Table 4. *IR spectrum of the* ClO_4 *group* (cm^{-1})

	$\nu_1 A$	ν_2	ν_3	ν_4
(1)	930 *m*		1070	625
			1110 *s*	630 *s*
			1145	637
Ionic	935 *w*	460 *s*	1050–1170 *s*	630 *s*

distances O(7)···N(3) 2·828 (5) and O(7)···O(2^i) 2·847 (5) Å.

The electronic reflectance spectrum of (1) involves a broad peak at 15 820 cm^{-1} with a weakly resolved shoulder at *ca* 10 000 cm^{-1} (Procter, Hathaway & Hodgson, 1972), and the polycrystalline ESR spectrum is axial, $g_\perp = 2·074$ and $g_{\parallel} = 2·284$. The single-crystal ESR spectrum of (1) yields three *g* factors 2·053, 2·065 and 2·274, but as the CuN_2O_2 plane is slightly misaligned by the monoclinic twofold axis, these crystal *g* factors cannot be unambiguously resolved into their local molecular *g* factors. Nevertheless, the electronic properties of (1) are consistent with the elongated rhombic octahedral $CuN_2O_2O'_2$ chromophore of (1) as reported above (Hathaway & Billing, 1970).

The authors acknowledge the award of a Senior Demonstratorship (to ST), help in data collection by Drs P. G. Owston, M. McPartlin, and D. K. Henrick (Chemistry Department, Polytechnic of North London, Holloway), the Computer Bureau, UCC, for computing facilities, Drs G. M. Sheldrick, S. Motherwell and R. Taylor (Cambridge University) for the use of their programs, and the Microanalysis Section, UCC, for analysis.

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Acta Cryst. (1982). B**38**, 1577–1580

Structure of Acetato(*N*-methyl-*N'*-salicylidene-1,3-propanediaminato)copper(II) Dimer

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(*Received* 14 *September* 1981; *accepted* 14 *December* 1981)

Abstract. $[Cu(C_{11}H_{15}N_2O)(C_2H_3O_2)]_2$, $(C_{13}H_{18}CuN_2O_3)_2$, $M_r = 627·68$, triclinic, $P\bar{1}$, $a = 8·247$ (3), $b = 9·173$ (2), $c = 10·239$ (3) Å, $\alpha = 108·88$ (2), $\beta = 111·20$ (3), $\gamma = 76·49$ (3)°, $V = 677·3$ (4) Å^3, $Z = 1$, $D_m = 1·53$ (flotation), $D_x = 1·539$ Mg m^{-3}, μ(Mo $K\alpha$) = 1·68 mm^{-1}. The structure was solved by direct methods and refined by the block-diagonal least-squares technique to $R = 0·043$ for 2246 reflections with $I > 2\sigma(I)$. The tridentate Schiff base derived from salicylaldehyde and *N*-methyl-1,3-propanediamine form together with the acetate O atom the coordination plane around Cu. The axial positions are occupied by the more distant carboxyl O atoms (2·51 and 2·83 Å). The acetate ion acts under these conditions as an unsymmetrically chelating and monoatomic bridging group.

Introduction. Several Schiff-base Cu^{II} complexes derived from L amino acids and salicylaldehyde have been analysed by X-ray methods (Ueki, Ashida, Sasada & Kakudo, 1967, 1969; Fujimaki, Oonishi, Muto, Nakahara & Konijama, 1971; Hämäläinen, Ahlgrén, Turpeinen & Rantala, 1978; Hämäläinen, Turpeinen, Ahlgrén & Rantala, 1978; Korhonen & Hämäläinen, 1979, 1981). The coordination sphere of the Cu^{II} ion in these compounds has almost invariably

0567-7408/82/051577-04$01.00

been found to be square-pyramidal (4 + 1). We have now replaced the amino acid in this type of complex with a diamine group and performed a structural analysis on the derived Schiff-base complex.

The compound was synthesized by the method given in the literature (Tokii, Emori & Muto, 1979), except that the Schiff-base ligand was prepared first and then the copper(II) acetate in equimolar ratio was gradually added with stirring. Recrystallizations were performed from ethanol.

