a distorted octahedral geometry. The Cr—N distance is 2·082 (4) Å which is greater than Cr—O(W1) and Cr—O(W2) [1·970 (4), 1·968 (4) Å]. This is explained by the fact that the N atom is attached to an electron-withdrawing group (phenyl ring with a carboxyl substituent) which causes the depletion of electron density at the N atom resulting in a weaker Cr—N bond. The Cr—N distance is nearly equal to that of a similar compound (Swaminathan, Sinha, Chatterjee, Patel & Padmanabhan, 1988). Cr—O(2) of the carboxylate [1·929 (3) Å] is shorter than the Cr—O(6) and Cr—O(4) distances of the glycinato rings [1·963 (3), 1·949 (3) Å]. The deviations from the octahedral angles at the Cr atom are within 6·5°. The axial oxygens make an angle O(2)—Cr—O(4) of 175·3 (1)°. The N—C(7) distance (1·484 Å) is less than the N—C(8) and N—C(10) distances of the glycinato rings [1·517 (6), 1·507 (6) Å]. This is due to part of the (cpida) ligand undergoing resonance (Martell & Calvin, 1956; Naveen Chandra, 1984). The phenyl ring is oriented at an angle of 109·5 (4)° to the equatorial coordination plane. The ring N,C(7),C(2),C(1),O(2),-Cr should be planar (Chatterjee & Phadke, 1987) but owing to the chelation and strain the planarity is disturbed. This plane is at an angle of 18·9 (3)° with respect to the phenyl ring. The corresponding C—C and C—O distances of the two glycinato rings are equal. C(11)=O(5) [1·241 (6) Å] is longer than C(9)=O(3) [1·217 (6) Å]. This is because O(5) forms two hydrogen bonds whereas O(3) forms only one. It has previously been observed (Weakliem & Hoard, 1959; Okazaki, Tomioka & Yoneda, 1983) that the G ring (the glycinato ring in plane with the equatorial plane) is more strained than the R ring [the glycinato ring bonding through O(4) out of the equatorial plane].

However, in the present work no marked difference is observed. The structure is stabilized by a network of hydrogen bonds involving the water molecules.

References

CHATTERJEE, C. & PHADKE, S. V. (1987). *J. Chem. Soc. Dalton Trans.* pp. 2095–2098.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
MARTELL, A. E. & CALVIN, M. (1956). *Chemistry of the Metal Chelate Compounds.* New York: Prentice Hall.
MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*78. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
NAVEEN CHANDRA (1984). PhD thesis. Department of Chemistry, Indian Institute of Technology, Bombay, India.
NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* A24, 351–359.
OKAZAKI, H., TOMIOKA, K. & YONEDA, H. (1983). *Inorg. Chim. Acta,* 74, 169–178.
SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.
STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination.* New York: Macmillan.
Structure Determination Package (1982). B. A. FRENZ and Enraf–Nonius, Delft, The Netherlands.
SWAMINATHAN, K., SINHA, U. C., CHATTERJEE, C., PATEL, R. P. & PADMANABHAN, V. M. (1988). *Acta Cryst.* C44, 447–449.
TOMITA, T., KYUNO, E. & TSUCHIA, R. (1969). *Bull. Chem. Soc. Jpn,* 42, 947–951.
WEAKLIEM, H. A. & HOARD, J. L. (1959). *J. Am. Chem. Soc.* 81, 549–555.

Structure of Bis[μ-iminodiacetato(1−)-μ-O,O',O'']-bis[pentaaquabarium(II)] Bis[iminodiacetato(2−)-N,O,O']cuprate(II)

BY PETER SIVÝ, BRANISLAV KOREŇ AND FEDOR VALACH

Faculty of Chemical Technology, Slovak Technical University, Department of Chemical Physics and Nuclear Technique, Radlinského 9, 812 37 Bratislava, Czechoslovakia

AND IVAN LUKEŠ

Department of Inorganic Chemistry, Charles University, 128 40 Prague, Czechoslovakia

