

The structure, which consists of *cis*-[CrCl₂-(cyclam)]⁺ cations and Cl⁻ anions, differs from that of (-)-*cis*-(*RRRR*)-[CrCl₂(cyclam)]ClO₄ (House & McKee, 1984) in that there is no crystallographically imposed C₂ symmetry and the compound crystallizes in a centrosymmetric space group with both the *RRRR* and *SSSS* cations present in the unit cell.

The perchlorate crystals were obtained from a resolved sample and it is not known whether or not the racemic perchlorate crystallizes differently.

The cyclam ligand is folded along the N(1) and N(3) direction with the four N atoms coordinated to the Cr atom in adjacent octahedral sites and the two Cl atoms *cis*-related, occupying the two remaining positions. Within the complex the five-membered ethylenediamine rings adopt a δ configuration (Purcell & Kotz, 1977) while the six-membered trimethylenediamine rings are in the chair (*c*) form.

Although the molecular geometries of the cation in the two salts are comparable, there are significant differences in some bond angles and torsional angles as seen for example in the greater folding at N(1) and N(3) [N(1)–Cr–N(3) bond angle 166.9 (1)° (chloride); 169.0 (4)° (perchlorate)] and the N(4)–Cr–N(2) bond angle [92.8 (1)° (chloride); 94.3 (3)° (perchlorate)].

It is likely that the interaction between the hydrogen-bonding system of the amine protons and the counter-anion is the major cause of these differences and of the differences in packing. The chloride anion is within strong hydrogen-bonding distance of the amine protons H(2) and H(4) [H(2)···Cl(3ⁱ) = 2.27 (3), H(4)···Cl(3ⁱ) = 2.26 (3) Å] with N–H···Cl angles of nearly 180° [174 (2) and 169 (2)° respectively] [(i) 0.5 + *x*, 0.5 – *y*, *z*] and there is a possible weaker interaction of H(1) and H(3) with other cations [H(3)···Cl(3) = 2.47 (3) Å and N(3)–H(3)···Cl(3) = 147 (2)°, H(1)···Cl(3ⁱⁱ) = 2.50 (3) Å and N(1)–H(1)···Cl(3ⁱⁱ) = 136 (2)°] [(ii) 0.5 + *x*, 0.5 – *y*, 1 + *z*].

In the perchlorate salt there appears to be, not unsurprisingly, no interaction between the amine

protons and the ClO₄⁻ anion, which remains disordered and presumably able to rotate freely; instead the complex cations are linked by significant intermolecular hydrogen-bonding interactions between the coordinated chloride and the amino protons on adjacent cation groups (N···Cl about 3.28 Å). These hydrogen bonds hold the molecules in chains along the twofold axis, while in the chloride salt it is the Cl(3) anion which forms hydrogen bonds with the amine protons of adjacent cations.

All bond lengths and angles within the cations are in the range expected for such compounds (Bang & Mønsted, 1982). The greater length of the Cr–N (mean 2.100 (1) Å) than the means 2.080 (6) Å in [CrCl₂-(cyclam)]⁺ (House & McKee, 1984) and 2.083 Å in [CrCl(H₂O)(hexamethylcyclam)]²⁺ (Temple, House & Robinson, 1984) is probably related to the hydrogen-bond system previously described.

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Structure of Diiodo(1,4,8,11-tetrathiacyclotetradecane)mercury(II)

BY N. GALEŠIĆ, M. HERCEG AND D. SEVDIĆ

Rudjer Bošković Institute, PO Box 1016, 41001 Zagreb, Yugoslavia

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Abstract. [HgI₂(C₁₀H₂₀S₄)], *M*_r = 722.90, orthorhombic, *Pnam*, *a* = 10.641 (3), *b* = 8.507 (3), *c* = 20.087 (8) Å, *V* = 1818 (1) Å³, *Z* = 4, *D*_m = 2.62, *D*_x

= 2.640 Mg m⁻³, λ(Mo Kα) = 0.7107 Å, μ = 12.25 mm⁻¹, *F*(000) = 1320, *T* = 293 K, final *R* = 0.052 for 1726 observed reflections. The structure is

