la direction O(II)· · ·O(III) et fait un angle de 15° avec le plan moléculaire. D'après cet ensemble de données, l'hybridation sp^2 de l'oxygène apparaît moins évidente pour le DM-2,5 phénol que pour le DM-2,3 phénol.

Le mode d'édification des structures de ces deux xylénols est tout à fait semblable. Les molécules s'associent entre elles de façon à former des chaînes autour d'axes hélicoïdaux parallèles à a pour le DM-2,3 phénol, parallèles à b pour le DM-2,5 phénol. Entre les chaînes ainsi constituées n'existent que des interactions de van der Waals. La cohésion est meilleure suivant la direction des chaînes qui coïncide avec la direction d'allongement des cristaux.

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The Crystal and Molecular Structure of Aquo(ethylenediaminetriacetatoacetic acid)rhodium(III)

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The crystal structure of aquo(ethylenediaminetriacetatoacetic acid)rhodium (III), Rh(H$_2$O)HEDTA, has been determined by X-ray diffraction, using 2183 three-dimensional intensity data. The crystals belong to the monoclinic space group $P2_1/c$ with four molecules in a unit cell of dimensions $a = 8.454(2)$, $b = 8.780(3)$, $c = 17.639(3)$ Å and $\beta = 100.58(3)°$. The observed and calculated densities of the crystal are 2.12 and 2.116 g cm^{-3}, respectively. The structure was solved by the heavy-atom method and refined by full-matrix least squares to a final R value of 0.025. The estimated errors in the bond distances are 0.002–0.007 Å and in bond angles 0.3–0.6°. The complex is a distorted octahedral molecule with H$_2$O bonded to Rh in an equatorial site and with the pentadentate EDTA bearing a proton on its uncoordinated glycinate arm. The coordinated bond distances are Rh–N, 2.082, 1.988 Å and Rh–O, 2.096, 2.030, 2.001, 2.027 Å. The uncomplexed –CH$_2$COOH arm and the coordinated H$_2$O are involved in intermolecular hydrogen bonding.

Introduction

The structure of transition metal–ethylenediaminetetraacetic acid (EDTA)† complexes in aqueous solution has been studied extensively by various physicochemical methods (Garvan, 1964; Podlahova, 1965; Haines & Douglas, 1965; Podlahova & Podlaha, 1966; Sugiura & Yamasaki, 1967; and Smith & Sawyer, 1968). X-ray studies have shown that EDTA behaves as a pentadentate or hexadentate ligand in the coordination sphere of a six-coordinated complex and as a hexadentate ligand in a seven-coordinated complex (see references in Table 8).

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† EDTA denotes the tetra-anion [(OOCCH$_2$)$_2$NCH$_2$CH$_2$N(CH$_2$COO)]$^{4-}$ and HEDTA the tri-anion [(OOCCH$_2$)$_2$NCH$_2$CH$_2$N(CH$_2$COO) (CH$_2$COOH)]$^{3-}$.

Dwyer & Garvan (1960) suggested that EDTA always forms a pentadentate complex with Rh(III), whereas Smith & Sawyer (1968) showed that in Rh(III)–EDTA complexes EDTA acts as a pentadentate ligand with one uncoordinated carboxylate group at low pH and ionization of the unbound carboxylic acid proton is accompanied by coordination to form the hexadentate complex at pH above 5. Dwyer & Garvan (1961) also observed a mutarotation of (−)-Rh^{III}-D-(−)-PDTA* which was interpreted to be due to the photoaquation of the complex in which a water molecule is substituted for a carboxylate ligand in the octahedral complex. However, Blackmer, Sudmeier, Thibedeau & Wing (1972) have reached a dif-

* PDTA is an abbreviation of 1,2-propylenediaminetetraacetate.

ferent conclusion from the investigation of the photolysis products of optically active Rh[III]PDTA and Rh[III]EDTA complexes in neutral solutions ($pH \sim$ 6·5), in which the ligands are hexadentate.

The structure of Rh(H_2O)HEDTA presented here provides information about the complex predominant in acid solution.

Experimental

The compound Rh(H_2O)HEDTA was prepared according to Dwyer & Garvan (1960). Yellowish-orange prismatic crystals were obtained by slow evaporation of an aqueous solution ($pH = 1$) at room temperature. One of these, having dimensions 0·4 × 0·2 × 0·2 mm, was used for collection of all the data. The crystal was mounted with the elongated direction (a axis) parallel to the φ axis of the goniostat. Precession and Weissenberg photographs showed monoclinic symmetry with systematically absent reflections $h0l$ with $l = 2n + 1$ and $0k0$ with $k = 2n + 1$, consistent with the centrosymmetric space group $P2_1/c$. The unit-cell dimensions and other crystal data are summarized in Table 1.

