Table 3. *Atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters* ($Å^2 \times 10^3$) *for* [Fe(3-OH-1,5-*dithiacyclooctane*)$_2$](ClO$_4$)$_2$

	x	y	z	U_{eq}/U_{iso}
Fe	0	0	0	13 (1)*
Cl	4928 (2)	2849 (2)	1328 (1)	40 (1)*
S(1)	−357 (1)	232 (1)	1603 (1)	19 (1)*
S(2)	103 (2)	−2907 (1)	210 (1)	21 (1)*
O(1)	2455 (4)	−269 (4)	516 (2)	23 (1)*
O(2)	5205 (6)	2118 (6)	2145 (3)	65 (2)*
O(3)	3120 (7)	3009 (6)	1129 (4)	75 (2)*
O(4)	5177 (7)	1447 (7)	745 (4)	34 (1)
O(5)	5904 (13)	3979 (12)	1149 (7)	41 (2)
O(6)	5066 (12)	4516 (11)	1746 (6)	44 (2)
O(7)	6607 (20)	2832 (19)	1036 (10)	26 (4)
O(8)	4118 (36)	2518 (33)	611 (18)	72 (7)
O(9)	5372 (32)	4120 (31)	748 (16)	61 (7)
C(1)	1674 (6)	−655 (6)	1951 (3)	24 (1)*
C(2)	2611 (6)	−1319 (6)	1240 (3)	24 (1)*
C(3)	2077 (6)	−2908 (6)	887 (3)	31 (2)*
C(4)	−1426 (7)	−3546 (5)	930 (3)	32 (2)*
C(5)	−2618 (6)	−2316 (5)	1231 (3)	26 (1)*
C(6)	−1913 (6)	−1183 (5)	1913 (3)	24 (1)*
HO(1)	3193 (80)	349 (73)	575 (41)	55 (21)

* $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

found here [2·565 (1) and 2·514 (1) Å] are no doubt a reflection of the low bond strength. Previous values for Fe—S(thiolate) are typically near 2·27 Å (Lane, Ibers, Frankel & Holm, 1975). The Fe—O(1) bond is tilted 14·6 (1)° from the normal to the FeS$_4$ plane. An ill-defined (owing to disorder in the ClO$_4^-$ group) hydrogen-bonding interaction exists between the hydrogen atom of the hydroxyl group and O(4) and O(8) of the perchlorate anion.

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Table 4. *Interatomic distances* (Å) *and angles* (°) *for* [Fe(3-OH-1,5-*dithiacyclooctane*)$_2$](ClO$_4$)$_2$

Fe–S(1)	2·565 (1)		
Fe–S(2)	2·514 (1)		
Fe–O(1)	2·062 (3)		
S(1)–C(1)	1·828 (5)		
S(1)–C(6)	1·835 (5)		
S(2)–C(3)	1·815 (5)		
S(2)–C(4)	1·825 (6)		
O(1)–C(2)	1·445 (6)		
C(1)–C(2)	1·513 (7)		
C(2)–C(3)	1·516 (7)	O(1)–HO(1)	0·79 (6)
C(4)–C(5)	1·526 (7)	O(1)···O(4)	2·62 (2)
C(5)–C(6)	1·513 (6)	O(1)···O(8)	2·73 (3)
S(1)–Fe–S(2)	87·4 (1)	C(3)–S(2)–C(4)	103·5 (2)
S(1)–Fe–O(1)	79·3 (1)	C(1)–S(1)–C(6)	104·5 (2)
S(2)–Fe–O(1)	79·6 (1)	S(1)–C(1)–C(2)	115·1 (3)
Fe–S(1)–C(6)	110·5 (1)	S(1)–C(6)–C(5)	116·9 (3)
Fe–S(1)–C(1)	94·7 (1)	S(2)–C(3)–C(2)	114·3 (3)
Fe–S(2)–C(3)	95·3 (2)	S(2)–C(4)–C(5)	117·3 (3)
Fe–S(2)–C(4)	111·3 (2)	O(1)–C(2)–C(1)	109·5 (4)
Fe–O(1)–C(2)	112·7 (3)	O(1)–C(2)–C(3)	105·8 (4)
		C(1)–C(2)–C(3)	117·8 (4)
		C(4)–C(5)–C(6)	117·5 (4)
Fe–O(1)–HO(1)	130 (5)		
C(2)–O(1)–HO(1)	109 (5)		

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Structure of *catena*-Tetraaqua-di-μ_3-(*N*-salicylidene-DL-glutamato)-tricopper(II) Heptahydrate, [Cu$_3$(C$_{12}$H$_{10}$NO$_5$)$_2$(H$_2$O)$_4$].7H$_2$O