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built up by chains stretched along the *c* axis composed of alternately connected HgI₂ moieties, located in the mirror planes, and centrosymmetric exodentate unstrained ligand molecules. The macrocyclic molecule acts as a doubly monodentate bridging ligand. One centrosymmetric pair of its S atoms coordinates two Hg atoms while the other centrosymmetric S pair remains uncoordinated. The Hg coordination polyhedron is a distorted tetrahedron with S—Hg—S and I—Hg—I bond angles of 84.36 (10) and 136.31 (6)° respectively. The Hg—S bond lengths are 2.752 (3) Å, and the Hg—I bond lengths are 2.653 (2) and 2.669 (2) Å.

Introduction. In recent years macrocyclic ligands have been widely studied because of the variety of their metal-binding properties (Melson, 1979). X-ray crystal-structure studies on the coordination chemistry of the mercury complexes with the potentially tetradentate macrocyclic polythiaether 1,4,8,11-tetrathiacyclotetradecane (ttp) have revealed different modes of bonding (Alcock, Herron & Moore, 1976, 1978; Herceg, Matković, Sevdic, Matković-Čalogović & Nagl, 1984). The objective of this paper is to study the crystal structure of the [HgI₂(ttp)] complex in order to determine the influence of the halogen-ion size on the type of complexes of mercury halogenides with ttp.

Experimental. The [HgI₂(ttp)] complex was prepared by the reaction of ttp and HgI₂ in acetone. The light-yellow crystalline product formed was filtered off, washed with acetone and dried. Crystals suitable for X-ray examination were obtained by recrystallization from benzene. *D_m* by flotation in a mixture of CCl₄ and CHBr₃. Intensity data collected from a crystal defined by the following planes/distances (in mm, from the crystal faces to the approximate crystal gravity centre): ±(110)/0.085, ±(110)/0.085, (011)/0.041, (011)/0.041, (011)/0.037, (011)/0.037, (001)/0.087, (001)/0.112. Philips PW 1100 four-circle diffractometer, θ - 2θ scanning technique, scan width 1.60°, scan rate 0.04° s⁻¹. Unit-cell parameters obtained from least-squares analysis of 18 reflections with 2θ values ranging from 10 to 18°. *Pnam*, a non-standard setting of space group No. 62, was determined by absent reflections *h*0*l*, *h* ≠ 2*n* and 0*kl*, *k*+*l* ≠ 2*n* and the structure determination. 2041 reflections scanned within the octant *h*, *k*, *l* (*h* 14, *k* 11, *l* 28) up to $\sin\theta/\lambda \leq 0.70 \text{ \AA}^{-1}$. Three standard reflections (205, 035, 420) measured every 2 h showed an average variation of 1%. Corrections applied for Lorentz and polarization effects and for absorption (Harkema, 1978); transmission factors from 0.15 to 0.25. Hg atom located by heavy-atom method, all other non-H atoms from Fourier map. H atoms located from difference map and theoretical calculations. In final calculations 12 strong low-order reflections strongly affected by extinction rejected. Full-matrix least-

squares refinement on *F* for 1726 remaining reflections with $I > 3\sigma(I)$ varying positional and anisotropic thermal parameters of non-H atoms, while parameters of H atoms with isotropic thermal factors 10% greater than those of bonded C atoms kept fixed; *R* and *wR* 0.052 and 0.072, respectively; function minimized $\sum w(|F_o| - |F_c|)^2$ with $w = A/\sigma^2(F_o)$ where *A* is an arbitrary scale factor for weights in the ninth weighting scheme of XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) giving *S* = 2.16 for *A* = 1.00. If *A* = 0.214 an *S* of 1.00 is obtained, but without any other repercussion on actual accuracy of the refinement. Parameter shifts < 0.1. Final difference map revealed no residuals greater than 1.4 e Å⁻³, except seven irregular maxima up to 4.6 e Å⁻³ near Hg and I atoms. Scattering factors of Cromer & Mann (1968) for non-H and those of Stewart, Davidson & Simpson (1965) for H atoms; anomalous-dispersion factors from Cromer & Liberman (1970). Calculations performed mainly with XRAY76 on a Univac 1110 computer at the University Computing Centre in Zagreb.

