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Structure of Magnesium [(*S*,*S*)-*N*,*N*′-Ethylenediaminedisuccinato]cuprate(II) Heptahydrate

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Abstract. $Mg[Cu(C_{10}H_{12}N_2O_8)].7H_2O$, $M_r = 502\cdot16$, orthorhombic, $P2_12_12_1$, $a = 8\cdot392$ (2), $b = 10\cdot855$ (2), $c = 21\cdot508$ (6) Å, $U = 1959\cdot2$ (8) Å^3, $Z = 4$, $D_m = 1\cdot70$ (2), $D_x = 1\cdot70$ Mg m^{-3}, Cu $K\alpha$ radiation ($\lambda = 1\cdot5418$ Å), $\mu = 2\cdot65$ mm^{-1}. Final $R = 0\cdot05$ for 1542 observed reflections. The structure consists of complex anions, Mg^{2+} cations and water molecules. The Cu atom is coordinated by two N atoms and one O atom from each of the four carboxylate arms of the complexing species. The coordination polyhedron of the Cu^{II} atom is an asymmetrically distorted tetragonal bipyramid. The complex anion has the absolute configuration (OC-6-13-A) with six-membered β-alanine chelate rings disposed equatorially, and five-membered glycine rings in the axial directions.

Introduction. Cupric complexes of *N*,*N*′-ethylenediaminedisuccinic acid (H_4edds) have been investigated as part of a study of the diastereoselectivity in compounds of the ligand with transition metals (Pavelčík & Majer, 1978; Pavelčík, Kettmann & Majer, 1979; Neal & Rose, 1972).

Single crystals were prepared by dissolving equimolar amounts of (*S*,*S*)-H_4edds and $Cu_2(OH)_2CO_3$ in water and adding excess MgO. The solution was heated and excess MgO filtered off. After evaporation, crystals of the cupric complex formed and were recrystallized from water. Elemental analysis gave: C 23·72, N 5·24, Cu 12·70, Mg 4·85%; $C_{10}H_{26}CuMgN_2O_{15}$ requires C 23·92, N 5·58, Cu 12·65, Mg 4·84%.

A blue crystal 0·40 × 0·28 × 0·25 mm was selected for data collection. Weissenberg photographs showed the crystal to be orthorhombic, with systematic absences $h00$ for $h = 2n + 1$, $0k0$ for $k = 2n + 1$, $00l$ for $l = 2n + 1$, uniquely indicating the space group $P2_12_12_1$. A Syntex $P2_1$ diffractometer and Cu $K\alpha$ radiation with a graphite monochromator were used for lattice-parameter and intensity measurements. The intensities were measured by the θ–2θ scan technique ($0 < 2\theta \leq 100°$) at a scan rate varying from 4·88 to 29·3° min^{-1} in 2θ. The background was measured at each end of the scan for one half of the scan time. Two standard reflections monitored after every 98 scans showed that no correction for instrument instability or crystal decay was required. The data were corrected for Lorentz and polarization effects and for absorption. 1542 reflections with $I > 1\cdot96\sigma(I)$ were used for the analysis.

The heavy-atom method was employed for the structure determination. The Cu–Cu vectors were identified in a Patterson function. All non-H atoms were found from Fourier syntheses. Twelve H atoms from the complex anion were placed in geometrically calculated positions at 0·9 Å from the bonded atoms and their positions confirmed by a difference synthesis. H atoms from water molecules were not resolvable. The structure was refined by block-diagonal least squares with anisotropic thermal parameters for non-hydrogen atoms and isotropic for H. The function $\sum w(|F_o| - |F_c|)^2$ was minimized; the weighting scheme $w^{-1} = \sigma^2(|F_o|) + (C|F_o|)^2$, where $\sigma(|F_o|)$ is derived from counting statistics and $C = 0\cdot03$, was employed. C was adjusted so that a constant value of $\langle w(|F_o| - |F_c|)^2\rangle$ was obtained in different $|F_o|$ intervals. The final $R = \sum|\Delta F|/\sum|F_o| = 0\cdot05$ for the observed reflections. The corresponding $R_w = [\sum w|\Delta F|^2/\sum w|F_o|^2]^{1/2} = 0\cdot076$. The maximum peak in the final difference synthesis was 0·35 e Å^{-3}.*

Scattering factors for Cu, Mg, O, N, C and H were taken from *International Tables for X-ray Crystallography* (1974). All calculations were performed on a Nova minicomputer with the Syntex XTL structure determination system, and on a Siemens 4004/150 computer at the Research Computing Centre of the Comenius University in Bratislava with the NRC program package (Ahmed, 1970). Coordinates for non-hydrogen atoms are listed in Table 1, bond distances and angles in Table 2, selected torsion angles in Table 3, and hydrogen-bond contacts in Table 4.