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Abstract. $M_r = 885{\cdot}23$, triclinic, $P\bar{1}$, $a = 7{\cdot}874\ (2)$, $b = 8{\cdot}702\ (3)$, $c = 13{\cdot}278\ (6)$ Å, $\alpha = 97{\cdot}32\ (4)$, $\beta = 104{\cdot}06\ (3)$, $\gamma = 97{\cdot}83\ (3)°$, $V = 862{\cdot}0$ Å^3, $Z = 1$, $D_m = 1{\cdot}68$ (flotation), $D_x = 1{\cdot}705$ Mg m^{-3}, μ(Mo $K\alpha$) = 1·99 mm^{-1}, λ(Mo $K\alpha$) = 0·71069 Å, $F(000) = 455$, room temperature, $R = 0{\cdot}037$ for 3054 reflections with $F_o \geq 6{\cdot}0\sigma(F_o)$. Each Schiff-base ligand is hexadentate, coordinated through N and four O atoms to two Cu atoms in the trimeric unit and through one carboxyl O atom to Cu in the adjacent trimeric unit, thus forming a polymeric structure. The coordination geometries around Cu atoms are square-pyramidal (4 + 1) and

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strongly tetragonally distorted octahedral (4 + 2). The structure is composed of sixteen-membered rings in addition to the usual five- and six-membered rings.

Introduction. We have continued the structural analysis of Schiff-base metal complexes formed from amino acid and salicylaldehyde fragments. In the present compound we found a racemization of the amino acid part without the use of abnormal conditions in the synthesis. Previously examined Schiff-base ligands belonging to this series have survived warming without undergoing racemization (Korhonen & Hämäläinen, 1979, 1981).

Experimental. To a warm aqueous solution (323 K) of L-glutamic acid (0·01 mol; E. Merck AG, for Biochemical Purpose) was added 0·01 mol of salicylaldehyde in 20 cm^3 of ethanol. The yellow mixture was stirred at this temperature for a few minutes and then 0·01 mol of copper(II) acetate monohydrate was gradually added. Stirring was continued at 343 K until all copper acetate was dissolved. The solution was left to cool for a few hours, after which the precipitated dark-green crude crystals were filtered off. This product was clearly unstable in air. The filtrate was then allowed to evaporate at 293 K. After about one month, more stable crystals were formed; these were washed with ethanol–water mixture (1:3) and dried in air. Electrolytic copper analysis gave Cu 20·97%, which is in agreement with the calculated value Cu 21·53% for the formula $C_{24}H_{42}Cu_3N_2O_{21}$.

Crystal 0·4 × 0·2 × 0·15 mm kept in the mother liquor and measured in a glass capillary as it had a tendency to decompose slowly in air. Lattice constants obtained by least-squares method from 16 centred reflections. Nicolet *P*3 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. 4574 independent reflections, $5·0 < 2\theta < 58·0°$, ω-scan method, measuring speed 2·0 to 20·0° min^{-1}. No significant change in the intensities of two standards measured after every 68 reflections. 3054 reflections with $F_o \geq 6·0\sigma(F_o)$ included in the refinement. Empirical absorption correction based on the ψ-scan method. Space group $P1$ initially selected. Positions of the three Cu atoms solved with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); all remaining atoms from subsequently derived electron density maps, calculated with the *XRAY*76 system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). During the refinement, however, the structure was found to be centrosymmetric and the amino acid parts of the ligands racemized. Refinement in space group $P\bar{1}$, including all non-hydrogen atoms with anisotropic thermal parameters, reduced R to 0·047. At this point, all H atoms except those of disordered lattice water O(11) were located on a difference Fourier map. A final least-squares refinement with non-hydrogen atoms allowed to vibrate anisotropically and H atoms isotropically gave $R = 0·037$ and $R_w = 0·044$. $\sum w(|F_o| - |F_c|)^2$ minimized, where $w = 1/(65·0 + |F_o| + 0·01|F_o|^2)$. $(\Delta/\sigma)_{max} = 0·8$. Max. $\Delta\rho$ excursion $|0·7|$ e Å^{-3}. Scattering factors for neutral atoms (Cromer & Mann, 1968) and for H atoms (Stewart, Davidson & Simpson, 1965). Anomalous-dispersion correction for Cu (Cromer & Liberman, 1970). No correction for secondary extinction.

Discussion. Final atomic coordinates and B_{eq} values (Hamilton, 1959) are reported in Table 1.† Fig. 1 shows the numbering of the asymmetric unit.

