Acta Cryst. (1984). C**40**, 960–962

(*N*-{2-[2-(2-Ammonioethylamino)ethylamino]ethyl}salicylideneaminato-*O*,*N*,*N*′,*N*″)-perchloratocopper(II) Perchlorate, $[Cu(ClO_4)(C_{13}H_{22}N_4O)].ClO_4$

By E. Rotondo, F. Cusmano Priolo, G. Bombieri and G. Bruno

Dipartimento di Chimica Inorganica e Struttura Molecolare, Università di Messina, Via dei Verdi, 98100 *Messina, Italy*

(*Received* 14 *October* 1983; *accepted* 27 *January* 1984)

Abstract. $M_r = 512{\cdot}8$, triclinic, $P\bar{1}$, $a = 8{\cdot}787\ (2)$, $b = 9{\cdot}907\ (1)$, $c = 12{\cdot}393\ (3)$ Å, $\alpha = 93{\cdot}05\ (6)$, $\beta = 109{\cdot}51\ (6)$, $\gamma = 97{\cdot}93\ (6)°$, $U = 1001{\cdot}5\ (6)$ Å^3, $Z = 2$, $D_x = 1{\cdot}70$ Mg m^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0{\cdot}71069$ Å, $\mu = 1{\cdot}413$ mm^{-1}, $F(000) = 526$, $T = 298$ K, final $R = 0{\cdot}047$ and $R_w = 0{\cdot}048$ for 2479 reflections. The coordination polyhedron around Cu is an irregular square pyramid with the protonated saltrien [saltrien $= 2\text{–}O^-\text{–}C_6H_4CH{=}N(CH_2)_2NH(CH_2)_2NH(CH_2)_2\text{-}NH_2$] acting as a tetradentate ligand through one O and three N atoms. The terminal nitrogen of the ligand is protonated and the apical position of the square pyramid is occupied by an oxygen of the perchlorate ligand.

Introduction. In many instances metal coordination compounds of Schiff bases have been suggested as models to describe energy transfer in naturally occurring systems and the coordination sphere about the metal ion is believed to play an important role in determining the nature of the model system (Wilkins, 1971).

In addition, the 'oxygen transfer' capability of some cobalt(II) salicylideneaminato compounds promoted a great deal of research concerning the correlation of redox potentials as well as chemical reactivity of the metal ion with the nature of the coordinated ligands (Jones, Summerville & Basolo, 1979). It has been shown that sharper changes of the metal-ion properties could be achieved through the use of non-symmetrical Schiff bases, *e.g.* of diprimary amines condensed with two different carbonylic moieties (Costes, Cross, Darbien & Laurent, 1982; Costa, Mestroni, Puxeddu & Reisenhofer, 1970).

Unfortunately, until now very few non-symmetrical ligands could be prepared. Recently, such a synthesis has been achieved in a two-step process having as isolable intermediate the 'half-unit' which is a 1:1 condensation product of diprimary amines which still has a primary amino group available for further reaction with carbonyl derivatives. The 'half-unit' therefore has been suggested as an intermediate of great potential usefulness in providing a facile extension to the available range of non-symmetrical Schiff bases (Bett, Fenton & Tate, 1981). In this perspective we have previously described the copper(II) and nickel(II) template synthesis of diethylenetriamine with one molecule of salicylaldehyde. The tetradentate behaviour of the resulting 'half-unit' was demonstrated by the crystal structure determination of the nickel and copper complexes (Cusmano Priolo, Rotondo, Rizzardi, Bruno & Bombieri, 1983; Rotondo, Cusmano Priolo, Romeo, Bruno & Bombieri, 1983). In the present paper we describe the crystal structure of the monoimine resulting from the copper(II) template condensation of one molecule of diethylenetetramine with one molecule of salicylaldehyde (1:1 molar ratio).

Experimental. 1 mmol of $Cu(NO_3)_2.3H_2O$ suspended in methanol [20 cm^3], 1 mmol of salicylaldehyde in methanol [10 cm^3] added; resulting solution added dropwise to a solution of triethylenetetramine (trien), 1 mmol in methanol [10 cm^3]; reaction mixture allowed to stand for two days at room temperature then 5 cm^3 of water saturated with $NaClO_4$ added; slow evaporation of solvent yielded dark-violet crystals of the title compound. Analytical data (wt%), calculated values in parentheses and the characteristic IR bands (cm^{-1}): C 30·38 (30·69), H 1·47 (1·41), N 10·90 (10·74); ν(NH) 3250 (*br*), ν(C=N) 1644 (*vs*).