The Cu was checked electroanalytically. Analysis: calculated: Cu, 20·25%; found: Cu, 20·18%. Also, the positions of the absorption maxima found in the IR spectrum were in good agreement with the positions given earlier (Tokii, Emori & Muto, 1979). A blue-green crystal with dimensions 0·25 × 0·35 × 0·20 mm was selected for the X-ray work. The unit-cell dimensions were calculated by the least-squares method applied to the angular values of 14 reflections measured on a Syntex $P2_1$ diffractometer (graphite-monochromatized Mo $K\alpha$ radiation). Intensities were collected between the 2θ values 3·0 and 53·0° using one check reflection every 60 reflections. The ω-scan method was employed with a variable scan speed of 2·0 to 15·0° min^{-1}, depending on the intensity of the measured reflection. The absorption effect was checked by empirical φ-scan method, but was so insignificant that correction was excluded.

Table 1. *Atomic coordinates* ($\times 10^4$; *for* H $\times$ 10^3) *and isotropic thermal parameters*

	x	y	z	B_{eq}/B (Å^2)
Cu	5310 (1)	3350 (1)	505 (1)	3·1 (1)
O(1)	3591 (4)	2644 (4)	−1332 (4)	3·6 (3)
O(2)	3662 (4)	5291 (4)	766 (4)	3·5 (3)
O(3)	2575 (6)	4091 (6)	1756 (6)	5·7 (5)
N(1)	6807 (5)	1332 (5)	352 (5)	3·5 (4)
N(2)	7101 (6)	4473 (5)	2319 (5)	3·7 (3)
C(1)	3756 (6)	1377 (6)	−2352 (6)	3·2 (4)
C(2)	2453 (7)	1179 (6)	−3723 (6)	3·8 (5)
C(3)	2542 (9)	−140 (7)	−4826 (6)	4·8 (6)
C(4)	3937 (9)	−1334 (8)	−4622 (7)	5·4 (6)
C(5)	5195 (8)	−1201 (7)	−3297 (7)	4·6 (6)
C(6)	5153 (7)	143 (6)	−2147 (6)	3·4 (4)
C(7)	6522 (6)	162 (6)	−772 (6)	3·4 (4)
C(8)	8197 (9)	1094 (8)	1705 (8)	6·3 (7)
C(9)	9509 (8)	2234 (9)	2350 (9)	6·8 (8)
C(10)	8917 (8)	3873 (9)	2385 (9)	6·3 (7)
C(11)	6807 (10)	4808 (9)	3744 (8)	6·3 (7)
C(12)	2579 (7)	5235 (6)	1373 (6)	3·8 (5)
C(13)	1251 (8)	6657 (8)	1610 (7)	4·9 (6)
H(1)	146 (7)	208 (7)	−391 (6)	6 (1)
H(2)	162 (9)	−9 (8)	−583 (8)	9 (2)
H(3)	387 (8)	−220 (7)	−537 (6)	6 (2)
H(4)	608 (8)	−203 (7)	−315 (6)	6 (2)
H(5)	733 (8)	−82 (7)	−71 (7)	6 (1)
H(6)	898 (10)	75 (9)	121 (9)	10 (2)
H(7)	866 (9)	−4 (8)	164 (7)	9 (2)
H(8)	−51 (11)	816 (10)	805 (9)	12 (2)
H(9)	90 (10)	798 (9)	689 (8)	11 (2)
H(10)	926 (11)	374 (10)	153 (9)	12 (2)
H(11)	986 (9)	463 (8)	331 (7)	9 (3)
H(12)	700 (8)	536 (7)	214 (7)	6 (2)
H(13)	698 (13)	376 (12)	422 (11)	17 (3)
H(14)	606 (10)	562 (9)	359 (8)	9 (2)
H(15)	767 (10)	565 (9)	449 (8)	11 (2)
H(16)	37 (9)	674 (8)	84 (8)	9 (2)
H(17)	170 (8)	764 (7)	164 (7)	7 (2)
H(18)	104 (9)	671 (9)	248 (8)	9 (2)

Table 2. *Interatomic distances* (Å) *and angles* (°)

Symmetry code: (i) $-x+1, -y+1, -z$.