Abstract. [Ba$_2$\{H$_2$N(CH$_2$COO)$_2$\}$_2$(H$_2$O)$_{10}$][Cu\{HN-(CH$_2$COO)$_2$\}$_2$], M_r = 1044·72, triclinic, $P\bar{1}$, a = 9·050 (4), b = 9·437 (5), c = 11·468 (5) Å, α = 108·05 (3), β = 93·68 (4), γ = 112·55 (4)°, V = 841·14 Å^3, Z = 1, D_m = 2·09, D_x = 2·06 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 3·09 mm^{-1}, F(000) =

Table 1. *Fractional coordinates and equivalent iso-tropic thermal parameters ($\AA^2$) with e.s.d.'s in parentheses for non-H atoms*

$$B_{eq} = \tfrac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j$$

	x	y	z	B_{eq}
Cu	0·5	0·0	0·5	1·58 (3)
N(1)	0·3853 (5)	0·1315 (5)	0·5904 (3)	1·5 (1)
C(1)	0·3758 (6)	0·2388 (6)	0·5227 (5)	1·8 (2)
C(2)	0·4798 (7)	0·2420 (6)	0·4247 (4)	1·9 (2)
O(1)	0·4921 (6)	0·3370 (5)	0·3667 (4)	2·9 (2)
O(2)	0·5488 (5)	0·1435 (5)	0·4033 (4)	2·2 (1)
C(3)	0·2261 (6)	0·0211 (6)	0·6046 (4)	1·6 (1)
C(4)	0·1341 (6)	−0·1289 (6)	0·4834 (4)	1·7 (1)
O(3)	−0·0013 (5)	−0·2331 (5)	0·4890 (3)	2·2 (1)
O(4)	0·1964 (5)	−0·1377 (5)	0·3891 (3)	3·0 (1)
Ba	0·2303 (1)	−0·3686 (1)	−0·0325 (1)	1·41 (1)
N(2)	−0·0497 (5)	−0·3112 (5)	−0·2998 (3)	1·6 (1)
C(5)	−0·0475 (6)	−0·1587 (6)	−0·2072 (5)	1·8 (1)
C(6)	0·1211 (6)	−0·0486 (5)	−0·1234 (4)	1·7 (1)
O(5)	0·1513 (5)	0·1001 (4)	−0·0704 (4)	2·5 (1)
O(6)	0·2156 (5)	−0·1153 (4)	−0·1139 (4)	2·4 (1)
C(7)	−0·2023 (6)	−0·4629 (5)	−0·3239 (4)	1·7 (1)
C(8)	−0·2181 (6)	−0·5072 (5)	−0·2066 (4)	1·5 (1)
O(7)	−0·3569 (5)	−0·6026 (5)	−0·2013 (3)	2·4 (1)
O(8)	−0·0914 (5)	−0·4450 (5)	−0·1238 (3)	2·4 (1)
O(1W)	0·1807 (5)	−0·4581 (5)	−0·3018 (3)	2·4 (1)
O(2W)	0·5305 (5)	−0·2558 (6)	−0·1043 (4)	3·4 (2)
O(3W)	0·0422 (6)	−0·2619 (6)	0·1363 (4)	3·5 (2)
O(4W)	0·3409 (6)	−0·6130 (5)	−0·1220 (5)	3·7 (2)
O(5W)	0·4694 (6)	−0·0791 (5)	0·1412 (4)	3·8 (2)

515, $T = 293$ K. Final $R = 0·039$ for 3846 observed reflections. The two iminodiacetate (ida) ions which coordinate Cu function as tridentate ligands and are related by a centre of inversion at the Cu atom, resulting in a *trans* configuration for the anion complex, Cu(ida)$_2^{2-}$. The coordination around Cu is in the shape of an octahedron, tetragonally distorted by Jahn–Teller distortion. The Cu–N, Cu–O$_{ax}$ and Cu–O$_{eq}$ bond distances are 2·005 (5), 1·948 (5) and 2·578 (4) Å, respectively. The Ba^{2+} ion is surrounded by nine O atoms, five from water molecules and four from acetate groups. The average Ba–O bond distance is 2·85 (7) Å.