Table 1. *Crystal data for* Rh(H_2O)HEDTA

Formula	Rh(H_2O)$C_{10}H_{13}N_2O_8$
Crystal dimensions	0·4 × 0·2 × 0·2 mm
Space group	$P2_1/c$
Cell constants	$a = 8\cdot454 \pm 0\cdot002$ Å
	$b = 8\cdot780 \pm 0\cdot003$
	$c = 17\cdot639 \pm 0\cdot003$
	$\beta = 100\cdot58 \pm 0\cdot03°$
Volume of unit cell	1287 Å³
Molecular weight	410·15
Density	$\varrho_{calc} = 2\cdot116$ g cm⁻³
	$\varrho_{obs}* = 2\cdot12$ g cm⁻³
Z	4
μ	13·53 cm⁻¹

* Measured by flotation using a mixture of bromoform and chloroform.

Intensity data were collected on a Picker FACS-I automated diffractometer, using Mo $K\alpha$ radiation ($\lambda = $ 0·71069 Å). Reflections with 2θ values up to 50° were collected by the $2\theta-\theta$ scan technique at a scan rate of 1° per min and a scan range of 1·70°. Stationary-counter background counts of 10 sec were taken at

each end of the scan. As a check for electronic and crystal stability during the period of data collection, the intensities of three standard reflections were measured at an interval of 50 reflections. They showed 2 % statistical fluctuations from the mean. Altogether, 2384 independent reflections were collected. Reflections with intensity I greater than 2·5 times its standard deviation $\sigma(I)$ were considered observed, leaving 2183 reflections after data reduction. The data were then corrected for Lorentz and polarization effects, but no absorption correction was made since the linear absorption coefficient is small (13·53 cm⁻¹). The estimated maximum and minimum absorption correction factors ($A*$) are approximately 1·5 and 1·3, respectively.

Determination and refinement of the structure

The structure was solved by the heavy-atom method. A three-dimensional Patterson map was calculated, from which the positional parameters of the rhodium atom were derived. Based on the rhodium atom, a three-dimensional electron-density map was computed. Subsequently, all non-hydrogen atoms were identified from the map.

Owing to an improper choice of the unit cell, the refinement was carried out in a non-reduced cell with $a = 8\cdot454$, $b = 8\cdot780$, $c = 22\cdot079$ Å, and $\beta = 128\cdot25°$. The results have been transformed in terms of the reduced cell.

Refinements of the atomic parameters and a scale factor were carried out through successive cycles of full-matrix least-squares calculations using the *ORFLS* program of Busing, Martin & Levy (1962). After five cycles of refinement with anisotropic thermal parameters for rhodium and isotropic thermal parameters for all other non-hydrogen-atoms, the discrepancy indices were reduced to $R_1 = 0\cdot062$ and $R_2 = 0\cdot068$ where $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_2 = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$. At this stage, a difference electron-density map was calculated, on which all hydrogen atoms were located. The structure was further refined for two cycles with anisotropic thermal parameters for all nonhydrogen atoms; hydrogen atoms were included in the structure factor calculation but not refined. R_1 and R_2 were 0·025 and 0·036, respectively. The data used up to this stage were 1181 reflections having 2θ values below 40°. Then data up to $2\theta = 50°$ were in-
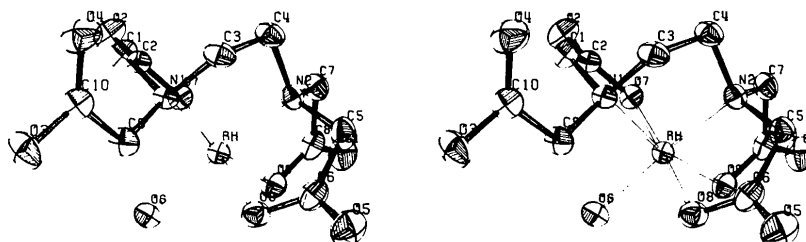

Fig. 1. A stereoscopic view of the molecule and the numbering of atoms.

Table 2. *Observed and calculated structure amplitudes*

The scale factor is 3·072. The indices are for the reduced unit cell.

