STRUCTURE OF A COPPER(II) COMPLEX WITH A NON-SYMMETRICAL TETRADENTATE SCHIFF BASE

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The structure of (1-phenyl-3-{2-[(2-aminoethyl)amino]ethylimino}-1-buten-1-olato-O,N,N′,N″)-copper(II) perchlorate, [Cu(baden)]ClO_4 was solved by Patterson and Fourier techniques and refined anisotropically to $R = 0{\cdot}066$ for 2 205 unique observed reflections. The title complex ($C_{14}H_{20}ClCuN_3O_5$) crystallizes in the $P2_1/c$ space group with the lattice parameters $a = 10{\cdot}435(1)$, $b = 20{\cdot}745(2)$, $c = 8{\cdot}457(1)$ Å, $\beta = 108{\cdot}56(1)°$, $Z = 4$. The complex cation including the baden ligand contains two five-membered and one six-membered chelate rings, and the phenyl ring. The perchlorate anion is disordered. Two perchlorate oxygen positions, O22A and O33B, each with one half occupation factor value and four N_3O donor atoms from the baden ligand complete the coordination geometry about the Cu atom on the square pyramid [Cu—O22A = 2·655(11)Å and Cu—O33B = 2·855(10) Å]. Weak hydrogen bonds among cations and anions were found in the structure.

So far the structures of the complexes with non-symmetrical tetradentate Schiff bases have been described with different ligands[1]. The structure determination of the title compound was undertaken to characterize a new series of the complexes containing the baden ligand – 1-phenyl-3-{2-[(2-aminoethyl)amino]ethylimino}-1-buten-1-olato-O,N,N′,N″ or 1-phenyl-3-methyl-4,7,10-triazadeca-1,3-dien-1-olato-O,N,N′,N″.

EXPERIMENTAL

To the methanolic solution containing 3·7 g (0·01 mol) $Cu(ClO_4)_2.6\,H_2O$ and the equimolar amount of the baden ligand was dropwise added 0·4 g (0·01 mol) NaOH (in aqueous methanol solution) under stirring. The crystalline product (1·1 g, 27%) was yielded by slow evaporation of a solvent during a few days. Dark violet crystals suitable for a structure-analysis were obtained by recrystallization from methanol. The density was determined by the flotation method in a mixture of diiodomethane–toluene. For $C_{14}H_{20}ClCuN_3O_5$ (409·3) calculated 41·08% C, 4·92% H, 15·53% Cu and 10·27% N; found 39·85% C, 5·05% H, 15·00% Cu and 10·46% N.

Crystal Structure Determination

Monoclinic, space group $P2_1/c$, $a = 10{\cdot}435(1)$, $b = 20{\cdot}745(2)$, $c = 8{\cdot}457(1)$ Å, $\beta = 108{\cdot}56(1)°$, $V = 1\,735{\cdot}5(5)$ Å^3, $Z = 4$, $D_o = 1{\cdot}57(1)$, $D_c = 1{\cdot}567$ g cm^{-3}, $\mu = 1{\cdot}443$ mm^{-1}, $F(000) = 844$.

The structure was solved by Patterson and Fourier techniques and refined by block-diagonal least-squares procedure. The hydrogen atoms were fixed in calculated positions with fixed U_{iso} values of 1·3 times the U_{eq} value of the attached atoms. The oxygen atoms of the perchlorate anion were assumed in two positions (A and B) with calculated occupancy factor values ($K = 0{\cdot}5$) and isotropically refined with constraints. Absorption and extinction effects were neglected.

The parameters of the intensity data collection, structure solution and refinement are listed in Table I.

