

Fig. 2. A stereo packing diagram of the ordered, (I), and disordered structures, (II).

[O(1) 2.330 (4); O(2) 2.351 (4) Å] than in the disordered form [O(1) = O(2) = 2.269 (3) Å]. The differences in the dimensions of the two cations may be related to the difference in hydrogen-bonding patterns in the two crystals (Table 3, Fig. 2). In the ordered structure, (I), on semicarbazone chain forms only one hydrogen bond while the other chain is involved in four hydrogen bonds. However, in (II), both semicarbazone chains form two hydrogen bonds involving the disordered chloride ion and water molecule. In both (I)

and (II) all the H atoms on the water molecules form hydrogen bonds but the hydrogen bonds to the water molecules are different. The differences in the packing in the two cases lead to a slightly higher density for the ordered structure compared to the disordered one. The formation of the disordered form (II) occurs at room temperature while the ordered form (I) comes from the heated solutions. Consequently, the rate of conversion of (II) to (I) is slow. Redissolving (II) will produce (I) but other reactions occur so that the result is a mixture of products. We are currently investigating these reactions.

We thank the Chemistry Department, University of Florida, for a Postdoctoral Fellowship (AEK), and the Center for Instructional Research Computing Activities for a grant of computer time. Purchase of the Nicolet Instrumentation was funded in part by NSF Grant CHE 8316675.

References

- CAMERON, A. F., TAYLOR, D. W. & NUTTALL, R. H. (1972). *J. Chem. Soc. Dalton Trans.* pp. 1603–1608.
 DREW, M. G. B. (1977). *Prog. Inorg. Chem.* **23**, 67–210.
 DREW, M. G. B., NELSON, J. & NELSON, S. M. (1981). *J. Chem. Soc. Dalton Trans.* pp. 1685–1690.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99–101. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
 KEPERT, D. L. (1979). *Prog. Inorg. Chem.* **25**, 41–144.
 PALENIK, G. J. & WESTER, D. W. (1978). *Inorg. Chem.* **17**, 864–870.
 SHELDRIK, G. M. (1986). Desktop *SHELXTL*. Nicolet XRD Corp., Madison, WI 53711–0508, USA.
 WESTER, D. W. & PALENIK, G. J. (1974). *J. Am. Chem. Soc.* **96**, 7565–7566.

Acta Cryst. (1988). **C44**, 88–92

Complexes of Cadmium(II) Bromide and Cadmium(II) Iodide with 18-Crown-6 Ether*

BY ALAN HAZELL

Institute of Chemistry, Aarhus University, DK-8000 Århus C, Denmark

(Received 16 July 1987; accepted 28 September 1987)

Abstract. [Cd(C₁₂H₂₄O₆)Br₂], *M_r* = 536.5, rhombohedral, *R* $\bar{3}$, *a* = 11.8127 (13), *c* = 11.9464 (15) Å (hexagonal setting), *V* = 1443.7 (4) Å³, *Z* = 3, *D_x* = 1.851 (1) Mg m⁻³, Mo *K*α, λ = 0.71073 Å, μ = 5.261 (1) mm⁻¹, *F*(000) = 786, *T* = 293 K, *R* = 0.028, *wR* = 0.031 for 528 reflexions [*I* > 3σ(*I*)] and 50

variables. [Cd(C₁₂H₂₄O₆)I₂], *M_r* = 630.5, orthorhombic, *Pnma*, *a* = 16.563 (3), *b* = 27.996 (5), *c* = 8.382 (2) Å, *V* = 3887 (1) Å³, *Z* = 8, *D_x* = 2.155 (1) Mg m⁻³, Mo *K*α, λ = 0.71073 Å, μ = 4.283 (2) mm⁻¹, *F*(000) = 2384, *T* = 294 K, *R* = 0.037, *wR* = 0.039 for 1287 reflexions [*I* > 3σ(*I*)] and 201 variables. The CdBr₂ complex is isostructural with the corresponding CdCl₂ and HgCl₂ compounds [Paige & Richardson (1984). *Can. J. Chem.* **62**, 332–335],