Table 3. *Positional parameters and anisotropic thermal parameters of the nonhydrogen atoms*

Standard deviations given in parentheses are in the least significant digit. Anisotropic thermal parameters have been multiplied by 10^4. The temperature factor is of the form $\exp[-(\beta_{11}h^2 + \ldots + 2\beta_{12}hk + \ldots)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh	0·2014 (0)	0·8219 (0)	0·1418 (0)	49 (1)	45 (0)	13 (0)	4 (0)	5 (0)	0 (0)
O(1)	−0·1931 (4)	0·7289 (3)	0·2281 (2)	60 (6)	125 (4)	30 (1)	3 (4)	8 (2)	−5 (2)
O(2)	0·0424 (4)	0·7762 (3)	−0·0866 (1)	91 (6)	124 (4)	17 (1)	28 (4)	9 (2)	7 (2)
O(3)	0·7547 (3)	0·8999 (3)	0·0542 (1)	81 (6)	79 (3)	32 (1)	−12 (4)	12 (2)	−2 (2)
O(4)	0·6657 (4)	0·6639 (3)	0·0248 (2)	81 (6)	115 (4)	30 (1)	25 (4)	10 (2)	19 (2)
O(5)	0·4820 (4)	0·7086 (3)	0·3408 (1)	131 (7)	117 (4)	18 (1)	−2 (4)	11 (2)	−3 (2)
O(6)	0·2273 (4)	1·0523 (2)	0·1146 (1)	93 (6)	56 (3)	20 (1)	−4 (4)	9 (2)	0 (1)
O(7)	0·0482 (3)	0·8042 (2)	0·0391 (1)	54 (5)	69 (3)	16 (1)	5 (3)	7 (2)	1 (1)
O(8)	0·3647 (4)	0·8423 (2)	0·2389 (1)	84 (6)	65 (3)	16 (1)	2 (3)	7 (2)	3 (1)
O(9)	0·0161 (3)	0·8576 (3)	0·1981 (1)	54 (5)	71 (3)	19 (1)	10 (3)	5 (2)	4 (1)
N(1)	0·3693 (4)	0·7387 (3)	0·0793 (1)	52 (6)	48 (3)	15 (1)	6 (4)	6 (2)	2 (1)
N(2)	0·1744 (4)	0·6089 (3)	0·1755 (1)	62 (6)	51 (4)	15 (1)	−7 (4)	6 (2)	−3 (1)
C(1)	0·2929 (5)	0·7352 (4)	−0·0041 (2)	65 (7)	90 (5)	15 (1)	5 (5)	7 (3)	1 (2)
C(2)	0·1145 (5)	0·7742 (4)	−0·0200 (2)	65 (7)	53 (4)	15 (1)	4 (4)	7 (2)	2 (2)
C(3)	0·4047 (5)	0·5802 (4)	0·1112 (2)	79 (8)	51 (4)	22 (1)	15 (5)	9 (3)	4 (2)
C(4)	0·2492 (5)	0·5069 (4)	0·1231 (2)	66 (7)	47 (4)	23 (1)	10 (5)	8 (3)	4 (2)
C(5)	0·2605 (5)	0·5947 (4)	0·2576 (2)	96 (8)	79 (5)	16 (1)	−22 (5)	8 (3)	−11 (2)
C(6)	0·3800 (5)	0·7220 (4)	0·2819 (2)	67 (8)	89 (5)	14 (1)	9 (5)	6 (3)	1 (2)
C(7)	−0·0033 (5)	0·5888 (4)	0·1706 (2)	62 (7)	67 (5)	20 (1)	−11 (5)	7 (3)	−2 (2)
C(8)	−0·0673 (5)	0·7326 (4)	0·2023 (2)	65 (8)	100 (5)	14 (1)	1 (5)	5 (3)	−5 (2)
C(9)	0·5144 (5)	0·8375 (4)	0·0917 (2)	57 (7)	70 (5)	22 (1)	3 (5)	8 (3)	6 (2)
C(10)	0·6504 (5)	0·7866 (4)	0·0523 (2)	72 (8)	78 (5)	16 (1)	6 (5)	8 (3)	1 (2)

cluded for two additional cycles of anisotropic refinement. The final residuals were $R_1 = 0\cdot026$ and $R_2 = 0\cdot035$ for 2183 reflections. The shifts in the last cycle of refinement were less than $0\cdot3\sigma$ for all parameters, and the standard deviation of an observation of unit weight was $1\cdot12$.

The weighting scheme used throughout the refinement is given by $w = 4F^2/L^2\sigma^2(I)$ where L is the reciprocal Lorentz–polarization correction and $\sigma(I) = [P + (t/20)^2 B + (0\cdot045I)^2]^{1/2}$. P is the peak intensity, t the scan time in seconds, and B the background count. The atomic scattering power of Rh was corrected for the real and imaginary part of the anomalous dispersion. The scattering factors for all elements were from *International Tables for X-ray Crystallography* (1962).