Cu–O(1)	1·918 (3)	Cu–N(1)–C(7)	124·3 (3)
Cu–O(2)	1·978 (3)	Cu–N(1)–C(8)	116·6 (3)
Cu–N(1)	1·965 (4)	Cu–N(2)–C(10)	113·9 (4)
Cu–N(2)	2·045 (4)	Cu–O(1)–C(1)	127·4 (3)
N(1)–C(7)	1·286 (6)	Cu–O(2)–C(12)	112·6 (4)
N(1)–C(8)	1·487 (8)	N(1)–Cu–N(2)	94·2 (2)
N(2)–C(10)	1·455 (8)	N(1)–C(8)–C(9)	114·1 (7)
N(2)–C(11)	1·488 (11)	O(1)–Cu–N(1)	93·5 (2)
O(1)–C(1)	1·305 (6)	O(1)–Cu–N(2)	168·7 (2)
O(2)–C(12)	1·277 (8)	O(1)–Cu–O(2)	86·4 (1)
O(3)–C(12)	1·235 (9)	O(1)–C(1)–C(2)	118·9 (4)
C(1)–C(2)	1·412 (7)	O(1)–C(1)–C(6)	123·5 (4)
C(1)–C(6)	1·422 (7)	O(2)–Cu–N(1)	173·4 (2)
C(2)–C(3)	1·371 (7)	O(2)–Cu–N(2)	86·9 (1)
C(3)–C(4)	1·397 (9)	O(2)–C(12)–O(3)	123·3 (5)
C(4)–C(5)	1·366 (8)	O(2)–C(12)–C(13)	116·8 (6)
C(5)–C(6)	1·406 (7)	N(1)–Cu–O(2^i)	103·5 (2)
C(6)–C(7)	1·449 (7)	N(2)–Cu–O(2^i)	83·7 (2)
C(8)–C(9)	1·505 (11)	O(1)–Cu–O(2^i)	86·5 (2)
C(9)–C(10)	1·461 (11)	O(2)–Cu–O(2^i)	83·1 (2)
C(12)–C(13)	1·510 (8)	O(3)–C(12)–C(13)	119·9 (6)
		Cu–N(2)–C(11)	118·0 (5)
Cu–O(2^i)	2·512 (5)	C(1)–C(2)–C(3)	121·4 (5)
Cu–O(3)	2·828 (6)	C(2)–C(3)–C(4)	120·6 (5)
Cu–Cu^i	3·379 (2)	C(3)–C(4)–C(5)	119·5 (5)
		C(4)–C(5)–C(6)	121·3 (5)
		C(5)–C(6)–C(1)	119·6 (5)
		C(5)–C(6)–C(7)	117·3 (5)
		C(6)–C(7)–N(1)	126·3 (5)
		C(8)–C(9)–C(10)	119·9 (5)
		C(9)–C(10)–N(2)	118·1 (7)
		C(10)–N(2)–C(11)	112·4 (5)
		O(2)–Cu–O(3)	51·1 (2)
		O(2)–Cu–O(2^i)	83·1 (2)

The approximate coordinates of the nonhydrogen atoms were obtained from the E map calculated with *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). All remaining calculations were based on the programs of XRAY 76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Block-diagonal least-squares refinement of atomic coordinates and thermal parameters converged for the anisotropic model to an R value of 0·054. At this stage the ΔF map revealed the positions of the H atoms. The final least-squares refinement including the H atoms with isotropic thermal parameters converged at R = 0·043 and R_w = 0·056, with $w = 1/(60{\cdot}0 + |F_o| + 0{\cdot}01|F_o|^2)$.* The average shift/error ratio in the last

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36605 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

cycle was 0·11. The scattering factors for non-hydrogen neutral atoms (Cromer & Mann, 1968) and for H atoms (Stewart, Davidson & Simpson, 1965) were used. The anomalous-dispersion correction for Cu was employed (Cromer & Liberman, 1970). The atomic coordinates and B_{eq} values (Hamilton, 1959) are given in Table 1 and bond lengths and angles in Table 2.