* 1,4,7,10,13,16-Hexaoxacyclooctadecane.

whereas the CdI_2 complex has two crystallographically independent molecules, one on a symmetry centre and one on a mirror plane. The Cd atom can be regarded as eight-coordinated with the complex having hexagonal bipyramidal geometry, rather than as two-coordinated with the linear CdX_2 groups 'threaded' through the 18-crown-6 cavity since the Cd–X distances are ca 0.1 Å longer than in the free CdX_2 molecules, indicating bonding between Cd and the equatorial O atoms. The bromide has Cd–Br = 2.506 (1) and Cd–O = 2.752 (3) Å, in the iodide the mean Cd–I distance is 2.692 (1) Å, Cd–O distances range from 2.69 (1) to 2.81 (2) Å with a mean of 2.768 (4) Å. The geometries of the Cd and Hg compounds are discussed in relation to softness parameters and bond distances are predicted for the Zn complexes.

Introduction. Complexes of macrocyclic ligands with metals have been studied extensively as models for more complicated biological systems. In particular, cadmium compounds have been studied since cadmium readily replaces zinc in metalloenzymes which can then be studied by ^{113}Cd NMR spectroscopy. Crown ethers have also been considered (Cram & Cram, 1978) as models for studying the transport of metal ions across membranes. The structures of the 18C6 complexes (18C6 = 18-crown-6 ether) of CdBr_2 and of CdI_2 have been determined in connection with solid-state ^{113}Cd CP/MAS (cross-polarization magic-angle spinning) NMR studies (Jakobsen, Jacobsen, Bildsøe & Ellis, 1987) of the cadmium halide complexes. Of particular interest here is the question as to whether the additional splittings observed for the spinning sidebands in the ^{113}Cd CP/MAS spectrum of the CdBr_2 complex should be attributed to there being non-equivalent Cd atoms or to the effect of the ^{113}Cd – $^{79/81}\text{Br}$ dipolar couplings. This question is independently being pursued by ^{113}Cd CP/MAS NMR studies of the complex at different magnetic-field strengths.

Experimental. 18C6 CdBr_2 was recrystallized from acetonitrile. A crystal was mounted on a Huber 4-circle diffractometer. The cell dimensions were determined from the setting angles of 55 reflexions with $18.3 < 2\theta < 31.0^\circ$. Intensities were measured out to $2\theta_{\text{max}} = 60^\circ$ using an ω – 2θ scan with Nb-filtered Mo $K\alpha$ radiation, the scan width was $(1.2 + 0.692\tan\theta)^\circ$ which was divided into 50 steps, the counting time was 2 s step^{-1} . Reflexions with $-16 \leq h \leq 16$, $-16 \leq k \leq 16$, $-16 \leq l \leq 0$ were measured giving 976 independent reflexions, $R_{\text{int}} = 0.073$, of which 528 had $I > 3\sigma(I)$. Reflexions 044 and 404 were monitored every 50 reflexions, the overall fall off in intensity was negligible. Reflexions were integrated using the Nelmes (1975) method; the data were corrected for absorption (crystal $0.15 \times 0.15 \times 0.18$ mm), transmission factors

ranging from 0.43 to 0.74. The structure was determined from a Patterson function. H-atom positions were calculated assuming C–H = 0.95 Å and were refined together with isotropic temperature factors. All non-H atoms were refined anisotropically. An isotropic extinction factor was refined giving $g = 5.5 (4) \times 10^{-4}$, which corresponds to a minimum value of I/I_{corr} of 0.63. $w = 1/\sigma(F)$, where $\sigma(F) = \{[\sigma_c(F^2) + 1.03F^2]\}^{1/2} - |F|$, where $\sigma_c(F^2)$ is the standard deviation of F^2 . The final R^* (on F) = 0.028, $wR = 0.031$, $S = 1.047$, $(\Delta/\sigma)_{\text{max}} = 0.34$, $\Delta\rho = -0.19 (3)$ to $0.15 (3) \text{ e } \text{Å}^{-3}$.