TABLE I

Data collection and structure refinement parameters

Crystal dimensions, mm	0·35 × 0·24 × 0·22
Diffractometer and radiation used	Enraf–Nonius CAD4 equipped with a graphite monochromator, MoK$_\alpha$, $\lambda = 0{\cdot}71073$Å
Scan technique	$\omega/2\theta$
Number and θ range of reflections for lattice parameter refinement[a]	20; 18·65—21·09°
Range of h, k and l	$-12 \rightarrow 12$, $0 \rightarrow 25$, $-10 \rightarrow 10$
Standard reflections	−2 1 0, 2 −1 0
Interval of standard reflection monitoring, intensity fluctuation	120 min; 0·3%
Total number of reflections measured, 2θ range	6 962; 0 → 50°
Number of unique observed reflections	2 205
Criterion for observed reflections	$I > 1{\cdot}96\sigma(I)$
Value of R_{int}	0·033
Function minimized	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Weighting scheme	$w = 0{\cdot}8699/[\sigma^2(F_o) + 0{\cdot}0009F_o^2]$
Parameters refined	88
Value of R	0·066
Value of wR	0·075
Value of S	1·926
Ratio of max. LS shift to e.s.d. (Δ/σ)	0·02
Max. and min. heights [b] in final $\Delta\varrho$ map	1·19 e Å^{-3} (1·50 Å away from Cl); −0·73 e Å^{-3}
Source of atomic scattering factors	ref.[3]
Programs used	SDP (ref.[2]), SHELX-76 (ref.[3]), PARST (ref.[4])
Computer used	DEC PDP 11/73, EC 1033

[a] No reflections indicating multiplicity of lattice parameters were found; [b] estimated standard deviations are not available.

DISCUSSION

The final atomic coordinates and equivalent isotropic temperature factors of non-hydrogen atoms (isotropic factors for perchlorate oxygens) are given in Table II. Bond distances and angles are listed in Table III. The complex cation is shown in Fig. 1 and the disordered perchlorate anion in Fig. 2.

The Cu atom of the [Cu(baden)]ClO_4 complex has a nearly square coordination with N_3O donor atoms from the baden ligand. The largest displacement from the

TABLE II

Final coordinates (.10^4) for non-hydrogen atoms and their equivalent isotropic thermal parameters (.10^3) as $U_{eq} = (1/3)\,[U_{22} + 1/\sin^2 \beta(U_{11} + U_{33} + 2U_{13} \cos \beta)]$

Atom	*x*	*y*	*z*	U_{eq}, Å^2
Cu	2130·7(8)	−550·1(4)	2459(1)	51·3(3)
Cl	−1361(2)	3702(1)	7011(3)	69(1)
O1	2325(5)	256(2)	1559(6)	56(1)
O11A[a]	−1120(19)	3103(4)	7768(18)	165(8)
O22A[a]	−1955(15)	3627(8)	5308(6)	237(16)
O33A[a]	−148(10)	4029(9)	7326(22)	183(8)
O44A[a]	−2217(14)	4051(7)	7649(17)	138(6)
O11B[a]	−207(10)	3358(6)	7849(14)	140(6)
O22B[a]	−2489(10)	3370(7)	7092(19)	181(8)
O33B[a]	−1431(14)	3779(8)	5361(8)	137(7)
O44B[a]	−1315(16)	4302(3)	7751(18)	139(7)
N1	4026(6)	−772(3)	3199(8)	57(3)
N2	1956(6)	−1345(3)	3728(8)	65(3)
N3	105(6)	−490(3)	1876(8)	60(3)
C1	4311(8)	−1387(4)	4076(10)	66(3)
C2	3034(9)	−1764(4)	3669(14)	86(4)
C3	534(7)	−1566(4)	3030(11)	68(3)
C4	−336(9)	−985(4)	2843(11)	70(3)
C5	3473(7)	511(3)	1614(8)	53(3)
C6	4725(7)	226(4)	2300(10)	57(3)
C7	4999(7)	−378(4)	3077(9)	58(3)
C8	6452(8)	−573(4)	3827(12)	80(4)
C9	3350(8)	1187(4)	904(9)	62(3)
C10	2304(9)	1572(4)	988(10)	68(3)
C11	2129(11)	2175(5)	353(13)	87(4)
C12	3000(16)	2399(5)	−411(13)	115(6)
C13	4091(14)	2049(6)	−493(12)	103(5)
C14	4301(10)	1425(5)	185(10)	80(4)

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[a] The occupancy factor is 0·5.

least-squares plane through Cu, N1, N2, N3, O1 is shown by atom N2[−0·170(6)Å]. The Cu—N2 and Cu—N3 bonds are approximately of equal lengths and significantly longer than the remaining Cu—O1 and Cu—N1 ones.