Discussion. Crystals of Mg[Cu{(*S*,*S*)-edds}]$.7H_2O$ are composed of [Cu{(*S*,*S*)-edds}]$^{2-}$ complex anions, Mg^{2+} cations and molecules of crystal water. The

* Lists of structure factors, anisotropic thermal parameters and H atom positions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35605 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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ligand $\{(S,S)\text{-edds}\}^{4-}$ binds with the central atom *via* six donors, Fig. 1. The coordination polyhedron of Cu is an asymmetrically deformed square bipyramid, elongated in the axial directions, as in $K_2[Cu(edta)].3H_2O$ (Porai-Koshits, Novožilova, Polynova, Filippova & Martynenko, 1973). A Cu atom binds in its coordination sphere the two N atoms from an ethylenediamine residue and four O atoms from carboxyl groups. This sixfold coordination results in five chelate rings: a five-membered ethylenediamine ring (*E* ring), two six-membered β-alanine rings (*G* rings), and two five-membered glycine rings (*R* rings) (nomenclature according to Weakliem & Hoard,

Table 1. *Final atomic coordinates* ($\times 10^4$) *and* B_{eq} *for nonhydrogen atoms*

E.s.d.'s are given in parentheses. $B_{eq} = \frac{4}{3}\sum_i \sum_j B_{ij}\,\mathbf{a}_i.\mathbf{a}_j$.

	x	*y*	*z*	B_{eq} (Å^2)
Cu(1)	76 (1)	1790 (1)	1971 (0)	2·20
N(1)	−2003 (5)	1304 (5)	1590 (2)	1·69
N(2)	−442 (6)	541 (4)	2632 (2)	1·55
C(1)	−2472 (8)	141 (6)	1856 (3)	2·15
C(2)	−2141 (8)	196 (6)	2554 (3)	2·21
C(3)	−132 (7)	1093 (6)	3246 (3)	1·98
C(4)	−872 (7)	2402 (5)	3253 (3)	1·83
C(5)	1659 (8)	1175 (6)	3348 (3)	2·20
C(6)	2707 (8)	1872 (6)	2872 (3)	2·03
C(7)	−1892 (7)	1340 (6)	899 (3)	2·05
C(8)	−1742 (7)	2678 (6)	681 (3)	2·12
C(9)	−194 (8)	3292 (5)	834 (3)	2·11
C(10)	−449 (7)	598 (5)	673 (2)	1·54
O(1)	−909 (6)	3008 (4)	2759 (2)	2·31
O(2)	−1369 (6)	2757 (4)	3778 (2)	2·54
O(3)	4018 (6)	2251 (5)	3040 (2)	3·21
O(4)	2252 (5)	1980 (4)	2321 (2)	1·99
O(5)	493 (5)	3095 (4)	1349 (2)	1·96
O(6)	348 (6)	4044 (5)	462 (2)	3·27
O(7)	645 (5)	392 (4)	1047 (2)	1·96
O(8)	−518 (6)	251 (5)	118 (2)	3·14
Mg(1)	2698 (2)	−715 (2)	965 (1)	1·63
W(1)	2245 (6)	−1059 (5)	28 (2)	2·63
W(2)	4045 (5)	794 (4)	685 (2)	2·46
W(3)	4648 (6)	−1873 (5)	882 (2)	3·06
W(4)	3360 (5)	−270 (4)	1864 (2)	2·29
W(5)	4269 (6)	−1771 (5)	2978 (2)	3·65
W(6)	3724 (5)	3336 (5)	977 (2)	3·01
W(7)	1878 (6)	−3584 (5)	31 (2)	3·38

Table 2. *Interatomic distances* (Å) *and angles* (°) *in the complex anion and the* MgO_6 *octahedron, with e.s.d.'s in parentheses*