18C6 CdI_2 was recrystallized from water. A crystal was mounted on a Huber 4-circle diffractometer. The cell dimensions were determined from the setting angles of 50 reflexions with $16.8 < 2\theta < 21.9^\circ$. Intensities were measured out to $2\theta_{\text{max}} = 45^\circ$ using an ω – 2θ scan with Nb-filtered Mo $K\alpha$ radiation, the scan width was $(2 + 0.692\tan\theta)^\circ$ which was divided into 50 steps, the counting time was 2 s step^{-1} . Reflexions with $0 \leq h \leq 17$, $0 \leq k \leq 30$, $0 \leq l \leq 9$ were measured giving 2583 reflexions of which 1287 had $I > 3\sigma(I)$. Reflexions 0,12,0 and 602 were monitored every 50 reflexions, the overall fall off in intensity was 2.6%. Reflexions were integrated using the Nelmes (1975) method; the data were corrected for absorption (crystal $0.35 \times 0.14 \times 0.08$ mm), transmission factors ranging from 0.53 to 0.71. The positions of the heavy atoms were determined with *MULTAN80* (Main *et al.*, 1980) and subsequent Fourier syntheses; H-atom positions were calculated assuming C–H = 0.95 Å and were not refined. H atoms were refined with a common isotropic temperature factor. All non-H atoms were refined anisotropically. An isotropic extinction factor was refined giving $g = 0.18 (3) \times 10^{-4}$, which corresponds to a minimum value of I/I_{corr} of 0.83. $w = 1/\sigma(F)$, where $\sigma(F) = \{[\sigma_c(F^2) + 1.03F^2]\}^{1/2} - |F|$, where $\sigma_c(F^2)$ is the standard deviation of F^2 . The final R^* (on F) = 0.037, $wR = 0.039$, $S = 0.984$, $(\Delta/\sigma)_{\text{max}} = 0.09$, $\Delta\rho = -0.9 (2)$ to $0.9 (2) \text{ e } \text{Å}^{-3}$. Fractional coordinates are listed in Tables 1 and 2, bond distances and angles are shown on Fig. 1 or listed in Table 3 which also includes torsion angles. Computations were carried out on a VAX 11/780 with the following programs: *INTEG* – integration; *DATAP* and *DSORTH* (State University of New York, Buffalo) – absorption correction and sorting; modified *ORFLS* (Busing, Martin & Levy, 1962) – least-squares refinement; *ORFFE* (Busing & Levy, 1964) – geometry and errors; *ORTEP* (Johnson, 1965) – drawings. Scattering curves: Cromer & Mann (1968) for Cd, I, Br, N and C; Stewart,

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44404 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Davidson & Simpson (1965) for H; anomalous-dispersion corrections for Cd, Br and I from Cromer & Liberman (1970).

Discussion. 18C6 CdBr₂ (Fig. 2) is isostructural with the corresponding CdCl₂ and HgCl₂ compounds (Paige & Richardson, 1984), Cd—Br is 2.506 (1), Cd—O 2.752 (3), C—C is 1.490 (8), the mean C—O distance is 1.417 (4), C—H ranges from 0.95 (5) to 1.07 (6) Å. The O atoms are ±0.150 (3) Å out of the equatorial plane. In 18C6 CdI₂ there are two crystallographically independent molecules, one is on a symmetry centre, the other on a mirror plane with Cd, two I and two O

atoms on the mirror plane. The Cd—I distances range from 2.684 (2)–2.697 (2) Å with a mean value of 2.692 (1) Å, Cd—O ranges from 2.69 (1) to 2.81 (2) Å with a mean of 2.768 (4) Å, the mean C—O and C—C distances are 1.420 (5) and 1.481 (10) Å. In the centrosymmetric molecule the O atoms are ±0.158 (10) Å out of the best plane, the second molecule is slightly squashed on one side so that the deviations from planarity range from -0.099 (11) to 0.220 (11) Å but the mean displacement, 0.157 (6) Å, is almost identical with that for the first molecule. Unlike the centrosymmetric molecules, the Cd atom is 0.023 (1) Å out of the best plane through the O atoms.

