are approximately tetrahedrally coordinated by crotonate O atoms, angular distortions being considerably greater around lithium than around zinc.

Comment

Both anhydrous and hydrated carboxylates of Li and of Zn have been prepared and their structures investigated. In the case of anhydrous Zn salts of monocarboxylic acids without other potentially ligating functional groups, several different types of polymeric structure have been found. One form of the acetate consists of a three-dimensional network (Capilla & Aranda, 1979). A second form of the acetate and two polymorphic forms of the propionate contain sheets of carboxylates and coordinated Zn ions (Clegg, Little & Straughan, 1986b; Goldschmied, Rae & Stephenson, 1977; Clegg, Little & Straughan, 1987). Linear polymeric chains are found in the benzoate (Guseinov, Musaev, Usubaliev, Amiraslanov & Mamedov, 1984), crotonate (Clegg, Little & Straughan, 1986a), 2-methyl-2-(phenylthio)propionate (Chan, Mak, Yip, Kennard, Smith & O'Reilly, 1987), 3,3-dimethylacrylate and one form of the 2-chlorobenzoate (Clegg, Harbron, Hunt, Little & Straughan, 1990), and in a disordered mixed benzoate/tiglate (Clegg, Harbron & Straughan, 1990); in these structures, pairs of Zn ions are bridged by three carboxylates in a *syn-syn* mode, and these units are linked together into chains by single *syn-anti* carboxylate bridges. A different type of polymeric chain, with pairs of *syn-syn* carboxylates bridging between adjacent Zn ions, is adopted in a second polymorphic form of the 2-chlorobenzoate (Nakacho, Misawa, Fujiwara, Wakahara & Tomita, 1976).

By contrast, the only known structure of an anhydrous Li salt of a monocarboxylic acid without other potentially ligating functional groups is that of the formate, which consists of a three-dimensional polymeric network (Kansikas & Hermansson, 1989).

Coordination of both metals is generally approximately tetrahedral in these compounds. The common mode of coordination by the carboxylates is as bridges, each O atom bonding to one metal centre.

As part of our studies of carboxylate complexes of Zn, we have prepared the anhydrous mixed dilithium zinc crotonate $Li_2Zn(O_2CCH=CHMe)_4$.

The structure consists of a two-dimensional sheet polymeric array. Fig. 1 shows the asymmetric unit together with additional atoms to complete the full set of bonds around it. Each Li is surrounded by four carboxylate O atoms: the Li—O distances vary between 1.882 (5) and 1.983 (4) Å, and O—Li—O angles show large deviations from the regular tetrahedral value of 109.5°, from 94.6 (2) to 126.4 (3)°. By contrast, the zinc coordination is much closer to regular tetrahedral, with smaller ranges of both
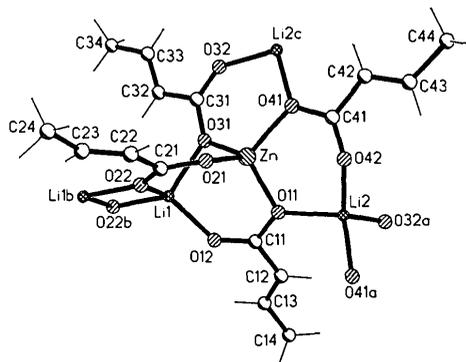

Fig. 1. The structure of one complete asymmetric unit, together with sufficient additional atoms to complete all bonds to the atoms of the asymmetric unit.

Zn—O distances [1.950 (2)–1.990 (2) Å] and O—Zn—O angles [103.54 (7)–119.09 (8)°], reflecting the greater degree of covalency in the Zn—O bonding.

Each crotonate binds to one Zn and two Li. Three of the four structurally independent crotonates are attached to Li through one O atom, and to Zn and a second Li through the other, but the fourth (ligand 2) has Zn at one end of the bridge and two Li at the other. Angles at O (M—O—M' and M—O—C) are far from constant, and the geometrical arrangement necessarily brings some pairs of metal atoms/ions into close proximity: the shortest Li···Zn distance is 2.876 (3) Å and the shortest Li···Li distance is only 2.647 (6) Å. By contrast, Zn atoms are all more than 6 Å apart.

The crotonate hydrocarbon side chains protrude on each side of the polymeric sheet. Even within one sheet, the arrangement is such as to bring the hydrophobic substituents together in clusters, seen as substantial voids in the projection of the $Li_2Zn(O_2C)_4$ framework (Fig. 2).