Discussion. The final atomic parameters are listed in Table 1* and bond lengths, angles and endocyclic torsion angles in Table 2. Fig. 1 shows an ORTEP diagram of two HgI₂ moieties bridged with a ligand molecule and the atomic numbering.

The ligand molecule (ttp) of the [HgI₂(ttp)] complex is centrosymmetric and shows an exodentate ('inside out') conformation, characterized by the lone (donor) electron pairs of the S atoms pointing outwards from the macrocycle (DeSimone & Glick, 1975, 1976). The HgI₂ moieties are placed in the mirror planes bound to the mirror symmetrical pairs of the ligand molecules. Each macrocyclic molecule acts as a doubly monodentate bridging ligand coordinating to two Hg atoms by a pair of its two mutually centrosymmetric S atoms, while the other pair of centrosymmetric S atoms remains uncoordinated. So, the structure is built of chains consisting of alternating HgI₂ and ligand moieties stretched along the *c* axis. In the structure of the [(NbCl₅)₂(ttp)] complex (DeSimone & Glick, 1975; DeSimone & Tighe, 1976), two NbCl₅ moieties are coordinated by the centrosymmetric ligand in a similar exodentate manner, but there are no chains.

The coordination polyhedron of Hg is a distorted tetrahedron. The I—Hg—I angle of 136.31 (6)° shows a considerable enlargement from the regular tetrahedral angle due to the repulsion between the I atoms. It is almost compensated by an analogous decreasing of the

* Lists of structure factors, anisotropic thermal parameters, a mean plane and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42694 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional positional parameters ($\times 10^4$) and equivalent isotropic temperature factors ($\times 10^2$) for non-H atoms

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
Hg	6390 (1)	7415 (1)	2500	3.60 (2)
I(1)	6691 (1)	10511 (2)	2500	4.48 (5)
I(2)	7890 (1)	4901 (2)	2500	4.46 (4)
S(1)	6760 (4)	8662 (4)	-114 (2)	4.3 (1)
S(2)	4579 (3)	6628 (4)	1580 (2)	3.3 (1)
C(1)	6384 (12)	7544 (20)	630 (6)	4.0 (4)
C(2)	5003 (12)	7700 (16)	833 (7)	3.7 (4)
C(3)	4917 (13)	4602 (17)	1369 (7)	3.7 (4)
C(4)	4013 (14)	3958 (18)	843 (8)	4.1 (5)
C(5)	4277 (14)	2213 (15)	731 (7)	3.6 (5)

Table 2. Bond lengths (\AA) and angles ($^\circ$) of non-H atoms and endocyclic torsion angles ($^\circ$)

Hg—I(1)	2.653 (2)	S(2)—C(2)	1.81 (1)
Hg—I(2)	2.669 (2)	S(2)—C(3)	1.81 (1)
Hg—S(2)	2.752 (3)	C(1)—C(2)	1.53 (2)
S(1)—C(1)	1.82 (1)	C(3)—C(4)	1.53 (2)
S(1)—C(5)	1.82 (1)	C(4)—C(5)	1.53 (2)
I(1)—Hg—I(2)	136.31 (6)	C(2)—S(2)—C(3)	103.6 (6)
I(1)—Hg—S(2)	109.02 (8)	S(1)—C(1)—C(2)	113 (1)
I(2)—Hg—S(2)	102.95 (8)	S(2)—C(2)—C(1)	115 (1)
S(2)—Hg—S(2 ⁱⁱ)	84.36 (10)	S(2)—C(3)—C(4)	112 (1)
C(1)—S(1)—C(5)	102.3 (6)	C(3)—C(4)—C(5)	110 (1)
Hg—S(2)—C(2)	105.1 (5)	C(4)—C(5)—S(1 ⁱ)	113 (1)
Hg—S(2)—C(3)	104.5 (5)		
C(5)—S(1)—C(1)—C(2)	-60 (1)	S(2)—C(3)—C(4)—C(5)	-175 (1)
S(1)—C(1)—C(2)—S(2)	-179 (1)	C(3)—C(4)—C(5)—S(1 ⁱ)	180 (1)
C(1)—C(2)—S(2)—C(3)	-61 (1)	C(4)—C(5)—S(1 ⁱ)—C(1 ⁱ)	61 (1)
C(2)—S(2)—C(3)—C(4)	-69 (1)		

Symmetry code: (i) $1-x, 1-y, -z$; (ii) $x, y, \frac{1}{2}-z$.