Table 4. *Observed positional parameters for hydrogen atoms**

Isotropic thermal parameters B for all hydrogen atoms were set at $2\cdot0$ Å².

	x	y	z
H(C1)	0·302	0·640	−0·024
H'(C1)	0·341	0·815	−0·027
H(C3)	0·458	0·515	0·074
H'(C3)	0·486	0·610	0·163
H(C4)	0·169	0·510	0·077
H'(C4)	0·260	0·408	0·147
H(C5)	0·198	0·590	0·294
H'(C5)	0·310	0·490	0·265
H(C7)	−0·051	0·570	0·117
H'(C7)	−0·028	0·490	0·196
H(C9)	0·541	0·832	0·138
H'(C9)	0·480	0·938	0·070
H(O3)	0·854	0·860	0·037
H(O6)	0·325	1·070	0·165
H'(O6)	0·130	1·120	0·120

Table 5. *Bond distances and angles in* Rh(H₂O)HEDTA

Standard deviations given in parentheses are in the least significant digit.

All angles involving Rh of the X–Rh–Y type range between $81\cdot8$ and $96\cdot0°$ $(\sigma = 0\cdot2°)$.

Bond distances (Å)

Rh–N(1)	2·082 (3)	C(1)–C(2)	1·522 (7)
Rh–N(2)	1·988 (3)	C(3)–C(4)	1·512 (6)
Rh–O(6)	2·096 (2)	C(5)–C(6)	1·515 (6)
Rh–O(7)	2·030 (3)	C(7)–C(8)	1·519 (5)
Rh–O(8)	2·001 (3)	C(9)–C(10)	1·516 (5)
Rh–O(9)	2·027 (3)	⟨C–C⟩	1·517
N(1)–C(1)	1·495 (5)	C(2)–O(2)	1·222 (5)
N(1)–C(3)	1·510 (4)	C(6)–O(5)	1·228 (6)
N(1)–C(9)	1·486 (6)	C(8)–O(6)	1·233 (5)
N(2)–C(4)	1·507 (4)	⟨C–O$_u$⟩	1·228
N(2)–C(5)	1·502 (5)		
N(2)–C(7)	1·499 (6)	C(2)–O(7)	1·297 (3)
⟨N–C⟩	1·500	C(6)–O(8)	1·293 (4)
		C(8)–O(9)	1·314 (5)
C(10)–O(3)	1·326 (5)	⟨C–O$_c$⟩	1·301
C(10)–O(4)	1·198 (4)		

Bonds angles (°)

Rh—N(1)–C(1)	108·3 (3)	C(4)–N(2)—C(7)	115·3 (4)
Rh—N(1)–C(3)	103·6 (3)	N(1)–C(9)—C(10)	116·4 (4)
Rh—N(1)–C(9)	110·1 (3)	C(9)–C(10)–O(3)	109·9 (4)
Rh—N(2)–C(4)	107·0 (3)	C(9)–C(10)–O(4)	125·9 (4)
Rh—N(2)–C(5)	107·6 (3)	O(3)–C(10)–O(4)	124·2 (4)
Rh—N(2)–C(7)	105·0 (3)	C(1)–N(1)—C(9)	110·3 (4)
Rh—O(7)–C(2)	115·5 (3)	N(2)–C(7)—C(8)	107·8 (4)
Rh—O(8)–C(6)	114·0 (3)	C(7)–C(8)—O(1)	120·5 (4)
Rh—O(9)–C(8)	111·5 (3)	C(7)–C(8)—O(9)	116·3 (4)
N(1)–C(1)–C(2)	114·2 (4)	O(1)–C(8)—O(9)	123·2 (4)
C(1)–C(2)–O(2)	118·9 (4)	N(2)–C(5)—C(6)	113·5 (4)
C(1)–C(2)–O(7)	117·4 (4)	C(5)–C(6)—O(5)	116·4 (4)
O(2)–C(2)–O(7)	123·7 (4)	C(5)–C(6)—O(8)	120·3 (4)
N(1)–C(3)–C(4)	109·0 (4)	O(5)–C(6)—O(8)	123·3 (4)
C(3)–C(4)–N(2)	107·7 (4)		

Results and discussion

A list of the observed and calculated structure amplitudes is given in Table 2. The final positional and anisotropic thermal parameters are given in Table 3, and observed positional parameters for the hydrogen atoms are listed in Table 4. Derived intramolecular bond distances and bond angles involving non-hydrogen atoms are given in Table 5. A stereoscopic view of the molecule together with the numbering of atoms is shown in Fig. 1.

