

The Structures of the Mixed Complexes Cadmium(II)–1,4,10,13-Tetraoxa-7,16-diazacyclooctadecane Diiodide and Mercury(II)–1,4,10,13-Tetraoxa-7,16-diazacyclooctadecane Diiodide*

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Abstract. $\text{Cd}(\text{C}_{12}\text{H}_{26}\text{N}_2\text{O}_4)\text{I}_2$ and $\text{Hg}(\text{C}_{12}\text{H}_{26}\text{N}_2\text{O}_4)\text{I}_2$ are isostructural, monoclinic, $P2_1/c$, $Z = 2$. $a = 8.664$ (4), $b = 11.783$ (4), $c = 10.737$ (5) Å, $\beta = 114.78$ (4)°, $V = 995.1$ Å³ for the Cd and $a = 8.723$ (1), $b = 11.437$ (2), $c = 10.916$ (5) Å, $\beta = 115.64$ (2)°, $V = 981.8$ Å³ for the Hg compound. The structures were determined at 298 and 193 K for the Cd and Hg compounds respectively. The main differences between the two structures are a decrease in the M –I distance and an increase in the M –O and M –N distances when the central ion changes from Cd^{2+} to Hg^{2+} . These differences can be related to differences in hardness/softness of the metal ions and the various donors.

Introduction. Complex formation with cyclic oxoaza compounds is well known both in aqueous solution (Anderegg, 1975; Arnaud-Neu, Spiess & Schwing-Weill, 1977) and in the solid state (Herceg & Weiss, 1970, 1972; Moras, Metz, Herceg & Weiss, 1972). The geometry and the rigidity of the ring system in 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (2,2) offers a possibility for formation of ternary complexes M –2,2– X_2 , where the ligands X occupy axial positions perpendicular to the ring plane. Whether coordination on these sites will occur or not depends on the coordination geometry and the donor properties of the axial ligands.

In the present study, the structures of ternary metal complexes with 2,2 and I^- will be described. I^- is a well known complexing agent which forms very stable complexes particularly with the soft Hg^{2+} (Gerding, 1968; Sillén, 1949). A solution-chemical investigation of these complexes is in progress. Because of the low solubility of Hg –2,2– I_2 only the Cd^{2+} –2,2– I^- system can be studied. The present investigation of the mixed complexes in the solid state was undertaken in order to obtain structural information, particularly about the differences in the bond lengths M –N, M –O and M –I, which will give a measure of differences in affinity between the two metal ions and the various donors.

Cd –2,2– I_2 was prepared by mixing acetonitrile solutions of CdI_2 and 2,2 followed by recrystallization from acetonitrile (m.p. 538–543 K). Hg –2,2– I_2 was prepared by adding an acetonitrile solution of 2,2 to $\text{HgI}_2(\text{s})$, which thus was converted to the mixed complex. The product was recrystallized from acetonitrile (m.p. 438–442 K).

Weissenberg photographs indicated the Laue class $2/m$ for both Cd –2,2– I_2 and Hg –2,2– I_2 . Systematically absent reflexions $0k0$: $k = 2n + 1$ and $h0l$: $l = 2n + 1$ indicate the space group $P2_1/c$ in both cases. Intensities were collected on a computer-controlled four-circle diffractometer (Enraf–Nonius CAD-4 for Hg –2,2– I_2 and Syntex $P2_1$ for Cd –2,2– I_2). Cell dimensions were obtained by a least-squares procedure from 41 reflexions for Hg –2,2– I_2 and 44 for Cd –2,2– I_2 . The data for Hg –2,2– I_2 were collected at 193 K with a low-temperature attachment (Danielsson, Grenthe & Oskarsson, 1976). The intensities of two standard reflexions were checked at regular intervals. No systematic variation was observed. The values of I and $\sigma_c(I)$ (σ_c is based on counting statistics) were corrected for Lorentz, polarization and absorption effects. For