Fast-atom bombardment (FAB) mass spectrometric analysis (with a *m*-nitrobenzyl alcohol matrix) of a
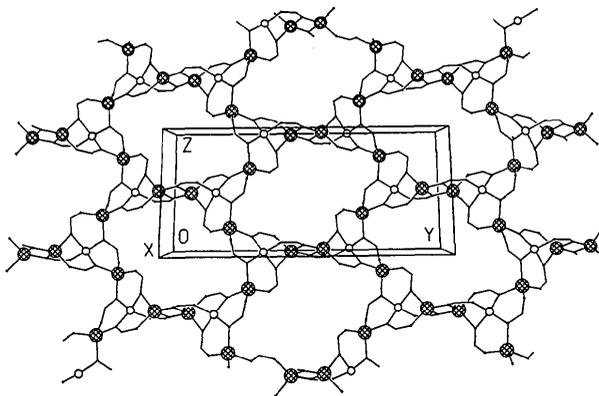

Fig. 2. The structure of the framework of one polymeric sheet, with crotonate side chains omitted.

methanol solution of the compound indicates that discrete mixed-metal species also exist in solution. Peaks are observed corresponding to ions [ZnLi(crotonate)]$^+$ (m/z 241), [ZnLi$_2$(crotonate)$_3$]$^+$ (m/z 333) and [ZnLi$_3$-(crotonate)$_4$]$^+$ (m/z 425).

Experimental

Crystal data

[Li$_2$Zn(C$_4$H$_5$O$_2$)$_4$]	D_x = 1.343 Mg m^{-3}
M_r = 419.57	Cu $K\alpha$ radiation
Monoclinic	λ = 1.54184 Å
$P2_1/c$	Cell parameters from 32
a = 10.730 (2) Å	reflections
b = 21.081 (4) Å	θ = 15.86–20.02°
c = 9.868 (2) Å	μ = 1.963 mm^{-1}
β = 111.62 (2)°	T = 295.0 (10) K
V = 2075.1 (7) Å^3	0.64 × 0.56 × 0.12 mm
Z = 4	Colourless

Data collection

Stoe Siemens diffractometer	3193 observed reflections
ω/θ scans with on-line pro-	[$I > 2\sigma(I)$]
file fitting (Clegg, 1981)	R_{int} = 0.0348
Absorption correction:	θ_{max} = 64.96°
empirical	h = -12 → 12
T_{min} = 0.379, T_{max} =	k = -24 → 12
0.603	l = -11 → 11
4453 measured reflections	3 standard reflections
3492 independent reflections	frequency: 60 min
	intensity variation: 1%

Refinement

Refinement on F^2	$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$R(F)$ = 0.0378 [$F^2>2\sigma(F^2)$]	$\Delta\rho_{min}$ = -0.35 e Å^{-3}
$wR(F^2)$ = 0.1064	Extinction correction:
S = 1.046	SHELXL93 (Sheldrick,
3491 reflections	1992)
249 parameters	Extinction coefficient:
Calculated weights	0.0014 (2)
$w = 1/[\sigma^2(F_o^2) + (0.0619P)^2$	Atomic scattering factors
$+ 0.6672P]$	from International Tables
where $P = (F_o^2 + 2F_c^2)/3$	for Crystallography (1992,
$(\Delta/\sigma)_{max}$ < 0.001	Vol. C, Tables 4.2.6.8,
	6.1.1.4)

H atoms were located in a difference synthesis and were refined with constraints. Data collection: *DIF4* (Stoe & Cie, 1988). Cell refinement: *DIF4*. Data reduction: local programs. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1992). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93* and local programs.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)

$$U_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Zn	0.15152 (3)	0.339332 (13)	-0.00572 (3)	0.0452 (2)
Li1	-0.0322 (4)	0.4395 (2)	-0.0116 (6)	0.059 (2)
Li2	0.1716 (5)	0.2148 (2)	0.1950 (5)	0.054 (3)
O11	0.0736 (2)	0.29477 (8)	0.1190 (2)	0.0538 (10)
O12	-0.0505 (2)	0.37873 (8)	0.1195 (2)	0.0688 (13)
C11	-0.0193 (3)	0.32282 (12)	0.1499 (3)	0.0532 (14)
C12	-0.0904 (3)	0.28335 (13)	0.2229 (3)	0.065 (2)
C13	-0.1937 (3)	0.3012 (2)	0.2493 (4)	0.078 (2)
C14	-0.2710 (4)	0.2618 (2)	0.3174 (6)	0.119 (3)
O21	0.2820 (2)	0.40657 (8)	0.0783 (2)	0.0562 (9)
O22	0.1400 (2)	0.48640 (7)	0.0521 (2)	0.0582 (9)
C21	0.2552 (2)	0.46521 (11)	0.0766 (3)	0.0487 (13)
C22	0.3708 (3)	0.50830 (13)	0.1022 (3)	0.0612 (14)
C23	0.3652 (3)	0.56903 (13)	0.0828 (3)	0.067 (2)
C24	0.4805 (3)	0.6121 (2)	0.0981 (4)	0.082 (2)
O31	-0.0008 (2)	0.38424 (8)	-0.1547 (2)	0.0559 (10)
O32	0.0638 (2)	0.35895 (9)	-0.3362 (2)	0.071 (2)
C31	-0.0061 (3)	0.39019 (11)	-0.2872 (3)	0.0538 (14)
C32	-0.1040 (3)	0.43727 (14)	-0.3780 (4)	0.073 (2)
C33	-0.1232 (3)	0.4477 (2)	-0.5148 (4)	0.086 (2)
C34	-0.2192 (4)	0.4941 (2)	-0.6129 (5)	0.131 (2)
O41	0.2405 (2)	0.27953 (7)	-0.0925 (2)	0.0516 (10)
O42	0.3023 (2)	0.22212 (10)	0.1090 (2)	0.0695 (13)
C41	0.3043 (2)	0.23271 (11)	-0.0123 (3)	0.0475 (13)
C42	0.3818 (3)	0.19225 (13)	-0.0741 (3)	0.059 (2)
C43	0.4403 (4)	0.1409 (2)	-0.0121 (4)	0.081 (2)
C44	0.5204 (4)	0.0971 (2)	-0.0684 (5)	0.119 (3)