Description of the structure

The complex exists in *dl*-stereoisomeric pairs, related by the centers of symmetry of the space group $P2_1/c$. The potentially sexadentate ethylenediaminetetra-
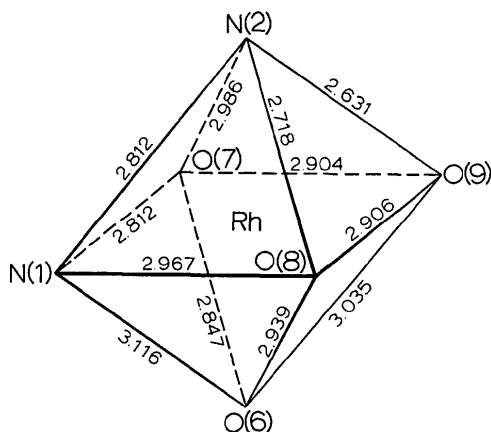

Fig. 2. Lengths of edges (in Å, $\sigma = 0.005$ Å) showing the distortion of the octahedron.

acetate ligand is acting as a pentadentate ligand with one acetate group remaining free and with a water molecule occupying the sixth position, forming a six-coordinated complex with the Rh(III) ion (Fig. 1). The complex is a distorted octahedron. The lengths of the twelve edges of the octahedron vary significantly from 2·631 to 3·116 Å (average 2·883 Å) as shown in Fig. 2. Moreover, based on the Rh atom and the six atoms bonded to Rh, the three least-squares planes given in Table 6 (planes I, II, III) are not exactly planar.

One may expect the Rh–N bonds to exceed the Rh–O lengths by 0·04 Å (the difference of the covalent radii for N and O). However, the differences are much larger than that. Rh–N(2), 1·988 Å, is extremely short compared with Rh–O(7), 2·030 Å, Rh–O(8), 2·001 Å, and Rh–O(9), 2·027 Å. Rh–N(1), 2·082 Å, is probably normal compared to Rh–O(7) and Rh–O(9). On the other hand, Rh–O(6), 2·096 Å, is much longer than other Rh–O bonds. The long Rh–O(6) bond may be caused by the hydrogen bonds. The C–O bond lengths within a carboxylate group differ according to whether the oxygen atoms are or are not complexed to the Rh, the C–O bond with complexed oxygen atoms being much longer. In the uncomplexed carboxylate group C(10)–O(4) is a double bond while C(10)–O(3) a single bond. The C–C and C–N bond lengths and all bond angles of the ligand are the same as those found in other structures (see references in Table 8).

The isostructural

Ga(H₂O)HEDTA,
Cr(H₂O)HEDTA
and   Fe(H₂O)HEDTA

Table 6. *Least-squares planes in* Rh(H₂O)HEDTA *and deviations of atoms* (*in* Å) *from planes*

Atoms used in the calculation of planes are indicated with standard deviations in parentheses (in the least significant digit)*

Atom	Plane I	Plane II	Plane III	Atom	Plane IV
Rh	0·069 (0)	−0·023 (0)	0·001 (0)	Rh	0·057 (0)
N(1)	−0·135 (3)	0·079 (2)		N(1)	−0·061 (3)
N(2)		−0·082 (2)	−0·062 (2)	C(1)	0·036 (4)
O(6)		−0·062 (2)	−0·060 (1)	C(2)	0·033 (3)
O(7)	0·104 (2)		0·060 (2)	O(7)	−0·066 (2)
O(8)	0·093 (2)		0·063 (2)	r.m.s. Δ	0·052
O(9)	−0·132 (2)	0·087 (2)			
r.m.s. Δ	0·109	0·071	0·055		

Atom	Plane V	Atom	Plane VI	Atom	Plane VII
Rh	−0·052 (0)	Rh	0·619 (0)	Rh	0·000 (0)
N(2)	0·097 (2)	N(2)	0·032 (3)	N(1)	0·000 (2)
C(5)	−0·110 (2)	C(7)	0·122 (3)	C(3)	−0·359
C(6)	0·057 (2)	C(8)	−0·423 (3)	C(4)	0·371
O(8)	0·008 (2)	O(9)	−0·350 (2)	N(2)	0·000 (2)
r.m.s. Δ	0·074	r.m.s. Δ	0·374	r.m.s. Δ	0·000

Table 7. *Comparison of the cell constants of* Rh(H₂O)HEDTA *with those of the isomorphous compounds*