Introduction. Structural data previously obtained for iminodiacetate acid (H₂ida) complexes with transition metals (Cambridge Structural Database, 1987), show that this ligand normally coordinates from the N atom, and also the O atoms of both carboxylate groups. It forms complexes with molar ratio of metal–ligand 1:1 and 1:2. Only for complexes with Cu has the ratio 1:4 been found (Lukeš, Šmídová, Vlček & Podlaha, 1984). Hitherto only spectroscopic data have been available to identify the coordination mode of the ligand.

Experimental. Blue prismatic crystal with dimensions 0·18 × 0·27 × 0·36 mm; D_m by flotation in CHBr₃/CH₃OH; Syntex P2₁ diffractometer, λ(Mo Kα) = 0·71069 Å, graphite monochromator, $\theta/2\theta$ scan, $2\theta_{max} = 60°$; time per reflection ca 60 s, two standard reflections, variation 3·6%; 25 reflections with 3·8 < 2θ < 23·0° used for refinement of lattice parameters; an absorption correction was applied, maximum and

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

Cu–N(1)	2·005 (5)	Ba–O(6)	2·866 (5)
Cu–O(2)	1·948 (5)	Ba–O(7')	2·979 (4)
Cu–O(4)	2·578 (4)	Ba–O(8)	2·761 (5)
N(1)–C(1)	1·477 (8)	Ba–O(8')	2·904 (4)
N(1)–C(3)	1·474 (6)	Ba–O(1W)	2·893 (4)
C(1)–C(2)	1·512 (8)	Ba–O(2W)	2·794 (5)
C(2)–O(1)	1·249 (8)	Ba–O(3W)	2·862 (6)
C(2)–O(2)	1·280 (9)	Ba–O(4W)	2·795 (6)
C(3)–C(4)	1·535 (5)	Ba–O(5W)	2·767 (4)
C(4)–O(3)	1·264 (6)	Ba–Ba'	4·207 (1)
C(4)–O(4)	1·246 (6)		
		N(2)–C(5)	1·493 (7)
		N(2)–C(7)	1·491 (5)
		C(5)–C(6)	1·519 (6)
		C(6)–O(5)	1·253 (6)
		C(6)–O(6)	1·258 (8)
		C(7)–C(8)	1·527 (7)
		C(8)–O(7)	1·252 (6)
		C(8)–O(8)	1·249 (6)

N(1)–Cu–O(2)	85·8 (2)	Cu–O(2)–C(2)	114·7 (4)
N(1)–Cu–O(4)	70·6 (1)	N(1)–C(3)–C(4)	111·7 (4)
Cu–N(1)–C(1)	107·9 (3)	C(3)–C(4)–O(3)	115·7 (4)
Cu–N(1)–C(3)	110·2 (3)	C(3)–C(4)–O(4)	118·5 (4)
C(1)–N(1)–C(3)	114·6 (5)	O(3)–C(4)–O(4)	125·8 (4)
N(1)–C(1)–C(2)	112·6 (5)	Cu–O(4)–C(4)	98·7 (3)
C(1)–C(2)–O(1)	119·2 (6)		
C(1)–C(2)–O(2)	117·3 (5)		
O(1)–C(2)–O(2)	123·0 (6)		
O(6)–Ba–O(7')	138·0 (1)	O(2W)–Ba–O(3W)	142·1 (1)
O(6)–Ba–O(8)	70·4 (1)	O(2W)–Ba–O(4W)	66·7 (2)
O(6)–Ba–O(8')	141·8 (2)	O(2W)–Ba–O(5W)	65·4 (1)
O(6)–Ba–O(1W)	66·7 (1)		
O(6)–Ba–O(2W)	78·6 (2)	O(3W)–Ba–O(4W)	143·6 (2)
O(6)–Ba–O(3W)	81·5 (2)	O(3W)–Ba–O(5W)	78·6 (1)
O(6)–Ba–O(4W)	134·2 (2)		
O(6)–Ba–O(5W)	75·4 (1)	O(4W)–Ba–O(5W)	112·9 (2)
O(7')–Ba–O(8)	126·1 (1)		
O(7')–Ba–O(8')	44·4 (1)	C(5)–N(2)–C(7)	114·4 (4)
O(7')–Ba–O(1W)	150·5 (2)	N(2)–C(5)–C(6)	111·2 (5)
O(7')–Ba–O(2W)	96·4 (1)	C(5)–C(6)–O(5)	116·2 (5)
O(7')–Ba–O(3W)	77·7 (2)	C(5)–C(6)–O(6)	117·1 (4)
O(7')–Ba–O(4W)	77·0 (2)	O(5)–C(6)–O(6)	126·7 (4)
O(7')–Ba–O(5W)	65·0 (1)	Ba–O(6)–C(6)	139·6 (4)
		N(2)–C(7)–C(8)	110·6 (3)
O(8)–Ba–O(8')	84·1 (1)	C(7)–C(8)–O(7)	117·4 (4)
O(8)–Ba–O(1W)	71·7 (1)	C(7)–C(8)–O(8)	117·2 (4)
O(8)–Ba–O(2W)	137·5 (1)	O(7)–C(8)–O(8)	125·4 (5)
O(8)–Ba–O(3W)	60·7 (1)	Ba–O(7)–C(8)	93·0 (3)
O(8)–Ba–O(4W)	117·6 (1)	Ba–O(8)–C(8)	155·1 (4)
O(8)–Ba–O(5W)	129·5 (2)		
O(8')–Ba–O(1W)	131·9 (1)		
O(8')–Ba–O(2W)	136·0 (2)		
O(8')–Ba–O(3W)	61·1 (2)		
O(8')–Ba–O(4W)	82·6 (2)		
O(8')–Ba–O(5W)	102·2 (1)		
O(1W)–Ba–O(2W)	69·7 (1)		
O(1W)–Ba–O(3W)	129·4 (2)		
O(1W)–Ba–O(4W)	73·6 (2)		
O(1W)–Ba–O(5W)	125·4 (1)		