Discussion. The unit cell contains a centrosymmetric dimer (Fig. 1) which is formed from two monomeric units linked together by two single O bridges, consisting in each case of one of the acetate O atoms between the Cu atoms, and by two hydrogen bonds [O(1)···N(2^{i}) = 2·991 (7) Å; (i) $-x+1, -y+1, -z$] between the salicylidene O and amine N atoms (Fig. 2). The Cu···Cu distance is 3·379 (2) Å. This fairly short carboxyl O-bridged Cu—Cu distance is not, however, revealed as magnetic interaction between the central atoms in the temperature range 80–300 K, as is seen from the measurements of Tokii, Emori & Muto (1979). Normally the two O atoms of a carboxylate group are each bonded to a different metal atom in binuclear complexes, owing to the residual negative charge on each O, to form Cu—O—C—O—Cu bridging instead of Cu—O—Cu bridging. It is worth noting also that in the present compound the nonbridging O atom of the acetate group interacts weakly with the Cu atom [2·828 (6) Å].

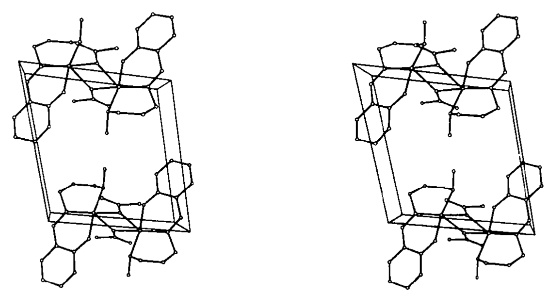

Fig. 1. A stereoview of the molecular ring.

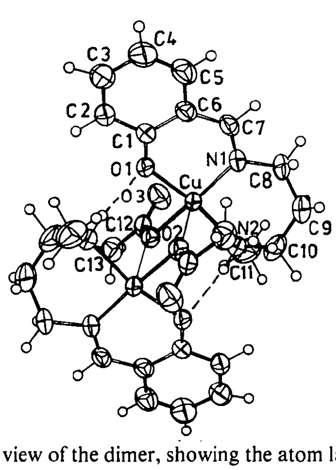

Fig. 2. A view of the dimer, showing the atom labelling.

Table 3. *Deviations* (Å) *of some atoms from the least-squares planes*

x,y,z refer to direct-space coordinates.

(1) Plane through O(2), O(3), C(12) and C(13)

$$3·4426x + 2·1391y + 6·3712z = 2·8809$$

O(2)	−0·000 (4)	O(3)	−0·000 (6)	C(12)	0·001 (6)
C(13)	−0·000 (7)	Cu	−0·015 (1)		

(2) Plane through O(1), O(2), N(1) and N(2)

$$-5·9820x - 5·6116y + 8·5886z = -4·6405$$

O(1)	−0·136 (4)	O(2)	0·139 (4)	N(1)	0·123 (8)
N(2)	−0·126 (5)	Cu	0·018 (1)		

(3) Plane through C(1), C(2), C(3), C(4), C(5) and C(6)

$$-6·5842x - 6·3421y + 7·0714z = -5·0012$$

C(1)	−0·008 (5)	C(2)	0·006 (6)	C(3)	0·004 (7)
C(4)	−0·013 (8)	C(5)	0·011 (7)	C(6)	−0·000 (6)
O(1)	0·017 (4)	N(1)	−0·077 (8)	C(7)	0·058 (6)

Angles (°) between	planes (1) and (2)	84·4 (5)
	planes (1) and (3)	82·4 (5)
	planes (2) and (3)	13·4 (7)

The *N*-methyl-1,3-propanediamine chelate ring is in a skew-boat conformation although this form is more unstable than the possible chair form, as Gollogly & Hawkins (1972) have pointed out.