	Space group	a	b	c	β
Ga(H₂O)HEDTA	$P2_1/c$	8·347 (5) Å	8·840 (5) Å	17·565 (10) Å	99·86 (5)°
Fe(H₂O)HEDTA	$P2_1/c$	8·364 (5)	8·942 (5)	17·83 (1)	99·46 (5)
Cr(H₂O)HEDTA	$P2_1/c$	8·40 (1)	8·78 (1)	17·64 (2)	99·9 (1)
Rh(H₂O)HEDTA	$P2_1/c$	8·454 (2)	8·780 (3)	17·639 (3)	100·58 (3)

have been found to be isomorphous in the crystalline state (Hoard, Kennard & Smith, 1963), having the same space group $P2_1/c$ and nearly identical cell constants. Based on the powder photographs Dwyer & Garvan (1960) found that $Rh(H_2O)HEDTA$ was isomorphous with $Cr(H_2O)HEDTA$. The space group and cell constants of the present structure further indicate that $Rh(H_2O)HEDTA$ is isomorphous with the Ga(III), Cr(III), and Fe(III) complexes. A comparison of the cell constants is given in Table 7. The present structure is probably the best representative of this general type, since the detailed structure for other complexes in this type have not been reported.

The structure of $Rh(H_2O)HEDTA$ is also quite similar to the structures of $Cu(H_2O)H_2EDTA$ and $Ni(H_2O)H_2EDTA$, all being pentadentate octahedral

complexes with a free $-CH_2COOH$ arm and a water molecule bonded to the metal except that the Cu and Ni complexes are protonated on the complexed acetate *trans* to the free arm. In other cases, the EDTA ligand is fully complexed to the metal, forming a hexadentate octahedral or seven-coordinated complex depending upon whether a water molecule participates to the coordination. As for the $[VO_2(H_2EDTA)]^-$ and $[VO_2(EDTA)]^{-3}$ ions, they are tetradentate octahedral complexes. A comparison of the crystal structures of EDTA-metal complexes is listed in Table 8. It is interesting to note that $Fe(H_2O)HEDTA$ is a pentadentate octahedral complex while $[Fe(H_2O)EDTA]^-$ is a hexadentate seven-coordinated complex. Thus the octahedral aquo pentadentate EDTA complex is the equilibrium product of acid hydrolysis.

Table 8. *Comparison of the crystal structures of some metal–EDTA complexes*

Compound	Space group	Coordination	Type of ligand	Number of free acetate groups*	Reference
$Cu(H_2O)H_2EDTA$	$P2_1/c$	octahedral	pentadentate	1	Stephens (1969)
$Ni(H_2O)H_2EDTA$	$P2_1/c$	octahedral	pentadentate	1	Smith & Hoard, (1959)
$Ga(H_2O)HEDTA$	$P2_1/c$	octahedral	pentadentate	1	Hoard et al. (1963)
$Fe(H_2O)HEDTA$	$P2_1/c$	octahedral	pentadentate	1	Hoard et al. (1963)
$Cr(H_2O)HEDTA$	$P2_1/c$	octahedral	pentadentate	1	Hoard et al. (1963)
$Rh(H_2O)HEDTA$	$P2_1/c$	octahedral	pentadentate	1	This work
$[Mn(H_2O)HEDTA]^-$ in $Mn_3HEDTA.10H_2O$	$P2_1/c$	seven-coordinated	hexadentate	0	Richards et al. (1964)
$[CoEDTA]^-$ in $NH_4[CoEDTA].2H_2O$ & $Rb[CoEDTA].2H_2O$	$P2_12_12_1$ $P2_12_12_1$	octahedral	hexadentate	0	Weakliem & Hoard (1959)
$[CrEDTA]^-$ in $NH_4[CrEDTA].2H_2O$ & $Rb[CrEDTA].2H_2O$	$P2_12_12_1$ $P2_12_12_1$	octahedral	hexadentate	0	Hoard, Smith & Lind (1961)
$[AlEDTA]^-$ in $NH_4[AlEDTA].2H_2O$	$P2_12_12_1$	octahedral	hexadentate	0	Hoard, Smith & Lind (1961)
$[Fe(H_2O)EDTA]^-$ in		seven-	hexadentate	0	Hoard, Lind & Silverton (1961)
$Rb[Fe(H_2O)EDTA].H_2O$ & $Li[Fe(H_2O)EDTA].2H_2O$	$P2/a$ $Pbca$	coordinated			Hamor et al. (1964)
$[Mn(H_2O)HEDTA]^-$ in $Mn[Mn(H_2O)HEDTA]_2.8H_2O$	$P2_1/n$	seven-coordinated	hexadentate	0	Hoard, Pedersen, Richards & Silverton (1961)
$[VO_2(H_2EDTA)]^-$ in $NH_4[VO_2(H_2EDTA)].3H_2O$	$P2_1/c$	octahedral	tetradentate	2	Scheidt, Collins & Hoard (1971)
$[VO_2EDTA]^{-3}$ in $Na_3[VO_2EDTA].4H_2O$	$P2_1/c$	octahedral	tetradentate	2	Scheidt, Countryman & Hoard (1971)