Table 1. *Details of the intensity collection and the least-squares refinement*

	Cd–2,2– I_2	Hg–2,2– I_2
FW	628.6	716.8
D_m (Mg m^{-3})	2.13	2.44
D_x (Mg m^{-3})	2.10	2.42
Crystal size (mm)	0.10 × 0.10 × 0.25	0.22 × 0.20 × 0.18
Radiation	Mo $K\alpha$ (graphite-monochromatized)	Mo $K\alpha$
Take-off angle (°)	4	3
θ interval (°)	0–22.5	3–26
Scan type/width $\Delta\omega$ (°)	$\omega/1.2$	ω –2 $\theta/0.7$ + 0.5 tan θ
Maximum recording time (min)	2.4	3
μ (mm^{-1})	2.0	11.2
Range of transmission factor	–	0.13–0.21
Number of measured reflexions	1193	2009
Number of reflexions with zero weight $ I < 2\sigma_c(I)$	435	237
Number of reflexions used in the final refinements, m	758	1772
Number of parameters refined, n	97	97
$R = \sum F_o - F_c / \sum F_o $	0.063	0.033
$R_w = [\sum w(F_o - F_c)^2 / \sum w F_o ^2]^{1/2}$	0.079	0.049
$S = [\sum w(F_o - F_c)^2 / (m - n)]^{1/2}$	1.80	2.0
$C =$ weighting function in $w^{-1} = \sigma_c^2(F_o ^2) / 4 F_o ^2 + (C F_o)^2$	0.030	0.018

* Diaza-crown Ethers. III.

Cd-2,2-I₂, no absorption correction was made. Table 1 gives the details of the data collection and refinement.

The metal ion was placed at the centre of symmetry. Successive difference syntheses combined with least-squares refinements revealed the positions of all the non-H atoms. The final model included anisotropic temperature factors. The choice of this model compared with a model with isotropic temperature factors was confirmed by the Hamilton *R*-factor ratios (Hamilton, 1965). Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The values for Cd, Hg and I were corrected for anomalous dispersion. The positional parameters are given in Table 2.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34348 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Atomic coordinates ($\times 10^4$) with e.s.d.'s for Cd-2,2-I₂ and Hg-2,2-I₂

	<i>x</i>	<i>y</i>	<i>z</i>
Cd	0	0	0
I	1539 (2)	2146 (1)	181 (2)
N	-147 (29)	493 (15)	2195 (23)
C(1)	818 (47)	-131 (28)	3357 (34)
C(2)	2671 (44)	-187 (30)	3582 (33)
O(1)	2612 (23)	-825 (14)	2424 (22)
C(3)	4299 (48)	-926 (25)	2542 (40)
C(4)	4119 (41)	-1625 (29)	1194 (40)
O(2)	3092 (25)	-915 (17)	118 (25)
C(5)	2851 (45)	-1441 (29)	-1197 (41)
C(6)	1846 (51)	-529 (25)	-2257 (34)
Hg	0	0	0
I	1431 (1)	2107 (1)	187 (1)
N	-222 (13)	570 (10)	2341 (11)
C(1)	850 (20)	-171 (12)	3498 (14)
C(2)	2674 (20)	-185 (12)	3657 (15)
O(1)	2693 (11)	-845 (9)	2530 (9)
C(3)	4374 (16)	-892 (15)	2575 (15)
C(4)	4219 (17)	-1554 (13)	1344 (15)
O(2)	3268 (12)	-859 (8)	194 (10)
C(5)	3096 (18)	-1385 (13)	-1048 (14)
C(6)	1975 (18)	-601 (15)	-2207 (14)

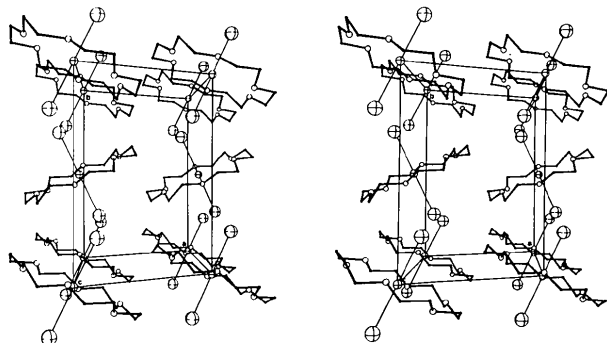


Fig. 1. A stereoscopic view of the unit cell.