Magnetic susceptibility, $\mu = 1{\cdot}82$ BM (1 BM $= 9{\cdot}274078 \times 10^{-24}$ JT^{-1}), obtained at 296 K with a Faraday balance equipped with a Bruker BMN 50/50 electromagnet and an *R*-100 Cohn microbalance; conductivity value obtained with a Radiometer CDM3 conductivity bridge, electronic spectrum recorded on a Cary 219 double-beam spectrophotometer. Prismatic crystal $0{\cdot}15 \times 0{\cdot}20 \times 0{\cdot}25$ mm, 20 reflections with $7 \leq \theta \leq 15°$ used for measuring lattice parameters; 2 standard reflections $35\bar{7}$ and 419 measured every 120 min, no significant intensity variation; 4632 independent reflections collected on a Siemens–Stoe four-circle diffractometer, scan range $2\theta = 3\text{–}50°$ $(-10 \leq h \leq 10, -12 \leq k \leq 12, -14 \leq l \leq 0)$, ω/θ scan mode, 2479 with $I \geq 2{\cdot}5\sigma(I)$, Lp correction, absorption ignored; structure solved by Patterson and Fourier methods and refined by full-matrix least-squares techniques; H atoms [except those belonging to N(4)] introduced at calculated positions (C—H 0·95 Å) with isotropic $B = 6$ Å^2, anisotropic temperature factors

0108-2701/84/060960-03$01.50

assigned to non-hydrogen atoms; perchlorate groups distributed on two positions with occupancy factors K 0·6 and 0·4, $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 3{\cdot}5578[\sigma^2(F_o) + 24{\cdot}8 \times 10^{-5} (F_o)^2]^{-1}$ in last refinement cycles, final $R = 0{\cdot}047$ and $R_w = 0{\cdot}048$ (297 parameters refined); atomic scattering factors (corrected for anomalous dispersion of Cu) from *International Tables for X-ray Crystallography* (1974); final $(\Delta/\sigma)_{\max} = 0{\cdot}02$, final $\Delta\rho$ excursions $\leq |0{\cdot}3|$ e Å^{-3}; computation carried out using *SHELX* (Sheldrick, 1976) on an IBM 4341 computer.*

Discussion. Table 1 gives the atomic coordinates and Table 2 bond lengths and angles. Fig. 1 shows a view down **c** of the cationic [Cu(saltrien)perchlorate] and anionic (perchlorate) units and Fig. 2 the crystal packing.

The weighted mean plane through the four basal donor atoms shows a lack of planarity with N(3) and N(1) deviating by 0·117 (4) and 0·124 (4) Å, respectively, while N(2) and O(9) are −0·167 (5) and −0·088 (4) Å on the opposite side, indicating a distortion of the basal plane towards tetrahedral. The copper atom is out of the plane by −0·078 (1) Å in the direction of the apical oxygen. The angles N(1)—Cu—N(3) and N(2)—Cu—O(9) are 164·3 (2)° and 177·7 (2)°. The remaining nitrogen N(4) of the ligand is not coordinating, being 3·468 (4) Å from copper.

The conformations of the five-membered rings of the saltrien ligand, as defined by ethylenic carbon-atom displacements from the corresponding donor–metal–donor planes, are for N(1)—Cu—N(2) envelope [C(8) and C(9) deviating by −0·006 (6) and −0·613 (6) Å, respectively] and for N(2)—Cu—N(3) half-chair [C(10) 0·343 (6) and C(11) −0·328 (6) Å out of the plane, respectively].

The torsion angles of the two ethylenic bridges are 52·2 (6)° for N(2)—C(10)—C(11)—N(3) and −46·6 (6)° for N(1)—C(8)—C(9)—N(2).

The ring $\overline{\text{O(9)—Cu—N(1)}}$ is approximately planar; the deviations of the atoms from their weighted mean plane are: Cu 0·005 (5), O(9) −0·053 (4), C(7) 0·033 (5), C(2) 0·044 (5), C(1) −0·012 (5) and N(1) −0·039 (4) Å.