* All free (or uncomplexed) acetate groups except those in $[VO_2EDTA]^{-3}$ were found to be protonated.

Table 9. *Distances and angles involving hydrogen bonding*

Atom A	Atom B	Symmetry code	Distance	Bond	Angle
O(7)	O(3)	I	2·673 Å		
O(7)	H(O3)	I	1·71	O(3)–H(O3)···O(7)	161°
O(3)	H(O3)	II	1·00	C(10)–O(3)–H(O3)	126
O(6)	O(5)	III	2·799		
H(O6)	O(5)	III	2·05	O(6)–H(O6)···O(5)	122
O(6)	O(2)	IV	2·695		
H'(O6)	O(2)	IV	1·73	O(6)–H'(O6)···O(2)	155
O(6)	H(O6)	II	1·11	H(O6)–O(6)–H'(O6)	110
O(6)	H'(O6)	II	1·03		

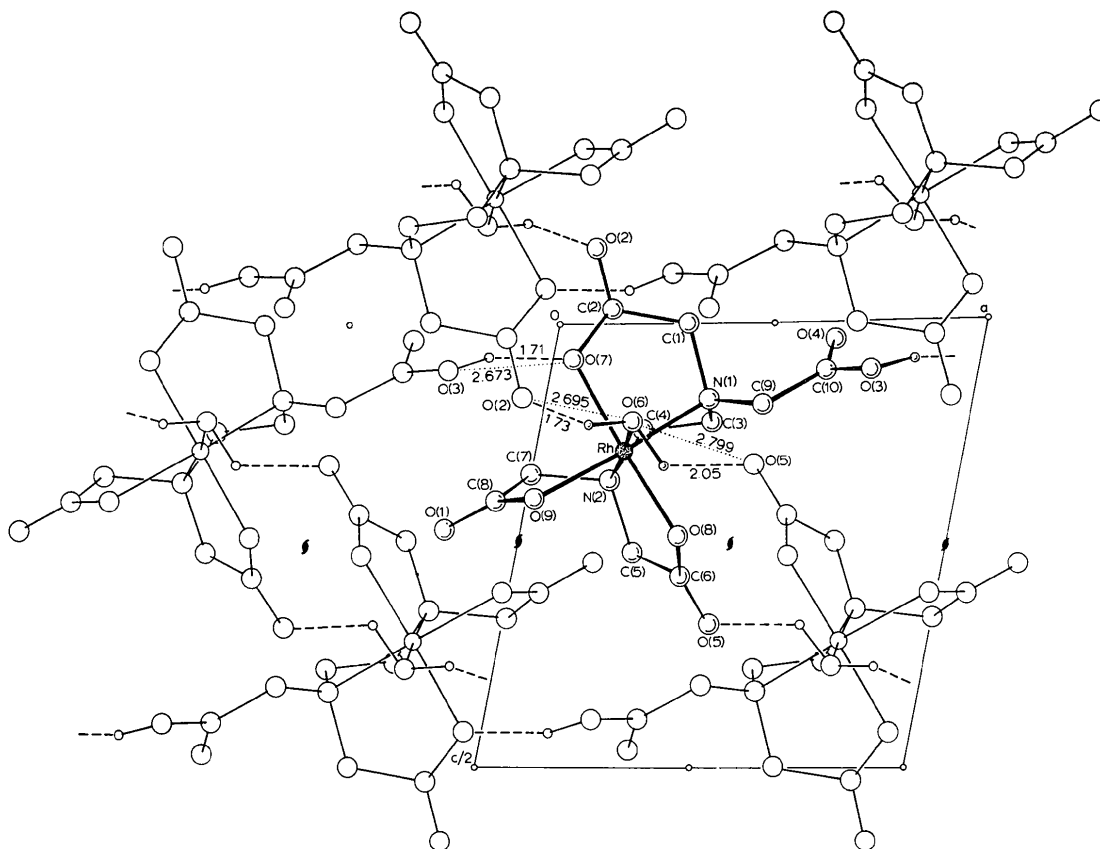| Symmetry codes:				
	I	$x-1$	y	z
	II	x	y	z
	III	$1-x$	$y-\frac{1}{2}$	$\frac{1}{2}-z$
	IV	$\bar{x}$	$\bar{y}$	$\bar{z}$

Fig. 3. Projection along the *b* axis showing the packing and the intermolecular hydrogen bonding scheme. Only those hydrogen atoms involving hydrogen bonding are indicated.