In 18-crown-6 ether complexes with MX₂, the metal atom may be regarded as eight-coordinated with two strong axial and six weak equatorial bonds, the complex having hexagonal bipyramidal geometry (Hughes & Truter, 1982), or as two-coordinated with the linear

Table 1. 18C6 CdBr₂; fractional atomic coordinates ($\times 10^5$ for Cd and Br, $\times 10^4$ for O and C, $\times 10^3$ for H), equivalent isotropic temperature parameters ($\text{\AA}^2 \times 10^{-4}$ for Cd, $\text{\AA}^2 \times 10^{-3}$ for O, C and H) and displacements D ($\text{\AA} \times 10^{-3}$) from the best planes through the O atoms together with the e.s.d.'s of the atoms

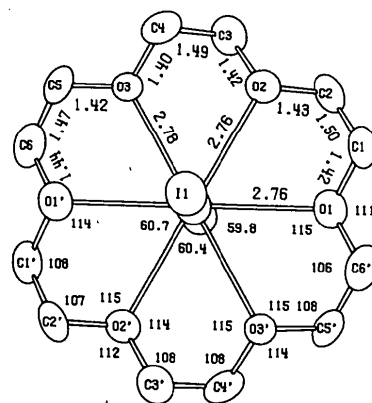
	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^*	<i>D</i>
Cd	0	0	0	586 (4)	0
Br	0	0	20975 (6)	608 (4)	2506 (1)
O(1)	2485 (3)	2125 (3)	126 (2)	63 (2)	150 (2)
C(1)	2627 (5)	3359 (5)	147 (5)	72 (3)	176 (6)
C(2)	1532 (6)	3456 (5)	373 (5)	72 (3)	446 (6)
H(11)	256 (4)	349 (5)	-93 (4)	68 (14)	-1107 (49)
H(12)	359 (6)	418 (7)	11 (5)	119 (21)	129 (55)
H(21)	165 (6)	431 (6)	21 (4)	87 (16)	247 (50)
H(22)	147 (5)	326 (5)	125 (4)	79 (16)	1496 (53)

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

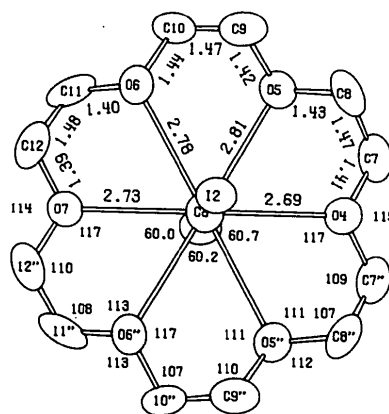
Table 2. 18C6 CdI₂; fractional atomic coordinates ($\times 10^5$ for Cd and I, $\times 10^4$ for O and C), equivalent isotropic temperature parameters ($\text{\AA}^2 \times 10^{-4}$) and displacements D ($\text{\AA} \times 10^{-3}$) from the best planes through the O atoms together with the e.s.d.'s of the atoms