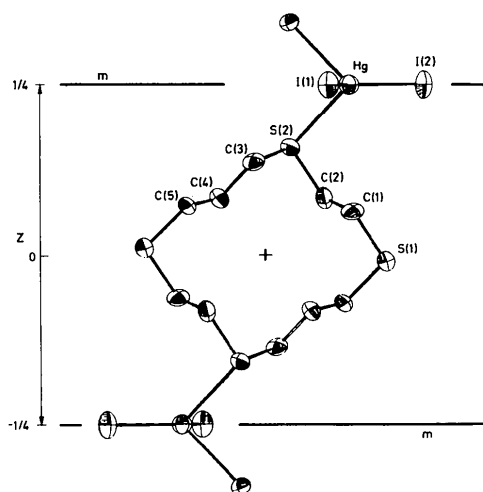


Fig. 1. ORTEP diagram (Johnson, 1965) showing two HgI_2 moieties bridged by the ligand molecule and the atom numbering. The symmetry centre at $\frac{1}{2}, \frac{1}{2}, 0$ is denoted by +. For clarity the H atoms are omitted.

S—Hg—S angle to $84.36(10)^\circ$. The Hg—I bond lengths of 2.653 (2) and 2.669 (2) \AA are slightly shorter, while the Hg—S bond lengths of 2.752 (3) \AA are about 0.2 \AA longer than expected for the Hg—S bond lengths of a tetrahedrally coordinated Hg atom (Grdenić, 1965). There are no other atoms around the Hg atoms at a distance shorter than the sum of the corresponding van der Waals radii.

The endocyclic bond lengths and angles (Table 2) do not show any peculiarities. The conformation of the ligand molecule can be described by displacements of the C atoms from the plane through the four S atoms and especially by the endocyclic torsion angles (DeSimone & Glick, 1976). The displacements of the C atoms from the S_4 plane are: C(1) 0.60 (1), C(2) -0.54 (1), C(3) 0.97 (1), C(4) 0.10 (2), C(5) 0.95 (1) \AA . Both the torsion angles (Table 2) and the displacements are in good agreement with two essentially equal conformations of the free ligand molecules, denoted as α and β_1 (DeSimone & Glick, 1976). These *exo* conformations, characterized by nearly synclinal and antiperiplanar torsion angles along the S—C and C—C bonds, respectively, show that the rings are unstrained. The third, also *exo*, conformer of the free ligand molecule, denoted as β_2 , and the ligand molecule in the $[(\text{NbCl}_5)_2(\text{ttp})]$ complex show energetically less convenient endocyclic torsion angles.

It is interesting to mention that the ttp ligand always forms the $[\text{HgI}_2(\text{ttp})]$ complex with HgI_2 , regardless of the metal/ligand ratios used. It was found that HgCl_2 and HgBr_2 can form two types of complexes with ttp as a ligand: $[\text{HgCl}_2(\text{ttp})]$ or $[(\text{HgCl}_2)_2(\text{ttp})]$ and $[\text{HgBr}_2(\text{ttp})]$ or $[(\text{HgBr}_2)_2(\text{ttp})]$, respectively, depending on the metal/ligand ratio used in their preparation (Sevdic & Meider, 1977; Mink, Sevdic & Meic, 1985). Our further experiments proved that during the recrystallization $[\text{HgCl}_2(\text{ttp})]$ was transformed into the $[(\text{HgCl}_2)_2(\text{ttp})]$ complex. Conversely, by recrystallization of $[(\text{HgBr}_2)_2(\text{ttp})]$, the complex $[\text{HgBr}_2(\text{ttp})]$ was formed. So it is inferred that for the complexes of HgCl_2 the complex with metal/ligand ratio 2:1 is the most convenient structural form, while for the complexes of HgBr_2 , the 1:1 ratio is preferred.