The hexadentate Schiff-base ligand acts as a bridging group between three Cu atoms, of which two [Cu(1) and Cu(2)] belong to the asymmetric unit. The distances of the non-side-chain carboxyl O atoms to Cu atoms are almost equal (1·962 and 1·953 Å) so that the carboxyl group provides a symmetrical bridge between Cu(1) and Cu(2*)($x-1,y,z$). The coordination geometry around the Cu(1) atom is square pyramidal, the basal plane consisting of three donor atoms of the Schiff-base ligand [O(1), O(3) and N(1)] and one water O atom [O(4)]. The angle Cu(1)—O(1)—C(1) is 114·7 (2)° and close to the value of 114° which is found to be typical for the five-membered chelate ring. The apical position is occupied by a second water O atom [O(5)].

In the side chain of the glutamic acid part, the carboxyl group itself acts as a bidentate ligand, forming an unsymmetrical chelate ring with the Cu(2) atom. The Cu—O distances are 1·944 and 2·708 Å. This type of joining necessarily causes distortion, since the less strongly connected O(7) atom occupies an irregular coordination position with respect to the Cu(2) atom (Table 2). This unsymmetrical connection is also reflected in the C—O bond lengths of the carboxyl group. The C—O lengths in cases of distortion like this commonly lie in the ranges 1·25–1·30 Å and 1·22–1·27 Å, as in this structure too. The other positions in the tetragonally distorted octahedral coordination sphere of Cu(2) are occupied by symmetrically situated O(6*) and O(7*) ($-x,-y,-z$) and carboxyl O(2*) atoms of neighbouring units ($x+1,y,z$ and $-x-1,-y,-z$). In the structure as a whole, such bonding leads to a polymeric structure, where the usual five- and six-membered rings of the asymmetric complex units alternate with sixteen-membered rings derived from the glutamic acid parts and two Cu atoms (Fig. 2). The crystal packing is completed by the water molecules, which join the complex units together *via* hydrogen bonds.

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† Tables of structure factors, anisotropic thermal parameters, H-atom coordinates, intermolecular distances and atomic displacements from mean planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39324 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent values of the anisotropic temperature factor coefficients*

	x	y	z	B_{eq}(Å^2)
Cu(1)	−5845 (1)	1599 (1)	3705 (1)	2·34
Cu(2)	0	0	0	2·17
O(1)	−7453 (3)	1002 (3)	2282 (2)	2·60
O(2)	−8170 (3)	1812 (3)	730 (2)	2·77
O(3)	−4255 (4)	2257 (3)	5081 (2)	2·84
O(4)	−7373 (4)	149 (3)	4282 (2)	3·06
O(5)	−4207 (5)	−590 (4)	3406 (2)	4·32
O(6)	−1392 (4)	335 (4)	1008 (2)	3·21
O(7)	−2283 (5)	2059 (5)	24 (3)	5·17
O(8)	−5312 (6)	−2846 (5)	1629 (3)	5·65
O(9)	−2042 (9)	−3265 (9)	1175 (6)	13·21
O(10)	−682 (6)	−736 (7)	−6921 (5)	8·48
O(11)*	0	5000	−365 (10)	20·45
N(1)	−4884 (4)	3366 (3)	3152 (2)	2·05
C(1)	−7235 (4)	1947 (4)	1662 (3)	2·22
C(2)	−5699 (5)	3336 (4)	2027 (3)	2·16
C(3)	−4359 (5)	3132 (5)	1365 (3)	2·58
C(4)	−3675 (5)	1604 (5)	1409 (3)	2·70
C(5)	−2357 (5)	1348 (5)	763 (3)	2·80
C(6)	−3769 (5)	4589 (4)	3692 (3)	2·53
C(7)	−2874 (5)	4773 (4)	4794 (3)	2·40
C(8)	−1657 (6)	6182 (5)	5239 (3)	3·19
C(9)	−704 (6)	6459 (5)	6288 (4)	3·73
C(10)	−932 (6)	5322 (6)	6900 (4)	3·80
C(11)	−2120 (5)	3927 (5)	6496 (3)	3·17
C(12)	−3122 (5)	3621 (4)	5432 (3)	2·46

* Population parameter 0·5.