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^*	<i>D</i>
Cd(1)	0	50000	0	38 (1)	0
I(1)	-14510 (6)	48125 (4)	13080 (13)	39 (1)	-2693 (1)
O(1)	548 (6)	4079 (4)	485 (14)	60 (8)	158 (11)
O(2)	675 (6)	4761 (4)	2899 (12)	39 (6)	-158 (10)
O(3)	379 (6)	5715 (3)	2168 (12)	54 (7)	158 (10)
C(1)	642 (10)	3956 (6)	2121 (23)	74 (13)	-346 (17)
C(2)	1148 (10)	4335 (6)	2894 (20)	59 (11)	319 (16)
C(3)	1077 (9)	5146 (6)	3674 (21)	37 (9)	356 (16)
C(4)	506 (9)	5555 (6)	3734 (20)	50 (10)	-292 (16)
C(5)	-101 (10)	6135 (6)	2049 (21)	48 (11)	-289 (17)
C(6)	-113 (13)	6285 (6)	367 (26)	77 (15)	367 (20)
Cd(2)	-22622 (10)	25000	-38727 (22)	48 (1)	23 (1)
I(2)	-36135 (10)	25000	-56671 (18)	48 (1)	-2673 (1)
I(3)	-8815 (10)	25000	-21974 (21)	52 (1)	-2706 (1)
O(4)	-1455 (10)	2500	-6661 (19)	72 (11)	-99 (11)
O(5)	-1764 (7)	1626 (4)	-5198 (13)	59 (8)	125 (11)
O(6)	-2824 (6)	1646 (4)	-2587 (13)	52 (7)	-185 (11)
O(7)	-3041 (11)	2500	-1004 (18)	92 (13)	220 (11)
C(7)	-1056 (12)	2074 (8)	-7090 (23)	86 (15)	267 (20)
C(8)	-1620 (13)	1671 (7)	-6879 (21)	88 (16)	-427 (19)
C(9)	-2324 (11)	1255 (6)	-4839 (24)	49 (11)	-497 (18)
C(10)	-2427 (11)	1216 (6)	-3102 (25)	72 (14)	139 (19)
C(11)	-2934 (13)	1666 (6)	-928 (26)	105 (17)	405 (21)
C(12)	-3448 (12)	2085 (7)	-581 (22)	86 (15)	-159 (20)

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



(a)



(b)

Fig. 1. 18C6 CdI₂ showing the numbering of the atoms, bond distances and angles. Standard deviations are 0.01 Å for Cd—O and 0.02 Å for C—O or C—C distances, 0.3° for the O—Cd—O angles and 1° for O—C—C and Cd—O—C. Distances and angles not shown are listed in Table 2. Symmetry code: (i) *x*, 1-*y*, *z*; (ii) *x*, 0.5-*y*, *z*.

MX_2 group 'threaded' through the 18-crown-6 cavity (Henrick, Mathews, Podejma & Tasker, 1982). The question as to whether the metal is bonded to the O atoms or whether the MX_2 group just fits into the hole can be answered by examining the $M-X$ bond lengths. In *trans* CdI_2 complexes, the $Cd-I$ distances vary

Table 3. Bond distances (Å), angles (°) not shown on Fig. 1 and torsion angles (°)