The bond lengths and angles in the Schiff-base ligand have their usual values within error limits. The C—O bond distances of the acetate group [1·277 (8) and 1·235 (9) Å] are indicative of the partial delocalization on to the carboxylate group, as expected on the basis of the structure. The Cu atom deviates from its coordination plane by only 0·02 Å, which is the same order of magnitude as in the amino acid Schiff-base complex μ-(*N*-salicylidene-L-valinato-μ-*O*)-(*N*-salicylidene-L-valinato)copper(II) (Korhonen & Hämäläinen, 1979). The plane calculated through the benzene ring forms an angle of 13·4° with the coordination plane (Table 3).

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Structures of Di-μ-acetato-(O,O')-μ-aqua-bis[acetato(N,N,N',N'-tetramethylethylenediamine)cobalt(II)] and μ-Aqua-di-μ-chloroacetato-(O,O')-bis[chloroacetato(N,N,N',N'-tetramethylethylenediamine)cobalt(II)]

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(*Received* 26 *October* 1981; *accepted* 15 *December* 1981)

Abstract. $C_{20}H_{46}Co_2N_4O_9$, orthorhombic, *Pbca*, a = 12·056 (3), b = 15·917 (5), c = 31·330 (10) Å, M_r = 604·6, Z = 8, D_c = 1·336 Mg m^{-3}, final R = 0·038 for 3134 observed reflections; $C_{20}H_{42}Cl_4Co_2N_4O_9$, monoclinic, $P2/n$, a = 10·834 (3), b = 8·328 (3), c = 18·749 (3) Å, β = 105·9 (2)°, M_r = 742·4, Z = 2, D_c = 1·515 Mg m^{-3}, final R = 0·033 for 2248 observed reflections. The complexes are octahedral, with a dimeric structure in which Co atoms are joined by one water molecule and two carboxylate groups.

Introduction. This work is a continuation of earlier studies on the crystal structures of Cu^{II} and Ni^{II} carboxylate complexes with N,N,N',N'-tetramethylethylenediamine as the second ligand. The Cu^{II} complexes are monomeric and five- or six-coordinated depending upon the carboxylate ligands (Turpeinen, Ahlgrén & Hämäläinen, 1978; Ahlgrén, Hämäläinen & Turpeinen, 1978), and the Ni^{II} complexes are octahedral, with a dimeric structure in which bridging occurs *via* the water O atom and two carboxylate groups (Ahlgrén, Turpeinen & Hämäläinen, 1978). This type of bridging system is novel in the first-row transition elements and is of interest because of possible low-dimensional magnetic interaction.

The title compounds $C_{20}H_{46}Co_2N_4O_9$ (I) and $C_{20}H_{42}Cl_4Co_2N_4O_9$ (II) were obtained by mixing equal amounts of the appropriate Co^{II} carboxylate and N,N,N',N'-tetramethylethylenediamine. Compound (I) was crystallized from cyclohexane and compound (II) from aqueous ethanol solution. Unit-cell parameters and intensity data for both compounds were obtained with a Syntex $P2_1$ diffractometer and graphite-monochromatized Mo $K\alpha$ radiation. The ω-scan technique was used and the scan rate varied from 2·0 to 30·0° min^{-1} depending upon peak intensity. The total numbers of reflections collected for (I) and (II) were 5286 and 3235 respectively, of which 3134 and 2248 were considered observed, having $I > 3\sigma(I)$. Systematically absent reflections indicated the space groups to be *Pbca* for (I) and *Pn* or $P2/n$ for (II); $P2/n$ was verified by successful refinement. No absorption correction was applied.

The structures were solved with *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and Fourier methods of the XRAY 76 program system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) and refined by full-matrix least squares minimizing $\sum w(|F_o| - |F_c|)^2$ with unit weights for (I) and the weighting scheme $w = 1/(40 + |F_o| + 0·01|F_o|^2)$ for (II). After all non-hydrogen atoms were located difference Fourier maps showed the positions of the H atoms, which were then refined isotropically together with the anisotropic

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