Symmetry code: ' at $-x, -1-y, -z$.

minimum transmission factors 0·5376, 0·5128; index range $0 \le h \le 9$, $-11 \le k \le 11$, $-15 \le l \le 15$; 4586 reflections measured, 4188 unique, $R_{int} = 0·03$, 3846 reflections observed with $I > 2·5\sigma(I)$; lattice parameters and Bravais translation lattice found by program *UB* (Sivý, Sivý & Koreň, 1987). Data reduction was performed with program *XP*21 (Pavelčik, 1987). Cu

and Ba atoms were located from the three-dimensional Patterson map (Sheldrick, 1976). Fourier and difference syntheses gave the positions of all non-H atoms. Refinement by least-squares method based on F values (223 refined parameters); scattering factors and f', f'' from *International Tables for X-ray Crystallography* (1974).

At this stage absorption correction was applied by program *DIFABS* (Walker, 1983). Because of strong secondary extinction, reflections with indices of 011, $\bar{1}24$, $\bar{2}42$, 212, $\bar{3}25$ and $\bar{3}14$ were excluded from further calculations. After anisotropic refinement, all H atoms were located from difference map (held fixed). Maximum positive and negative electron density in final difference Fourier synthesis 0·8 and −0·8 e Å^{-3}; final $R = 0.039$, $wR = 0.046$, $w = 0.9061/[\sigma^2(F_o) + 0.0015F_o^2]$; $(\Delta/\sigma)_{max} = 0.02$ in final refinement cycle. Calulations performed using an M4030-1 computer, Slovak Technical University, Bratislava, Czechoslovakia.

Discussion. Coordinates and equivalent isotropic thermal parameters of non-H atoms are given in Table 1.* Bond lengths and angles are listed in Table 2. The molecular structure and the arrangement in the unit cell are shown in Fig. 1. From Fig. 1, iminodiacetate can be seen to bind both in the complex anion and in the cation. Both iminodiacetate groups in the anion Cu(ida)$_2^{2-}$ are tridentate. The donor atoms form a tetrahedrally distorted octahedron around Cu, under the influence of the Jahn–Teller effect. The Cu atom lies at a centre of symmetry. Its equatorial