TABLE III

Bond distances (in Å) and angles (in °)

Atoms	Distances	Atoms	Distance
Cu—O1	1·875(5)	C6—C7	1·401(12)
Cu—N1	1·930(6)	C7—C8	1·501(10)
Cu—N2	2·007(7)	C9—C10	1·372(13)
Cu—N3	2·016(6)	C10—C11	1·351(13)
O1—C5	1·297(9)	C11—C12	1·354(21)
N1—C1	1·458(10)	C12—C13	1·371(21)
N1—C7	1·333(10)	C13—C14	1·405(16)
N2—C2	1·435(12)	Cl—O11A	1·384(10)
N2—C3	1·484(9)	Cl—O22A	1·384(6)
N3—C4	1·475(12)	Cl—O33A	1·385(13)
C1—C2	1·488(12)	Cl—O44A	1·386(16)
C3—C4	1·487(12)	Cl—O11B	1·385(10)
C5—C6	1·382(10)	Cl—O22B	1·384(13)
C5—C9	1·515(10)	Cl—O33B	1·383(8)
C9—C14	1·408(14)	Cl—O44B	1·387(9)

Atoms	Angles	Atoms	Angles
N2—Cu—N3	85·1(3)	C2—N2—C3	119·7(7)
N1—Cu—N3	168·6(3)	Cu—N3—C4	108·0(5)
N1—Cu—N2	83·6(3)	N1—C1—C2	108·6(7)
O1—Cu—N3	94·9(3)	N2—C2—C1	109·1(7)
O1—Cu—N2	171·8(2)	N2—C3—C4	106·9(6)
O1—Cu—N1	96·5(3)	N3—C4—C3	109·6(7)
Cu—O1—C5	124·6(4)	O1—C5—C9	113·8(6)
Cu—N1—C7	123·8(5)	O1—C5—C6	125·4(6)
Cu—N1—C1	113·3(5)	C6—C5—C9	120·8(7)
C1—N1—C7	122·6(7)	C5—C6—C7	127·1(7)
Cu—N2—C3	106·9(5)	N1—C7—C6	122·5(7)
Cu—N2—C2	105·9(5)	C6—C7—C8	117·8(7)
N1—C7—C8	119·6(7)	C5—C9—C14	120·9(8)
C5—C9—C10	119·1(7)	C10—C9—C14	120·0(8)
C9—C10—C11	121·8(9)	C10—C11—C12	119(1)
C11—C12—C13	122(1)	C12—C13—C14	119(1)
C9—C14—C13	117(1)		

The arrangement of the Cu, N1, C7, C6, C5 and O1 atoms, forming the six-membered chelate ring, corresponds to a very flat chair conformation. The N1 and Cu atoms being displaced by 0·032(6) and −0·0006(9) Å from the least-squares plane fitted through all the atoms of the ring. The phenyl group is not in conjugation with the mentioned six-membered pseudoaromatic ring, the dihedral angle between their planes equals 29·3(3)°. The C5—C9 contact between the two non-saturated six-membered rings is surprisingly the longest C—C bond in the structure. Both five-membered chelate rings are distorted. One of them (Cu, N1, C1, C2 and N2) adopts an asymmetric envelope conformation with the N1—C1—C2—N2 torsion angle of −43·2(9)°. The C1 and C2 atoms are displaced from the least-squares plane of the ring by −0·054(8)Å and 0·443(11)Å, respectively. The conformation of the second five-membered chelate ring (Cu, N2, C3, C4 and N3) is a half-chair, the N2—C3—C4—N3 torsion angle equals 53·1(9)° and the C3 and C4 atoms show the deviations from the ring-plane by 0·359(9)Å and −0·245(9)Å.