(a) 18C6 $CdBr_2$; symmetry code (i) $x-y, x, -z$; (ii) $y, y-x, -z$			
$Cd-Br$	2.506 (1)	$C(1)-H(11)$	0.95 (5)
$Cd-O$	2.752 (3)	$C(1)-H(12)$	1.11 (7)
$C(1)-O$	1.420 (6)	$C(2)-H(21)$	0.96 (6)
$C(2)-O^i$	1.414 (6)	$C(2)-H(22)$	1.07 (5)
$C(1)-C(2)$	1.490 (8)		
$Br-Cd-O$	86.87 (6)	$O-C(1)-H(11)$	114 (3)
$Br-Cd-O^i$	93.13 (6)	$O-C(1)-H(12)$	112 (3)
$O-Cd-O^i$	60.30 (1)	$C(2)-C(1)-H(11)$	105 (3)
$Cd-O-C(1)$	116.6 (3)	$C(2)-C(1)-H(12)$	112 (3)
$Cd-O-C(2^{ii})$	114.1 (3)	$H(11)-C(1)-H(12)$	105 (4)
$C(1)-O-C(2^{ii})$	112.7 (4)	$O^i-C(2)-H(21)$	110 (4)
$O-C(1)-C(2)$	108.8 (4)	$O^i-C(2)-H(22)$	108 (3)
$C(1)-C(2)-O^i$	107.2 (4)	$C(1)-C(2)-H(21)$	108 (3)
		$C(1)-C(2)-H(22)$	111 (3)
		$H(21)-C(2)-H(22)$	113 (4)
$C(2^{ii})-O-C(1)-C(2)$	177.6 (3)	$C(1)-C(2)-O^i-C(1^i)$	169.2 (3)
$O-C(1)-C(2)-O^i$	64.0 (6)		
(b) 18C6 CdI_2 ; symmetry code: (i) $-x, 1-y, -z$; (ii) $x, 0.5-y, z$			
$Cd(1)-I(1)$	2.693 (1)	$Cd(2)-I(3)$	2.684 (2)
$Cd(2)-I(2)$	2.697 (2)		
$I(1)-Cd(1)-I(1^i)$	180.0	$I(2)-Cd(2)-O(6)$	86.5 (2)
$I(2)-Cd(2)-I(3)$	177.7 (1)	$I(2)-Cd(2)-O(7)$	95.7 (4)
$I(1)-Cd(1)-O(1)$	92.9 (2)	$I(3)-Cd(2)-O(4)$	91.8 (4)
$I(1)-Cd(1)-O(2)$	87.5 (2)	$I(3)-Cd(2)-O(5)$	87.5 (2)
$I(1)-Cd(1)-O(3)$	94.3 (2)	$I(3)-Cd(2)-O(6)$	94.7 (2)
$I(2)-Cd(2)-O(4)$	85.9 (4)	$I(3)-Cd(2)-O(7)$	86.7 (4)
$I(2)-Cd(2)-O(5)$	91.3 (2)		
$O(1)-C(1)-C(2)-O(2)$	68	$O(4)-C(7)-C(8)-O(5)$	-68
$C(1)-C(2)-O(2)-C(3)$	177	$C(7)-C(8)-O(5)-C(9)$	178
$C(2)-O(2)-C(3)-C(4)$	-175	$C(8)-O(5)-C(9)-O(10)$	178
$O(2)-C(3)-C(4)-O(3)$	-67	$O(5)-C(9)-C(10)-O(6)$	67
$C(3)-C(4)-O(3)-C(5)$	-174	$C(9)-C(10)-O(6)-C(11)$	-178
$C(4)-O(3)-C(5)-C(6)$	174	$C(10)-O(6)-C(11)-C(12)$	-172
$O(3)-C(5)-C(6)-O(1^i)$	67	$O(6)-C(11)-C(12)-O(7)$	-65
$C(5)-C(6)-O(1^i)-C(1^i)$	176	$C(11)-C(12)-O(7)-C(12^{ii})$	-174
$C(6^i)-O(1^i)-C(1^i)-C(2)$	176	$C(7^{ii})-O(4)-C(7)-C(8)$	-168

E.s.d.'s for torsion angles are 1–2°.

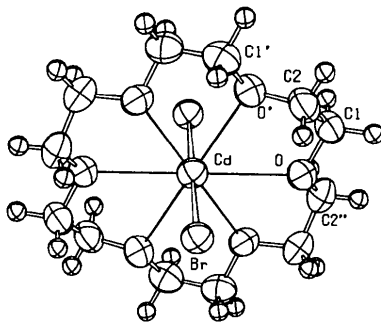


Fig. 2. 18C6 $CdBr_2$ showing the numbering of the atoms, H atoms are named after the C atom to which they are attached. Symmetry code: (i) $x-y, x, -z$; (ii) $y, y-x, -z$.

Table 4. Metal-oxygen and metal-halogen distances (Å) in the 18C6 compounds and metal-halogen distances in MX_2 , $\Delta = [M-X(\text{crown})] - [M-X(\text{gas})]$

	$M-O$	$M-X$	$M-X(\text{gas})$	Δ
$CdCl_2^a$	2.752 (1)	2.3645 (5)	2.235 ^d	0.130
$CdBr_2^b$	2.752 (3)	2.506 (1)	2.394 (2) ^c	0.112
CdI_2^b	2.768 (4)	2.692 (1)	2.58 ^f	0.112
$HgCl_2^a$	2.825 (4)	2.314 (1)	2.252 (5) ^{d,e}	0.062
$HgBr_2$			2.41 (2) ^h	
HgI_2^c	2.86 (2)	2.622 (1)	2.568 (4) ^f	0.054