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* Lists of structure amplitudes, anisotropic thermal parameters, H-atom parameters and details of least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51078 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
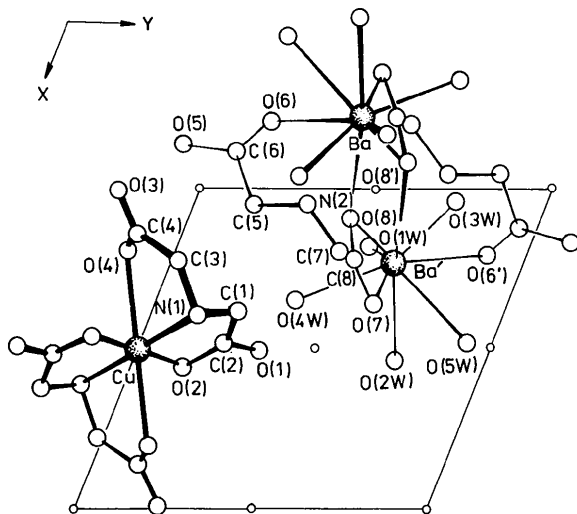
plane is formed by two chelate rings, with distances Cu—N(1) and Cu—O(2) 2·005 (5) and 1·948 (5) Å. The O(4) atoms of the carboxylate groups are bonded in axial positions and together with N(1) atoms create the other chelate rings. The angle O(4)—Cu—N(1) is 70·6 (1)°, and together with the distance Cu—O(4), 2·578 (4) Å, indicates the considerable distortion of the coordination polyhedron. In the complex cation, five molecules of H$_2$O and four O atoms of Hida$^-$ anion are coordinated to Ba^{2+} ions. The N atoms are protonated and take no part in the coordination. The Ba atoms form centrosymmetrical dimers connected by O(8), O(8'), O(6) and O(6') from the different iminodiacetate groups (Fig. 1). The average Ba—O distance is 2·85 (7) Å. From possible hydrogen bonds N(2)—H···O it appears that the hydrogen proton H(N2A) is an 'acid' one. It forms a hydrogen bond to O(1W) [length H···O 2·91 (8) Å]. Other possible interactions of H(N2A) are to O(6) [2·69 (5) Å] and to O(8) [2·67 (6) Å]. Thus the hydrogen proton is enclosed in a tetrahedral cavity formed by atoms N(2), O(1W), O(6) and O(8). The second atom H(N2B) is 'covalently' bound and does not form significant hydrogen-bond interactions. The coordination mode of ida to Cu is analogous to the complexes of other transition metals. On the other hand, the coordination mode of ida to the Ba atoms has not previously been observed with any of the following central atoms: Cu, Ni, Pd, V, Co, Mo, U, Yb, Nd, Zn and Pr (Cambridge Structural Database, 1987).

The present structure, containing two kinds of metal atoms, shows for the first time, iminodiacetate groups being bonded to the metal atoms in both the complex anion and the cation.

The Ba—Ba interatomic distance [4·207 (1) Å] indicates no chemical interaction. The carboxylate oxygens O(7) and O(8) (Fig. 1) are coplanar with atoms C(7) and C(8) ($\chi^2 = 0.01$ Å^2). The other atoms of the iminodiacetate ligands deviate from planarity.

Fig. 1. Projection of the crystal structure along the c axis.

References

Cambridge Structural Database (1987). Univ. Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 55, 99, 149. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
LUKEŠ, I., ŠMÍDOVÁ, I., VLČEK, A. & PODLAHA, J. (1984). *Chem. Zvesti*, **38**, 331–339.
PAVELČÍK, F. (1987). Computer program for Syntex $P2_1$ data reduction. Dept. of Analytical Chemistry, J. A. Komensky Univ., Faculty of Pharmacy, 832 32 Bratislava, Czechoslovakia.
SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.
SIVÝ, P., SIVÝ, J. & KOREŇ, B. (1987). *UB. Automatic Procedure for Unambiguous Choice of Lattice Parameters and Bravais Translation Lattice*. Dept. of Physics, CHTF SVŠT, Radlinského 9, 812 37 Bratislava, Czechoslovakia.
WALKER, N. (1983). *DIFABS*. Empirical absorption program. Chemistry Dept., Queen Mary College, London E1 4NS, England.