The goal of this structure determination has been the correct formulation of the compound. In fact, in principle, the presence of two perchlorate anionic units should have required the oxidation of copper(II) to copper(III), considering the saltrien as a negatively unicharged species. But an accurate examination of the final difference Fourier map allowed the discovery of

Table 1. *Atomic coordinates* (×10^4) *and equivalent isotropic and isotropic U values* (Å^2 ×10^3) *with e.s.d.'s in parentheses*

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

	x	y	z	U_{eq}/U_{iso}	K
Cu	1480 (1)	2059 (1)	2548 (1)	58·4 (3)	
Cl(1)	5571 (1)	2416 (1)	4916 (1)	61·2 (5)	
Cl(2)	7555 (2)	2946 (2)	348 (1)	70·7 (6)	
O(1)	4078 (5)	1625 (5)	4233 (4)	116 (2)	
N(1)	283 (5)	2221 (4)	3590 (3)	60 (2)	
N(2)	2238 (5)	4063 (4)	2986 (4)	66 (2)	
N(3)	2416 (5)	2312 (4)	1263 (3)	64 (2)	
N(4)	3748 (6)	−438 (6)	2233 (4)	71 (2)	
O(9)	828 (4)	139 (3)	2183 (3)	62 (2)	
C(1)	−664 (6)	1236 (5)	3781 (4)	61 (2)	
C(2)	−994 (5)	−143 (5)	3272 (4)	55 (2)	
C(3)	−2161 (6)	−1061 (6)	3547 (5)	73 (2)	
C(4)	−2615 (7)	−2387 (6)	3077 (6)	30 (3)	
C(5)	−1915 (7)	−2872 (6)	2335 (5)	78 (3)	
C(6)	−742 (6)	−2016 (5)	2069 (4)	66 (2)	
C(7)	−274 (6)	−634 (5)	2507 (4)	55 (2)	
C(8)	517 (7)	3614 (6)	4119 (5)	75 (2)	
C(9)	969 (7)	4576 (5)	3341 (5)	76 (2)	
C(10)	2628 (7)	4665 (6)	2039 (5)	80 (3)	
C(11)	3441 (7)	3689 (6)	1544 (5)	81 (2)	
C(12)	3137 (7)	1237 (6)	794 (4)	74 (3)	
C(13)	4441 (7)	674 (6)	1699 (5)	74 (2)	
O(2)	5045 (9)	3652 (8)	5242 (7)	122 (4)	0·6
O(3)	6549 (13)	1925 (10)	5855 (9)	138 (5)	0·6
O(4)	6524 (9)	2931 (12)	4269 (7)	113 (5)	0·6
O(5)	6137 (5)	2649 (5)	−622 (4)	108 (2)	
O(6)	7726 (19)	4335 (14)	648 (11)	181 (5)	0·6
O(7)	7615 (15)	2027 (15)	1124 (10)	192 (8)	0·6
O(8)	8817 (9)	2669 (11)	−75 (10)	135 (6)	0·6
O(21)	5845 (20)	2534 (16)	6042 (14)	115† (5)	0·4
O(31)	6390 (23)	1314 (19)	4722 (17)	172† (6)	0·4
O(41)	5993 (20)	3555 (16)	4505 (13)	117† (5)	0·4
O(61)	7174 (14)	3106 (13)	1389 (10)	88† (3)	0·4
O(71)	8413 (18)	4315 (18)	0481 (14)	94† (5)	0·4
O(81)	8691 (21)	2150 (16)	511 (14)	118† (5)	0·4

† U_{iso}.