Discussion. Fig. 1 shows a stereoscopic view of the unit cell and the packing of the complexes, which is nearly the same for both. Fig. 2 depicts the complex. The coordination polyhedron can be described either as a slightly distorted square made up of two N atoms and two I⁻ ions or as an approximate hexagonal bipyramid with two N and four O atoms in a plane (Table 3) and

Table 3. Deviations (δ_i in $\text{\AA} \times 10^2$) from the least-squares plane through the centre of symmetry

The mean deviation $\sigma = (\sum w_i \delta_i^2 / 3 \sum w_i)^{1/2}$ (three degrees of freedom) is also given; w_i is the inverted mean variance for the atomic coordinates. The lower sign refers to atoms with the transformed coordinates $-x, -y, -z$.

	Cd-2,2-I ₂	Hg-2,2-I ₂
N	± 22	± 28
O(1)	∓ 15	∓ 20
O(2)	± 20	± 22
σ	11	13

Table 4. Selected interatomic distances (\AA) with e.s.d.'s in 2,2, Cd-2,2-I₂ and Hg-2,2-I₂

Superscripts refer to the following transformations of coordinates x, y, z : (i) $-x, -y, -z$; (ii) $x, \frac{1}{2} - y, \frac{1}{2} + z$.

	2,2	Cd-2,2-I ₂	Hg-2,2-I ₂
<i>M</i> -I		2.827 (1)	2.680 (1)
<i>M</i> -N		2.482 (22)	2.724 (10)
<i>M</i> -O(1)		2.811 (20)	2.909 (9)
<i>M</i> -O(2)		2.841 (20)	2.935 (9)
N-C(1)	1.451 (9)	1.386 (40)	1.472 (18)
C(1)-C(2)	1.515 (8)	1.521 (51)	1.523 (22)
C(2)-O(1)	1.471 (5)	1.435 (39)	1.450 (17)
O(1)-C(3)	1.422 (7)	1.418 (42)	1.447 (15)
C(3)-C(4)	1.477 (9)	1.615 (53)	1.497 (21)
C(4)-O(2)	1.417 (9)	1.402 (42)	1.413 (17)
O(2)-C(5)	1.421 (6)	1.474 (46)	1.430 (17)
C(5)-C(6)	1.510 (11)	1.542 (49)	1.514 (21)
C(6)-N ⁱ	1.440 (7)	1.502 (46)	1.473 (17)
N-N ⁱ	5.841 (6)	4.964 (44)	5.448 (20)
O(1)-O(1 ⁱ)	5.612 (6)	5.622 (40)	5.818 (18)
O(2)-O(2 ⁱ)	5.670 (5)	5.682 (40)	5.870 (18)
I-I ⁱ		5.654 (2)	5.360 (2)
I-I ⁱⁱ		5.38 (2)	5.53 (1)
I-N		3.64 (2)	3.69 (1)
I-N ⁱ		3.88 (2)	3.95 (1)
I-N ⁱⁱ		4.03 (2)	3.86 (1)

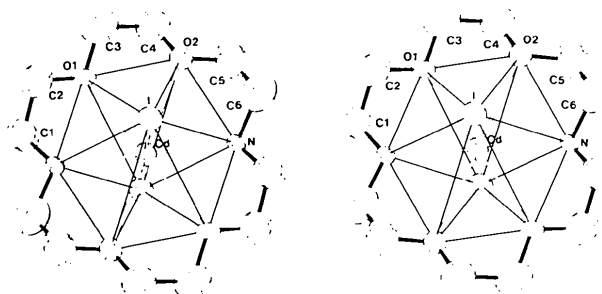


Fig. 2. A stereoscopic view of the coordination polyhedron of the Cd-2,2-I₂ complex.