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

Cu(1)–O(1)	1·962 (3)	O(4)–Cu(1)–N(1)	163·5 (1)
Cu(1)–O(3)	1·913 (3)	O(4)–Cu(1)–O(5)	87·4 (1)
Cu(1)–O(4)	1·977 (3)	O(5)–Cu(1)–N(1)	108·6 (1)
Cu(1)–N(1)	1·928 (3)	O(6)–Cu(2)–O(7)	53·1 (1)
Cu(1)–O(5)	2·485 (4)	O(1)–C(1)–O(2)	124·7 (3)
Cu(2)–O(6)	1·944 (3)	O(1)–C(1)–C(2)	119·2 (3)
Cu(2)–O(7)	2·708 (5)	O(2)–C(1)–C(2)	116·0 (3)
Cu(2$^{\rm i}$)–O(2)	1·953 (3)	Cu(1)–O(1)–C(1)	114·7 (2)
		Cu(1)–O(3)–C(12)	126·6 (2)
O(1)–C(1)	1·259 (5)	Cu(1)–N(1)–C(2)	114·1 (2)
O(2)–C(1)	1·259 (4)	Cu(1)–N(1)–C(6)	126·1 (3)
C(1)–C(2)	1·525 (5)	Cu(2$^{\rm i}$)–O(2)–C(1)	124·5 (3)
C(2)–N(1)	1·471 (4)	Cu(2)–O(7)–C(5)	74·3 (3)
C(2)–C(3)	1·542 (6)	C(1)–C(2)–C(3)	109·2 (3)
C(3)–C(4)	1·504 (6)	C(1)–C(2)–N(1)	107·5 (3)
C(4)–C(5)	1·520 (6)	C(2)–N(1)–C(6)	119·4 (3)
C(5)–O(6)	1·263 (6)	C(2)–C(3)–C(4)	113·1 (3)
C(5)–O(7)	1·234 (6)	C(3)–C(2)–N(1)	111·7 (3)
C(6)–N(1)	1·290 (4)	C(3)–C(4)–C(5)	114·9 (4)
C(6)–C(7)	1·439 (5)	C(4)–C(5)–O(6)	116·0 (4)
C(7)–C(8)	1·410 (5)	C(4)–C(5)–O(7)	121·4 (4)
C(7)–C(12)	1·416 (6)	O(6)–C(5)–O(7)	122·5 (4)
C(8)–C(9)	1·385 (6)	C(6)–C(7)–C(8)	116·8 (4)
C(9)–C(10)	1·378 (7)	C(6)–C(7)–C(12)	123·8 (3)
C(10)–C(11)	1·384 (6)	C(7)–C(8)–C(9)	121·3 (4)
C(11)–C(12)	1·413 (5)	C(8)–C(9)–C(10)	119·1 (4)
C(12)–O(3)	1·338 (4)	C(9)–C(10)–C(11)	121·5 (4)
		C(10)–C(11)–C(12)	120·6 (4)
O(1)–Cu(1)–O(3)	177·9 (1)	O(3)–C(12)–C(7)	123·6 (3)
O(1)–Cu(1)–O(4)	92·1 (1)	O(3)–C(12)–C(11)	118·2 (4)
O(1)–Cu(1)–O(5)	91·7 (1)		
O(1)–Cu(1)–N(1)	84·0 (1)	O(2$^{\rm ii}$)–Cu(2)–O(6)	87·6 (1)
O(3)–Cu(1)–N(1)	93·9 (1)	O(2$^{\rm ii}$)–Cu(2)–O(7)	95·3 (1)
O(3)–Cu(1)–O(4)	89·7 (1)	O(6)–Cu(2)–O(7)	126·9 (1)
O(3)–Cu(1)–O(5)	89·5 (1)	Cu(2)–O(6)–C(5)	109·9 (3)

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

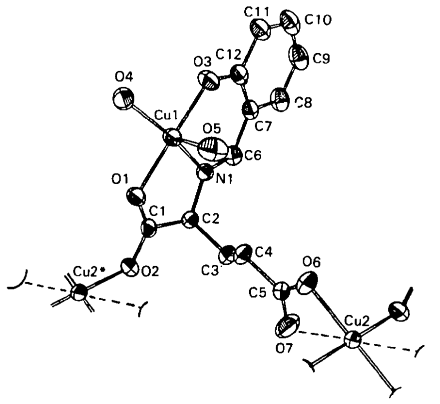

Fig. 1. View and numbering scheme of the asymmetric unit.

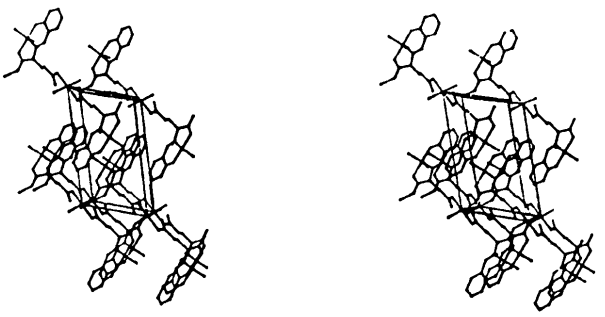

Fig. 2. Molecular packing. For clarity two positions of the complex units and the water molecules have been omitted.

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