Cu–N(1)	2·001 (5)	C(6)–O(3)	1·230 (8)
Cu–N(2)	2·013 (5)	C(6)–O(4)	1·252 (7)
Cu–O(1)	2·304 (4)	C(7)–C(8)	1·532 (9)
Cu–O(4)	1·987 (4)	C(7)–C(10)	1·534 (8)
Cu–O(5)	1·981 (4)	C(8)–C(9)	1·497 (9)
Cu–O(7)	2·546 (4)	C(9)–O(5)	1·268 (7)
N(1)–C(1)	1·442 (8)	C(9)–O(6)	1·231 (8)
N(1)–C(7)	1·491 (8)	C(10)–O(7)	1·243 (7)
N(2)–C(2)	1·485 (8)	C(10)–O(8)	1·254 (7)
N(2)–C(3)	1·473 (8)	Mg–O(2^{vii})	2·075 (5)
C(1)–C(2)	1·528 (9)	Mg–O(7)	2·109 (5)
C(3)–C(4)	1·551 (9)	Mg–*W*(1)	2·085 (5)
C(3)–C(5)	1·523 (9)	Mg–*W*(2)	2·080 (5)
C(4)–O(1)	1·251 (7)	Mg–*W*(3)	2·072 (5)
C(4)–O(2)	1·265 (7)	Mg–*W*(4)	2·070 (5)
C(5)–C(6)	1·548 (9)		

N(1)–Cu–N(2)	85·6 (2)	O(1)–C(4)–C(3)	118·9 (5)
N(1)–Cu–O(1)	98·0 (2)	O(2)–C(4)–C(3)	114·9 (5)
N(1)–Cu–O(4)	170·3 (2)	O(3)–C(6)–O(4)	121·4 (6)
N(1)–Cu–O(5)	93·8 (2)	O(3)–C(6)–C(5)	118·6 (6)
N(1)–Cu–O(7)	71·7 (2)	O(4)–C(6)–C(5)	119·9 (5)
N(2)–Cu–O(1)	77·8 (2)	O(5)–C(9)–O(6)	120·8 (6)
N(2)–Cu–O(4)	90·1 (2)	O(5)–C(9)–C(8)	120·8 (6)
N(2)–Cu–O(5)	176·3 (2)	O(6)–C(9)–C(8)	118·2 (5)
N(2)–Cu–O(7)	101·0 (2)	O(7)–C(10)–O(8)	126·7 (5)
O(1)–Cu–O(4)	89·6 (2)	O(7)–C(10)–C(7)	118·2 (5)
O(1)–Cu–O(5)	98·7 (2)	O(8)–C(10)–C(7)	115·0 (5)
O(1)–Cu–O(7)	169·7 (1)	C(1)–N(1)–C(7)	115·9 (5)
O(4)–Cu–O(5)	91·1 (2)	C(2)–N(2)–C(3)	112·0 (5)
O(4)–Cu–O(7)	100·7 (2)	C(3)–C(5)–C(6)	119·7 (5)
O(5)–Cu–O(7)	82·3 (2)	C(4)–C(3)–C(5)	109·9 (5)
Cu–O(1)–C(4)	108·3 (4)	C(7)–C(8)–C(9)	115·2 (5)
Cu–O(4)–C(6)	129·0 (4)	C(8)–C(7)–C(10)	109·6 (5)
Cu–O(5)–C(9)	129·1 (4)	O(2^{vii})–Mg–O(7)	89·6 (2)
Cu–O(7)–C(10)	105·1 (3)	O(2^{vii})–Mg–*W*(1)	91·0 (2)
Cu–N(1)–C(7)	110·3 (4)	O(2^{vii})–Mg–*W*(2)	178·5 (2)
Cu–N(1)–C(1)	107·8 (4)	O(2^{vii})–Mg–*W*(3)	87·9 (2)
Cu–N(2)–C(2)	107·3 (4)	O(2^{vii})–Mg–*W*(4)	94·7 (2)
Cu–N(2)–C(3)	108·7 (3)	O(7)–Mg–*W*(1)	92·0 (2)
N(1)–C(1)–C(2)	107·9 (5)	O(7)–Mg–*W*(2)	91·1 (2)
N(1)–C(7)–C(8)	109·6 (5)	O(7)–Mg–*W*(3)	177·4 (2)
N(1)–C(7)–C(10)	110·6 (5)	O(7)–Mg–*W*(4)	90·4 (2)
N(2)–C(2)–C(1)	107·2 (5)	*W*(1)–Mg–*W*(2)	87·7 (2)
N(2)–C(3)–C(4)	108·1 (5)	*W*(1)–Mg–*W*(3)	87·3 (2)
N(2)–C(3)–C(5)	109·1 (5)	*W*(1)–Mg–*W*(4)	173·9 (2)
O(1)–C(4)–O(2)	126·2 (6)	*W*(2)–Mg–*W*(3)	91·3 (2)
		W(2)–Mg–*W*(4)	86·6 (2)
		W(3)–Mg–*W*(4)	90·6 (2)