References: (a) Paige & Richardson (1984); (b) this work; (c) Pears, Stoddart, Crosby, Allwood & Williams (1986); (d) Lister & Sutton (1941); (e) Petrov, Utkin, Girichev & Ivanov (1985); (f) Hassel & Strømme (1938), 2.60 (2) Å; Lister & Sutton (1941), 2.56 (3) Å; (g) Kashiwabara, Konaka & Kimura (1973); (h) Akishin, Spirodonov & Khodchenkov (1959); (i) Gershikov (1984).

greatly according to the strength of the equatorial bonds, e.g. $Cd-I$ is 2.692 (1) Å for the 18-crown-6 ether where there are six weak 'bonds', 2.827 (1) Å in an azo-crown ether where there are two strong bonds to nitrogen and four weak 'bonds' to oxygen (Malmsten, 1979), and 2.969 (1) Å in a pyridine complex where there are four strong equatorial bonds (Ito, Shibata & Saito, 1984). If there was no bonding to oxygen one would expect $Cd-I$ to be as short as in the isolated CdI_2 molecule. In fact the $Cd-X$ distances in the crown ethers are about 0.1 Å longer than those in the free molecules (Table 4) showing that there is weak bonding to the O atoms. Weak bonds occur in other cadmium complexes, e.g. in (tetraphenylporphinato)-cadmium(II) there are $Cd \cdots C$ contacts of 2.845 (5) Å (Hazell, 1986) between pairs of molecules. Evidence for weak $Cd-O$ bonding in the $CdCl_2$ and $CdBr_2$ complexes is also obtained from the ^{113}Cd CP/MAS studies which show exceptionally high shielding values for the elements of the shielding tensor corresponding to out-of-plane shielding.

In the corresponding Hg crown ethers, the $Hg-O$ bonds are even weaker than in the Cd complexes, $Hg-O$ is 0.05 Å longer than $Cd-O$ and $Hg-X$ are 0.05 Å shorter than $Cd-X$. The $Hg-X$ distances are only about 0.05 Å longer than in the free molecules. The structure of 18C6 $HgBr_2$ has not been determined; the $Hg-Br$ distance should be 2.47 Å, i.e. the value for the free molecule plus 0.05 Å. The differences between the Hg and the Cd complexes are in accordance with Hg being a softer acceptor than Cd. Ahrlund (1968) lists two scales of softness, $\sigma_p = 0.115, 0.081, 0.064$ for Zn, Cd, Hg and $\sigma_A = 3.1, 3.5, 4.6$ for Zn, Cd, Hg, so that $Zn-O < Cd-O < Hg-O$ and $Zn-X$ should be more than 0.1 Å longer than $Zn-X$ in the free ZnX_2 molecule. The $Zn-X$ distances in the free molecules are $Zn-Cl = 2.072$ (4), $Zn-Br = 2.204$ (5) and $Zn-I = 2.401$ (5) Å (Hargittai, Tremmel & Hargittai, 1986); the values in 18C6 ZnX_2 are predicted to be 0.24 Å longer than in the free molecule if the differences are

linearly correlated with σ_p and 0.15 Å with σ_A . Similarly, the Zn—O distances are predicted to be 2.60 or 2.72 Å.

In 18C6 CdI₂ the molecules pack quite differently from the CdCl₂, CdBr₂ and HgCl₂ compounds which are all isomorphous and in which all the molecules have the same orientation. The HgI₂ compound has a distorted 18C6 CdCl₂ structure.

There is no evidence from this X-ray diffraction study that there is more than one type of Cd atom in the 18C6 CdBr₂ structure and the peak splitting in the NMR spectrum must be attributed to dipole spin-spin interactions.

I am indebted to Karl E. Holst for synthesizing the complexes and to the Danish Science Research Council and to the Carlsberg Foundation for the diffractometer.