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Cu–N(1)	1·931 (5)	C(2)–C(3)	1·415 (8)
Cu–N(2)	1·989 (4)	C(2)–C(7)	1·404 (8)
Cu–N(3)	2·033 (5)	C(3)–C(4)	1·358 (8)
Cu–O(1)	2·634 (5)	C(4)–C(5)	1·367 (10)
Cu–O(9)	1·894 (3)	C(5)–C(6)	1·380 (8)
N(1)–C(1)	1·278 (7)	C(6)–C(7)	1·399 (7)
N(1)–C(8)	1·453 (7)	C(8)–C(9)	1·498 (9)
N(2)–C(9)	1·468 (8)	C(10)–C(11)	1·498 (10)
N(2)–C(10)	1·463 (8)	C(12)–C(13)	1·505 (8)
N(3)–C(11)	1·482 (7)	Cl(1)–O(1)	1·398 (4)
N(3)–C(12)	1·497 (8)	Cl(1)–O(2)	1·451 (9)
N(4)–C(13)	1·479 (9)	Cl(1)–O(3)	1·355 (10)
N(4)–H(40)	0·88 (6)	Cl(1)–O(4)	1·407 (10)
N(4)–H(41)	0·80 (4)	Cl(2)–O(5)	1·395 (4)
N(4)–H(42)	0·94 (6)	Cl(2)–O(6)	1·381 (11)
O(9)–C(7)	1·333 (7)	Cl(2)–O(7)	1·353 (8)
C(1)–C(2)	1·424 (7)	Cl(2)–O(8)	1·427 (11)
N(2)–Cu–O(9)	177·7 (2)	C(3)–C(2)–C(7)	118·6 (5)
N(1)–Cu–O(9)	95·1 (2)	C(2)–C(3)–C(4)	121·8 (5)
N(1)–Cu–N(2)	84·7 (2)	C(3)–C(4)–C(5)	119·9 (6)
N(2)–Cu–N(3)	85·8 (2)	C(4)–C(5)–C(6)	120·0 (5)
O(9)–Cu–N(3)	94·9 (2)	C(5)–C(6)–C(7)	121·9 (5)
Cu–O(1)–Cl(1)	135·5 (3)	C(2)–C(7)–C(6)	117·8 (5)
Cu–N(1)–C(8)	112·8 (3)	O(9)–C(7)–C(6)	118·5 (5)
Cu–N(1)–C(1)	124·8 (3)	O(9)–C(7)–C(2)	123·7 (4)
C(1)–N(1)–C(8)	122·3 (5)	N(1)–C(8)–C(9)	108·2 (5)
Cu–N(2)–C(10)	108·7 (3)	N(2)–C(9)–C(8)	107·9 (5)
Cu–N(2)–C(9)	106·0 (3)	N(2)–C(10)–C(11)	108·2 (5)
C(9)–N(2)–C(10)	117·6 (4)	N(3)–C(11)–C(10)	109·4 (5)
C(11)–N(3)–C(12)	114·1 (4)	N(3)–C(12)–C(13)	114·0 (4)
Cu–O(9)–C(7)	125·6 (3)	N(4)–C(13)–C(12)	112·4 (5)
N(1)–C(1)–C(2)	125·7 (5)	O(1)–Cu–N(2)	88·6 (2)
C(1)–C(2)–C(7)	124·6 (5)	O(1)–Cu–N(3)	100·9 (2)
C(1)–C(2)–C(3)	116·8 (5)	O(1)–Cu–O(9)	89·1 (2)
O(1)–Cu–N(1)	91·4 (2)	N(1)–Cu–N(3)	164·3 (2)
N(3)–Cu–N(1)	164·3 (2)		

---

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39234 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

electron density residues of the order of 0·8 e Å^{-3} near to the non-coordinated nitrogen N(4) in positions characteristic for three hydrogen atoms bound to an sp^3-hybridized nitrogen atom. These were introduced in the structure-factor calculations and refined with a fixed isotropic thermal parameter ($B = 6$ Å^2). In particular, one of them, H(42), forms a short contact of 1·76 (3) Å with the oxygen of the saltrien ligand [the corresponding N(4)···O(9) distance is 2·686 (7) Å] which could be interpreted as a hydrogen bond. The coordinated Schiff base can be seen as the result of a proton transfer from the phenoxy oxygen to the terminal nitrogen. In order to effect sufficient charge dispersal copper(II) requires, in the solid state, that the apical position be occupied by a perchlorate anion which neutralizes one of the two positive charges of the metal. A second, not coordinated, perchlorate anion counterbalances the residual positive charge of the complex. The given formulation is in agreement with the value of $\mu_{\rm eff}$ (1·82 BM) for copper in the oxidation state +2 with a d^9 configuration.

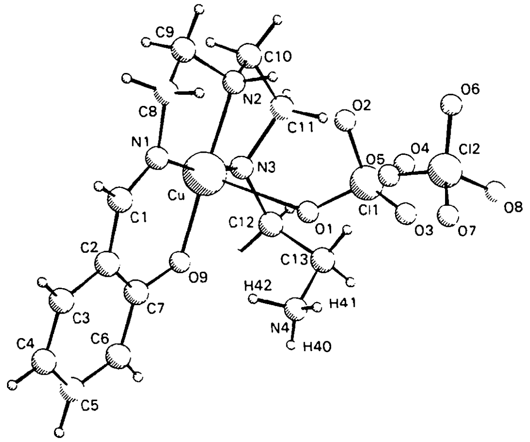

Fig. 1. View of the asymmetric unit down **c**.