Table 2. Geometric parameters (Å, °)

Zn—O21	1.950 (2)	Li1—O31	1.954 (5)
Zn—O41	1.959 (2)	Li1—O22	1.982 (5)
Zn—O11	1.964 (2)	Li2—O32^{ii}	1.894 (5)
Zn—O31	1.990 (2)	Li2—O42	1.894 (5)
Li1—O12	1.882 (5)	Li2—O41^{ii}	1.953 (5)
Li1—O22^i	1.896 (4)	Li2—O11	1.983 (4)
O21—Zn—O41	105.32 (7)	O41^{ii}—Li2—O11	107.0 (2)
O21—Zn—O11	119.09 (8)	C11—O11—Zn	118.3 (2)
O41—Zn—O11	110.81 (7)	C11—O11—Li2	130.6 (2)
O21—Zn—O31	103.54 (7)	Zn—O11—Li2	110.77 (14)
O41—Zn—O31	112.52 (7)	C11—O12—Li1	136.9 (2)
O11—Zn—O31	105.50 (7)	C21—O21—Zn	125.4 (2)
O12—Li1—O22^i	119.7 (2)	C21—O22—Li1^i	144.8 (2)
O12—Li1—O31	100.4 (2)	C21—O22—Li1	128.5 (2)
O22^i—Li1—O31	126.4 (3)	Li1^i—O22—Li1	85.4 (2)
O12—Li1—O22	116.3 (3)	C31—O31—Li1	135.9 (2)
O22^i—Li1—O22	94.6 (2)	C31—O31—Zn	120.8 (2)
O31—Li1—O22	97.9 (2)	Li1—O31—Zn	93.6 (2)
O32^{ii}—Li2—O42	120.2 (2)	C31—O32—Li2^{iii}	143.5 (2)
O32^{ii}—Li2—O41^{ii}	101.1 (2)	C41—O41—Li2^{iii}	127.6 (2)
O42—Li2—O41^{ii}	115.2 (2)	C41—O41—Zn	117.19 (14)
O32^{ii}—Li2—O11	115.4 (2)	Li2^{iii}—O41—Zn	112.15 (15)
O42—Li2—O11	98.0 (2)	C41—O42—Li2	137.3 (2)

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

The complex was prepared by mixing methanol solutions of anhydrous zinc crotonate and lithium crotonate in 1:2 molar ratio. Crystals were deposited at room temperature from the saturated solution. Satisfactory chemical analyses were obtained.

References

Capilla, A. V. & Aranda, R. A. (1979). *Cryst. Struct. Commun.* **8**, 795–798.

Chan, W. H., Mak, T. C. W., Yip, W. H., Kennard, C. H. L., Smith, G. & O'Reilly, E. J. (1987). *Aust. J. Chem.* **40**, 981–986.

Clegg, W. (1981). *Acta Cryst.* A37, 22-28.

Clegg, W., Harbron, D. R., Hunt, P. A., Little, I. R. & Straughan, B. P. (1990). *Acta Cryst.* C46, 750-753.

Clegg, W., Harbron, D. R. & Straughan, B. P. (1990). *J. Crystallogr. Spectrosc. Res.* 20, 17-22.

Clegg, W., Little, I. R. & Straughan, B. P. (1986a). *Acta Cryst.* C42, 919-926.

Clegg, W., Little, I. R. & Straughan, B. P. (1986b). *Acta Cryst.* C42, 1701-1703.

Clegg, W., Little, I. R. & Straughan, B. P. (1987). *Acta Cryst.* C43, 456-457.