The strain in the complex can be best expressed by the analysis of the glycinic (Rh–N–C–C–O–Rh) rings (Weakliem & Hoard, 1959). An unstrained ring should be planar. The least-squares planes calculated for the atoms in the glycinic rings are given in Table 6 (planes IV, V, and VI). The former two, axial glycinic rings, are unstrained, while the latter, equatorial glycinic ring, like those in other EDTA complexes, is highly strained.

The conformation of the ethylenediamine rings, Rh–N(1)–C(3)–C(4)–N(2)–Rh, is expressed by the N–C–C–N torsional angle, 56·6°. C(3) and C(4) are on the opposite sides and equidistant from the N(1)–Rh–N(2) plane (see plane VII in Table 6), similar to those found in other EDTA complexes.

All the acetate groups were calculated to be quite planar and the least-squares planes are not reported here.

Hydrogen bonding and crystal packing

The intermolecular hydrogen bond scheme is shown by broken lines in Fig. 3. The distances and angles involving hydrogen bond are given in Table 9. The hydrogen bond distances are also shown in Fig. 3. Each molecule of Rh(H$_2$O)HEDTA is involved in six

hydrogen bonds with surrounding molecules. The free acetate group is protonated as found in other metal–EDTA complexes with free acetate arms (see Table 8). The protonated acetate oxygen, O(3), serves as a proton donor to the bound oxygen O(7) of another molecule, while the water O(6) donates its protons to the uncomplexed oxygen atoms, O(2) and O(5), of two different molecules. Two molecules related by the two-fold screw axis at $a=0$, $c=\frac{1}{4}$ are linked together through the O(6)–H$\cdots$O(5) bond, forming an infinite helix parallel to the *b* axis. On the other hand, the molecules are held together through the O(6)–H$\cdots$O(2) and O(3)–H$\cdots$O(7) bonds, giving rise to infinite connection along the *a* axis. Except for the hydrogen bonded atoms, no atoms have distances shorter than the van der Waals contact distances.

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The Crystal Structure of a Naturally Occurring γ-Lactone Glucoside ($C_{11}H_{16}O_8.H_2O$) from *Helleborus Foetida* L.

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The crystal structure of the title compound has been determined. The cell is monoclinic, space group $P2_1$ with $Z = 2$. Cell parameters are $a = 11·41$ (2), $b = 10·82$ (2), $c = 5·33$ (2) Å, $\beta = 95·72$ (6)°. All reflexions with $I > 0$ and $2\theta \le 52°$ (1280 independent) were measured using a four-circle diffractometer equipped with a crystal monochromator and a scintillation counter. Mo $K\alpha$ radiation was employed. The structure was determined by the symbolic addition method and was refined by the least-squares method to a final R value of 0·051 using 1161 independent reflexions considered to be observable. The compound contains a β-glucose unit fused to a dioxane ring, onto which a γ-lactone ring is attached in spiro arrangement.

Introduction

The compound studied was isolated by Dr E. Wollenweber at the Botanical Institute of the Technical University of Darmstadt, and a sample was sent to Dr J. Lam of this department for chemical investigations. We undertook a crystallographic study, and at the time we determined the structure, a paper was published (Tschesche, Welmar, Wulff & Snatzke, 1972) describing a compound which appeared to be the same and proposing a structure which was qualitatively equivalent to the one which we had arrived at, except that the stereochemistry at C(4′) (Fig. 1) could not be

obtained by the methods used by Tschesche *et al.* Professor Tschesche kindly sent us a sample of the crystal isolated in his laboratory, and rotation and Weissenberg X-ray photographs of his and of our samples were completely identical as regards both lattice spacings and relative intensities. A preliminary communication was published (Mariezcurrena, Rasmussen, Lam & Wollenweber, 1972), emphasizing the stereochemistry at C(4′). This paper communicates details about the structure solution and quantitative details about bond lengths *etc.*

Experimental

Crystals were kindly supplied by Dr Wollenweber, Botanical Institute, Technical University of Darmstadt, through Dr J. Lam, Department of Organic

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* Now returned to Facultad de Quimica, Montevideo, Uruguay.

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