Table 5. Selected angles (°) with e.s.d.'s in 2,2, Cd-2,2-I₂ and Hg-2,2-I₂

The superscript refers to the following transformation of the coordinates *x, y, z*: (i) $-x, -y, -z$.

	2,2	Cd-2,2-I ₂	Hg-2,2-I ₂
I-M-N		86.3 (4)	86.2 (2)
I-M-O(1)		94.1 (4)	93.9 (2)
I-M-O(2)		85.9 (4)	83.7 (2)
N-C(1)-C(2)	109.7 (3)	111.4 (2.7)	110.4 (1.1)
C(1)-C(2)-O(1)	108.5 (3)	103.5 (2.5)	107.7 (1.1)
C(2)-O(1)-C(3)	111.5 (4)	107.8 (2.4)	112.0 (1.1)
O(1)-C(3)-C(4)	110.5 (4)	104.7 (2.6)	107.0 (1.1)
C(3)-C(4)-O(2)	110.1 (4)	102.9 (2.5)	107.7 (1.2)
C(4)-O(2)-C(5)	111.9 (6)	108.9 (2.4)	112.7 (1.1)
O(2)-C(5)-C(6)	108.1 (3)	102.9 (2.5)	107.9 (1.2)
C(5)-C(6)-N ⁱ	110.4 (3)	104.3 (2.5)	111.4 (1.2)
C(6)-N ⁱ -C(1 ⁱ)	114.2 (4)	102.0 (2.4)	110.2 (1.1)
I-N-I ⁱ		97.5 (5)	89.1 (2)
N-I-N ⁱ		82.5 (5)	90.9 (2)

two axial I⁻ ions. Tables 4 and 5 give selected interatomic distances and angles. Uncomplexed 2,2 is included for comparison (Herceg & Weiss, 1972).

The formation constants in aqueous solution for the first complex between the weak (*b*)-acceptor (Ahrlund, Chatt & Davies, 1958) Cd²⁺ and NH₃ and I⁻ respectively are of about the same order of magnitude. With the marked (*b*)-acceptor Hg²⁺ the difference is about four log units in favour of I⁻ (*Stability Constants of Metal-Ion Complexes*, 1964), indicating a very strong Hg²⁺-I⁻ interaction.

When the central ion is changed from Cd²⁺ to the larger Hg²⁺ a ring expansion should follow. The change in O-Oⁱ distance reflects this fact. However, the ionic radius change cannot be responsible for the large (~0.50 Å) N-Nⁱ expansion. The reason must be related to the very strong linear I⁻-Hg²⁺-I⁻ coordination which thus weakens the Hg²⁺-N interaction.

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N-rac-C-rac-(5,6,12,13-Tetramethyl-1,4,8,11-tetraaza-4,11-cyclotetradecadiene)-nickel(II) Diperchlorate

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Abstract. C₁₄H₂₈N₄Ni²⁺·2ClO₄⁻, [Ni(C₁₄H₂₈N₄)(ClO₄)₂ (isomer *c*), *M_r* = 510.0, monoclinic, *P*2₁/*c*, *a* = 10.99 (3), *b* = 13.46 (5), *c* = 16.28 (3) Å, β = 117.72 (2)° (from diffractometer measurements, Mo Kα radiation), *V* = 2131.8 Å³, *Z* = 4, *F*(000) = 1064,

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The Hg-I length is about the same as in other Hg²⁺-I⁻ complexes (Sandström, 1978). The similar affinities of Cd²⁺ for N and I⁻ result in a longer Cd-I distance than that found, for example, in CdI₂ (2.60 Å).

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μ = 0.80 mm⁻¹. The crystals contain *N-rac-C-rac*-[NiL]²⁺ cations, in which the N-H bonds at N(1) and N(8) are *cis* to the adjacent axial methyl groups at C(6) and C(13) respectively. The perchlorate anions are disordered.

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