Table 3. *Selected torsion angles* (°) *in the complex molecule*

Cu–N(1)–C(1)–C(2)	42·7 (6)	C(7)–C(10)–O(7)–Cu	−12·1 (6)	C(3)–N(2)–Cu–O(4)	54·9 (4)
N(1)–C(1)–C(2)–N(2)	−54·4 (6)	C(10)–O(7)–Cu–N(1)	31·4 (4)	N(2)–Cu–O(4)–C(6)	−30·7 (5)
C(1)–C(2)–N(2)–Cu	38·1 (5)	O(7)–Cu–N(1)–C(7)	−41·5 (3)	C(8)–C(7)–C(10)–O(7)	100·4 (6)
C(2)–N(2)–Cu–N(1)	−12·5 (4)	Cu–O(1)–C(4)–C(3)	3·6 (7)	C(8)–C(7)–N(1)–C(1)	167·8 (5)
N(2)–Cu–N(1)–C(1)	−17·2 (3)	O(1)–C(4)–C(3)–N(2)	−32·4 (7)	C(10)–C(7)–N(1)–C(1)	−71·2 (6)
Cu–O(5)–C(9)–C(8)	13·9 (8)	C(4)–C(3)–N(2)–Cu	46·2 (5)	C(1)–C(2)–N(2)–C(3)	157·4 (5)
O(5)–C(9)–C(8)–C(7)	−38·5 (8)	C(3)–N(2)–Cu–O(1)	−34·6 (4)	C(9)–C(8)–C(7)–C(10)	−51·9 (1)
C(9)–C(8)–C(7)–N(1)	69·7 (6)	N(2)–Cu–O(1)–C(4)	17·8 (4)	C(6)–C(5)–C(3)–C(4)	−62·1 (1)
C(8)–C(7)–N(1)–Cu	−69·3 (5)	Cu–O(4)–C(6)–C(5)	18·6 (8)	C(5)–C(3)–N(2)–C(2)	168·2 (1)
C(7)–N(1)–Cu–O(5)	39·0 (4)	O(4)–C(6)–C(5)–C(3)	−25·5 (9)	C(4)–C(3)–N(2)–C(2)	−72·2 (1)
N(1)–Cu–O(5)–C(9)	−13·4 (5)	C(6)–C(5)–C(3)–N(2)	56·3 (7)	C(5)–C(3)–C(4)–O(1)	80·6 (1)
Cu–N(1)–C(7)–C(10)	51·7 (5)	C(5)–C(3)–N(2)–Cu	−73·4 (5)	C(2)–C(1)–N(1)–C(7)	166·9 (1)
N(1)–C(7)–C(10)–O(7)	−20·6 (7)				

Table 4. *Hydrogen-bond contacts* (X—H$\cdots Y$) <3 Å

$N(1)\cdots W(5^{i})$	2·975 (7)	$O(8)\cdots W(1)$	2·729 (7)
$O(1)\cdots W(4^{i})$	2·897 (6)	$O(8)\cdots W(6^{iii})$	2·883 (7)
$O(2)\cdots W(7^{i})$	2·978 (6)	$O(8)\cdots W(7^{iv})$	2·856 (7)
$O(3)\cdots W(3^{ii})$	2·746 (6)	$W(1)\cdots W(7)$	2·759 (7)
$O(3)\cdots W(5^{ii})$	2·828 (7)	$W(2)\cdots W(6)$	2·844 (7)
$O(4)\cdots W(4)$	2·794 (6)	$W(3)\cdots W(7^{v})$	2·759 (7)
$O(5)\cdots W(6)$	2·841 (6)	$W(4)\cdots W(5)$	2·998 (7)
$O(6)\cdots W(2^{iii})$	2·705 (6)	$W(5)\cdots W(6^{vi})$	2·812 (7)