The O atoms of the perchlorate anion (O11, O22, O33 and O44) are disordered. The *R*-factor value decreased for a model in which each O atom assumes two positions, A and B, with calculated occupancy factors of 0·5. According to this model the perchlorate tetrahedron apparently oscillates between these two limiting states. The oscillating motion can be explained as a restricted rotation around an axis perpendicular to the Cl, O22A, O33A plane and passing through the Cl atom, approximately in the $[1\bar{1}0]$ direction. The ideal O11A—Cl—O11B and O44A—Cl—O44B angle values corresponding this operation are 45° and that is in good agreement with the observed values of 44·7(7)° and 45·6(9)°, respectively. The Cl—O distances listed in Table III correspond to those found in other perchlorate complexes with Schiff bases[5–8].

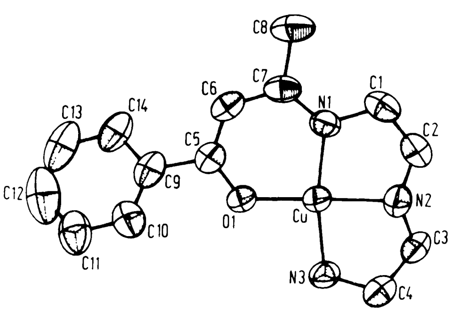

FIG. 1

View of the complex cation with thermal ellipsoids scaled to 50% probability

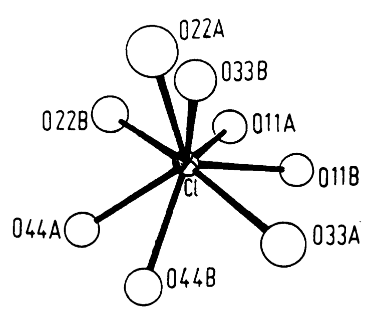

FIG. 2

View of the disordered perchlorate anion

Two oxygen positions, O22A and O33B, approximately situated in an axial site, with four N_3O donor atoms (in basal sites) complete the coordination geometry about the Cu atom on the square pyramid. The Cu—O22A and Cu—O33B distances equal 2·655(11) Å and 2·855(10) Å, respectively. An inspection of the molecular packing shows that the O11A, O33A and O11B perchlorate oxygens can serve as acceptors of weak hydrogen bonds as followed from the donor–acceptor lengths and the donor–hydrogen–acceptor angles: 3·10(2) Å and 165·4(8)° for N2—H···O11A, 3·08(2)Å and 157·9(8)° for N3—H···O33A and 3·09(1)Å and 160·2(7)° for N3—H···O22B. The perchlorate tetrahedron shows a regular shape, there are no sign of splitting t_2 stretching (1 083 cm^{-1}) or bonding (622 cm^{-1}) vibrations of the anion in the IR spectra. A weak peak at 3 055 cm^{-1}, assigned as ν_{N-H} seems to support the mentioned hydrogen bonding. A crystal packing is depicted in Fig. 3.

Comparison of the title complex with related [Pd(baden)]ClO_4 (ref.[1]) reveals considerable differences in the conformation of the six membered chelate rings and in the coordination geometry of a metal. The conformation of the six-membered chelate ring is a boat, in the palladium(II) complex and the coordination polyhedron around Pd is a distorted square, apical positions bellow and above the metal are empty up to 3·5 Å. Pd—N1 is the shortest bond contrary to the title complex, where Cu—O1 is the shortest one.

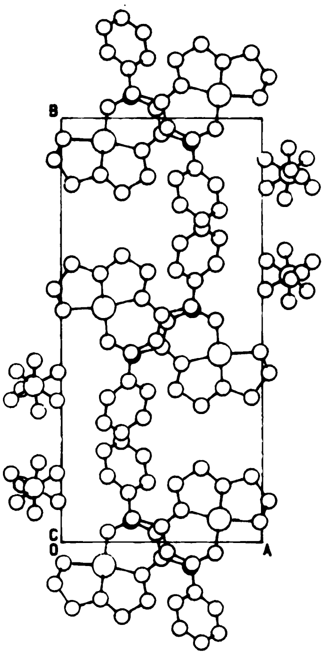

FIG. 3
Crystal packing

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