Goldschmied, E., Rae, A. D. & Stephenson, N. C. (1977). *Acta Cryst.* B33, 2117-2120.

Guseinov, G. A., Musaev, F. N., Usubaliev, B. T., Amiraslanov, I. R. & Mamedov, Kh. S. (1984). *Koord. Khim.* 10, 117-122.

Kansikas, J. & Hermansson, K. (1989). *Acta Cryst.* C45, 187-191.

Nakacho, Y., Misawa, T., Fujiwara, T., Wakahara, A. & Tomita, K. (1976). *Bull. Chem. Soc. Jpn*, 49, 58-61.

Sheldrick, G. M. (1990). *SHELXTL/PC User's Manual.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1992). *SHELXL93. Program for the Refinement of Crystal Structures.* Beta test version. Univ. of Göttingen, Germany.

Stoe & Cie (1988). *DIF4. Diffractometer Control Program.* Version 7.04. Stoe & Cie, Darmstadt, Germany.

Structure of [(3RS,7SR)-3,7-Dimethyl-3,7-diazanonane-1,9-diamine]-perchloratocopper(II) Perchlorate, [Cu(ClO4)(C9H24N4)](ClO4)

Tian-Huey Lu* and Jyh-Liong Lin

Department of Physics, National Tsing Hua University, Hsinchu 300, Taiwan

Kelun Shu, Yi-Zhong Yuan and Chung-Sun Chung

Department of Chemistry, National Tsing Hua University, Hsinchu 300, Taiwan

(*Received* 23 *November* 1992; *accepted* 7 *June* 1993)

Abstract

The Cu^{II} is coordinated in a slightly distorted square pyramid with the four N atoms equatorial and the O atom of the perchlorate group axial. The four donor N atoms are coplanar; Cu^{II} is 0.0165 Å out of this plane towards the perchlorate group. This complex has the (3RS,7SR) configuration at the chiral N centers, with the two N-methyl groups on the same side of the plane of the four N atoms. The tetraamine binds to the Cu^{II} atom in a relatively strain-free planar fashion; the central six-membered ring

exhibits a stable chair form and the two terminal five-membered rings take stable skew forms.

Comment

The crystal structures of open-chain tetraamine complexes containing primary and secondary amine groups have been extensively studied. However, analogous complexes containing tertiary amine groups have received very little attention. In order to study the steric effects of N-methyl groups on the structure of the copper(II) complex, we have prepared and studied the structure of the title complex.

1,9-Diamino-3,7-dimethyl-3,7-diazanonane was synthesized according to the method of Yoshikawa & Sekihara (1967). To its solution (3.76 g, 0.02 mol in 2-propanol, 80 ml), a solution of Cu(ClO4)2.6H2O (7.4 g, 0.02 mol in methanol, 80 ml) was added dropwise. The color of the solution changed rapidly to deep blue and blue precipitates formed. Single crystals were obtained from aqueous solution by slow evaporation.

As a result of the two bulky axial N-methyl groups lying above the metal ion and hindering the axial position, this complex is five coordinate; the geometry about the Cu^{II} ion is slightly distorted square pyramidal with a tetraamine N atom equatorial and an O atom of the perchlorate group axial. The four N atoms of tetraamine are coplanar within 0.011 (3) Å. The deviation of Cu^{II} ion from the best
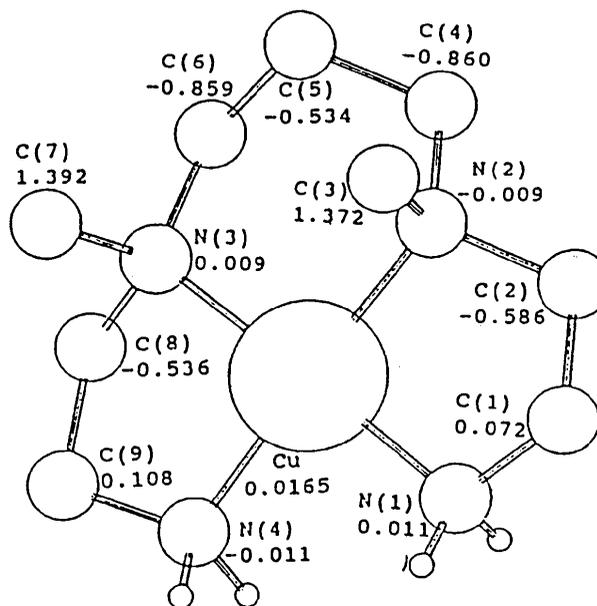

Fig. 1. A perspective view of the molecule with the numbering scheme excluding the H atoms attached to the C atoms and the perchlorate ions. The displacements (Å) of the atoms from the best plane formed by the four N atoms coordinated to the Cu^{II} ion are indicated.