In the structure of $[(\text{HgCl}_2)_2(\text{ttp})]$ (Alcock *et al.*, 1976, 1978) the centrosymmetric exodentate ligand is doubly bidentate bridging two HgCl_2 moieties. It should be noticed that the crystal data of the $[\text{HgBr}_2(\text{ttp})]$ complex which we obtained by oscillation and Weissenberg X-ray photographs are: $a = 10.35(2)$, $b = 8.37(1)$, $c = 19.89(3)$ \AA , $V = 1723(5)$ \AA^3 , space group $Pn\bar{m}$ ($Pna2_1$). The obvious similarity with the analogous data of the $[\text{HgI}_2(\text{ttp})]$ complex indicates that the structures of these complexes are probably similar. As expected, in accord with the difference in the iodine and bromine radii, the unit-cell volume of $[\text{HgBr}_2(\text{ttp})]$ is somewhat smaller than that of the $[\text{HgI}_2(\text{ttp})]$ complex.

The mentioned stability preferences of the different crystal species, as well as the two crystal structures of the $[(\text{HgCl}_2)_2(\text{ttp})]$ and $[\text{HgI}_2(\text{ttp})]$ complexes, illustrate the importance of the size of the coordinated halogen ion in forming mercury complexes with the potentially tetradentate macrocyclic polythiather ttp. While in the $[(\text{HgCl}_2)_2(\text{ttp})]$ complex ttp does not act as a tetradentate but as a doubly bidentate ligand, in $[\text{HgI}_2(\text{ttp})]$ and probably in $[\text{HgBr}_2(\text{ttp})]$, where the halogen ions are larger, the Hg-halogen units are placed at the side of the macrocycle which acts as a doubly monodentate ligand.

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Structure of *trans*-Dichlorobis(ethylenediamine)cobalt(III) Perchlorate

BY ERIC C. NIEDERHOFFER, ROBERTA PEASCOE, PHILIP R. RUDOLF, ABRAHAM CLEARFIELD AND ARTHUR E. MARTELL

Department of Chemistry, Texas A&M University, College Station, Texas 77843, USA

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Abstract. $[\text{CoCl}_2(\text{C}_2\text{H}_8\text{N}_2)_2]\text{ClO}_4$, $M_r = 349.45$, $P\bar{1}$, $a = 8.519$ (2), $b = 12.372$ (3), $c = 6.341$ (1) Å, $\alpha = 100.79$ (2), $\beta = 105.09$ (2), $\gamma = 77.40$ (2)°, $V = 623.7$ (4) Å³, $Z = 2$, $D_m = 1.88$ (2), $D_x = 1.86$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 20.71$ cm⁻¹, $F(000) = 356$, $T = 296$ K, $R = 0.035$ for 1575 unique observed data. There are two independent cations in the unit cell with nearly identical bond distances and angles. The cations are close to C_{2h} symmetry, the deviation arising from a twist of the ethylenediamine ligand. Each Co atom is found on an inversion center.

Introduction. Trivalent cobalt complexes are readily prepared from the oxygenation and subsequent oxidation of cobalt(II) compounds. Many *cis*- and *trans*-disubstituted cobalt(III) complexes may be synthesized from carbonatobis(ethylenediamine)cobalt(III) which is a product of the above reaction in the presence of

carbon dioxide (Springborg & Schaffer, 1973). The resulting cobaltic compounds are moderate oxidizing agents and isolation is usually performed at low temperature in order to minimize the production of cobalt(II) species. Thermal reactions of cobalt(III) complexes are important in the understanding of electron-transfer mechanisms. This report describes the product obtained in the thermal hydrolysis of carbonatobis(ethylenediamine)cobalt(III) in aqueous solutions of hydrochloric acid.

Experimental. Hydrolysis of carbonatobis(ethylenediamine)cobalt(III) chloride at 353 K in 6 M HCl resulted in a green crystalline material on standing at ambient temperature. The analysis of this product was in good agreement with that of the title compound. Crystal density by flotation in 1,2-dibromopropane–bromobenzene, crystal 0.08 × 0.09 × 0.10 mm, CAD-