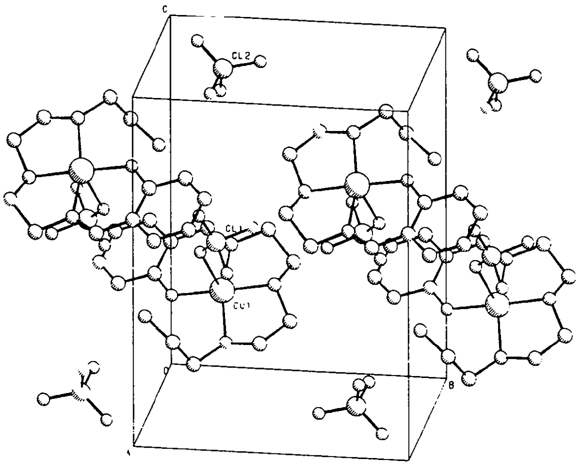

Fig. 2. Unit-cell contents.

A comparison of the structural parameters of the present compound with those of $[Cu(saldien)H_2O].PF_6$ (Cusmano Priolo *et al.*, 1983) shows a close similarity in bond distances and angles, the only difference being the conformation of one of the two five-membered rings [$\overline{\rm N(2)—Cu—N}(3)$ envelope conformation in the saldien complex and half-chair in the present complex].

The Cu—O(perchlorate) distance [2·634 (4) Å] is in the range of the distances [2·575 (6)–2·676 (10) Å] found in complexes containing the CuN_4O_2 coordination group, as for example Cu[*N,N'*-bis(2-aminoethyl)trimethylenediamine]$(ClO_4)_2$ (Fawcett, Rudich, Toby, Lalancette, Potenza & Schugar, 1980) where both perchlorates are bound to copper. The Cu—O(1)—Cl(1) angle of 135·5 (3)° is larger than that found in the previously quoted compound where the two Cu—O—Cl angles are 118·9 (3) and 121·1 (3)°, but it is very close to the value of 136·3 (9)° found in $\{Cu_3(OH)$-[3-(phenylimino)-2-butanone oxime]$_3(ClO_4)\}.ClO_4$ (Butcher, O'Connor & Sinn, 1981) where the Cu—O-(perchlorate) distance is 2·552 (9) Å.

The molar conductivity of the complex in methanol at 298 K is 206 Ω^{-1} cm^2 mol^{-1}; this value is in the range of a 2:1 electrolyte type and suggests that the complex in solution loses the coordinated perchlorate and acts as a dipositively charged species. The electronic spectrum of the compound in methanol has a maximum at 573 nm ($\varepsilon = 115$ cm^3 mol^{-1} cm^{-1}) attributable to a $d \rightarrow d$ transition of copper d^9 in a square-pyramidal arrangement (Hathaway & Tomlison, 1970). The molecular conductivity and the electronic spectrum, therefore, suggest that in solution the complex preserves its square-pyramidal configuration, substituting a perchlorate anion with a molecule of solvent.

References

Bett, G., Fenton, D. E. & Tate, J. R. (1981). *Inorg. Chim. Acta*, **54**, 101–102.

Butcher, R. I., O'Connor, C. I. & Sinn, E. (1981). *Inorg. Chem.* **20**, 537–545.

Costa, G., Mestroni, G., Puxeddu, A. & Reisenhofer, E. (1970). *J. Chem. Soc. A*, pp. 2870–2874.

Costes, J. P., Cross, G., Darbien, M. H. & Laurent, J. P. (1982). *Inorg. Chim. Acta*, **60**, 111–114.

Cusmano Priolo, F., Rotondo, E., Rizzardi, G., Bruno, G. & Bombieri, G. (1983). *Acta Cryst.* C**39**, 550–552.

Fawcett, T. G., Rudich, S. M., Toby, B. H., Lalancette, R. A., Potenza, J. A. & Schugar, H. J. (1980). *Inorg. Chem.* **19**, 940–945.

Hathaway, B. J. & Tomlison, A. A. G. (1970). *J. Chem. Soc. A*, pp. 806–811.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99–104. Birmingham: Kynoch Press.

Jones, R. D., Summerville, D. A. & Basolo, F. (1979). *Chem. Rev.* **79**, 139–179.

Rotondo, E., Cusmano Priolo, F., Romeo, M., Bruno, G. & Bombieri, G. (1983). *Acta Cryst.* C**39**, 1525–1527.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Wilkins, R. G. (1971). *Adv. Chem. Ser.* No. 100, pp. 111–126.