References

- AHRLAND, S. (1968). *Struct. Bonding (Berlin)*, **5**, 118–149.
 AKISHIN, P. A., SPIRODONOV, V. P. & KHODCHENKOV, A. N. (1959). *Zh. Fiz. Khim.* **33**, 20–24.
 BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142–146.
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE*. Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee, USA.
 CRAM, D. J. & CRAM, J. M. (1978). *Acc. Chem. Res.* **11**, 8–14.
 CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
 GERSHIKOV, A. G. (1984). *Zh. Strukt. Khim.* **25**, 30–34.
 HARGITTAI, M., TREMMEL, J. & HARGITTAI, I. (1986). *Inorg. Chem.* **25**, 3163–3166.
 HASSEL, O. & STRØMME, L. C. (1938). *Z. Phys. Chem. Abt. B*, **38**, 466–468.
 HAZELL, A. C. (1986). *Acta Cryst.* **C42**, 296–299.
 HENRICK, K., MATHEWS, R. W., PODEJMA, B. L. & TASKER, P. A. (1982). *J. Chem. Soc. Chem. Commun.* pp. 118–119.
 HUGHES, D. L. & TRUTER, M. R. (1982). *J. Chem. Soc. Chem. Commun.* pp. 727–729.
 ITO, M., SHIBATA, T. & SAITO, Y. (1984). *Acta Cryst.* **C40**, 2041–2043.
 JAKOBSEN, H. J., JACOBSEN, H., BILDSØE, H. & ELLIS, P. D. (1987). Unpublished.
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
 KASHIWABARA, K., KONAKA, S. & KIMURA, M. (1973). *Bull. Chem. Soc. Jpn.* **46**, 410–413.
 LISTER, M. & SUTTON, L. E. (1941). *Trans. Faraday Soc.* **37**, 406–419.
 MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
 MALMSTEN, L.-Å. (1979). *Acta Cryst.* **B35**, 1702–1704.
 NELMES, R. J. (1975). *Acta Cryst.* **A31**, 273–279.
 PAIGE, C. R. & RICHARDSON, M. F. (1984). *Can. J. Chem.* **62**, 332–335.
 PEARS, D. A., STODDART, J. F., CROSBY, J., ALLWOOD, B. L. & WILLIAMS, D. J. (1986). *Acta Cryst.* **C42**, 51–53.
 PETROV, V. M., UTKIN, A. N., GIRICHEV, G. V. & IVANOV, A. A. (1985). *Zh. Strukt. Khim.* **26**, 52–55.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1988). **C44**, 92–94

Structure du Trichloro(diméthylsulfoxyde)platinate(II) de Bis(propanediamine-1,3-N,N')platine(II) (2/1)

PAR BERNARD VIOSSAT

Laboratoire de Chimie Minérale, UFR de Médecine et de Pharmacie, 34, rue du Jardin des Plantes, 86034 Poitiers CEDEX, France

ET PATRICK TOFFOLI, PARVIZ KHODADAD ET NOËL RODIER

Laboratoire de Chimie Minérale, Faculté des Sciences Pharmaceutiques et Biologiques, 5, rue J.-B. Clément, 92296 Châtenay-Malabry CEDEX, France

(Reçu le 4 juin 1987, accepté le 15 septembre 1987)

Abstract. [Pt(C₃H₁₀N₂)₂]²⁺.2[Pt(C₂H₆OS)Cl₃]⁻, *M_r* = 1102.5, monoclinic, *P*2₁/*c*, *a* = 12.815 (4), *b* = 9.491 (2), *c* = 12.078 (4) Å, β = 112.02 (2)°, *V* = 1362 (1) Å³, *Z* = 2, *D_m* = 2.65 (4), *D_x* = 2.688 Mg m⁻³, λ(Mo *K*α) = 0.7107 Å, μ = 16.3 mm⁻¹, *F*(000) = 1008, *T* = 294 (1) K, *R* = 0.045 for 1959 independent reflections. The crystal contains {Pt[NH₂-

(CH₂)₃NH₂]₂}²⁺ and {PtCl₃[(CH₃)₂SO]}⁻ ions. In both groups the Pt atom displays an almost square-planar coordination. The structure is constituted of layers which spread out along (100) planes. Each layer contains a sheet of cations inserted between two sheets of anions. Cations and anions are linked together through hydrogen bonds.