Equivalent positions

(i)	$-x, y+\frac{1}{2}, \frac{1}{2}-z$	(v)	$x+\frac{1}{2}, -\frac{1}{2}-y, -z$
(ii)	$1-x, y+\frac{1}{2}, \frac{1}{2}-z$	(vi)	$1-x, y-\frac{1}{2}, \frac{1}{2}-z$
(iii)	$x-\frac{1}{2}, \frac{1}{2}-y, -z$	(vii)	$-x, y-\frac{1}{2}, \frac{1}{2}-z$
(iv)	$x-\frac{1}{2}, -\frac{1}{2}-y, -z$		

1959). The deviations of atoms from the defined planes and the torsion angles show that all chelate rings are non-planar. The E ring has a slightly asymmetric *gauche* conformation, the G rings have the conformation of an asymmetric twisted boat and the R rings have the conformation of an asymmetric envelope. The bond angles and lengths in the ligand are normal. Significant differences occur in the bonds of the Cu^{II} coordination polyhedron. The Cu—O lengths for the two axial bonds differ considerably from those in the equatorial plane (by as much as 0·43 Å), as in other Cu complexes (Gažo *et al.*, 1976). Very probably this is the result of the Jahn–Teller effect. The valency angle of Cu in the E ring and G rings is deformed only slightly, whereas in the R rings its deformation is considerable (up to 15 °).

The coordination polyhedron of the Mg^{2+} cation is a deformed octahedron. Mg^{2+} coordinates four water molecules and two O atoms from the carboxyl groups of the ligand $\{(S,S)\text{-edds}\}^{4-}$. The result is the interconnection of complex anions and cations in the **c** direction, Fig. 2. Every $\{(S,S)\text{-edds}\}^{4-}$ ligand reacts through the intermediary of O(7) and O(2) in two

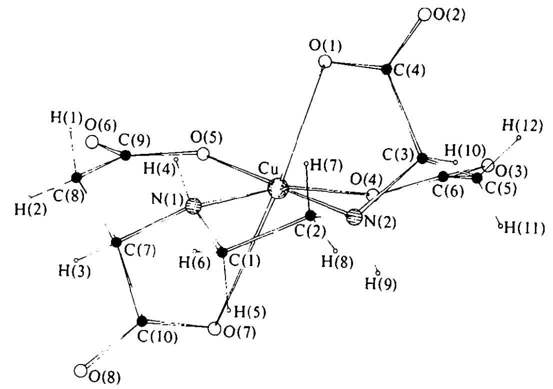

Fig. 1. A perspective drawing of (OC-6-13-A) $[Cu\{(S,S)\text{-edds}\}]^{2-}$ and the numbering scheme of the atoms.

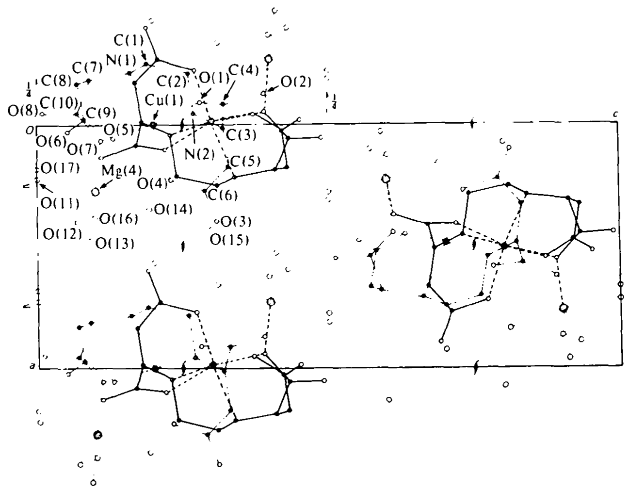

Fig. 2. The projection of the structure in the **b** direction. Coordination bonds are represented by dashed lines.

different coordination polyhedra (MgO_6). O(7) bridges Cu^{II} and Mg^{2+}. As a result of this, the axial binding length O(7)—Cu increases, so that it reaches 2·546 Å, whereas the other axial binding length [O(1)—Cu] is 2·305 Å. The whole structure is stabilized by hydrogen bonds, Table 4.

The $\{(S,S)\text{-edds}\}^{4-}$ ligand binds with Cu^{2+} stereospecifically, giving rise to the absolute configuration (OC-6-13-A) (Brown, Cook & Sloan, 1975). This configuration is the same as in the complexes of this ligand with Ni^{II}, Co^{III} and Fe^{III} (Pavelčik, 1980, unpublished), and points to a significant diastereoselectivity of optically active forms of $\{(S,S)\text{-edds}\}^{4-}$.

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