Crystal structure of the 2:1 complex of mercury(II) chloride with trithiapyridino-12-crown-4 having unusual mercury coordination

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(Received September 18, 1991; revised December 9, 1991)

Abstract

The single crystal X-ray analysis of the 1:2 complex between trithiapyridino-12-crown-4 (**1**) and $HgCl_2$ is reported. Crystals of the complex are monoclinic, $P2_1/n$, with $a=13.455(5)$, $b=15.627(2)$, $c=8.933(2)$ Å, $\beta=93.42(2)°$ and $D_c=2.844$ g cm^{-3} for $Z=4$. The host macrocycle has an approximate non-crystallographic mirror symmetry. The structure contains Hg in two very different environments. One Hg is fivefold coordinated in distorted square pyramidal geometry using the four heteroatoms of the macroring and an additional chloro atom as ligating sites. The other Hg remains uncoordinated by the macroring but is surrounded by three chloro atoms to form a trigonal-planar geometry. This complex is an example of unique coordination mode around Hg.

Introduction

Complexes of crown thioethers with transition and non-transition metal ions are of considerable interest [1–3] since their thermodynamical stabilities differ greatly from that of the normal oxygen containing crowns. In general, the binding of transition metal ions is enhanced for the crown thioethers (and azacrowns) while complexation of alkali and alkaline earth metal ions is reduced [4].

The current macrocycle **1**, a NS_3-hetero analogue of 12-crown-4, has been reported to form crystalline complexes with $AgNO_3$, $HgCl_2$, $PdCl_2$, $HAuPtCl_4$, H_2PtCl_6 and $Co(SCN)_2$ [5]. X-ray crystal structures of uncomplexed **1** [6] and of the 1:1 $AgNO_3$ complex of **1** [7] have already been studied. Marked conformational changes of **1** are observed when going from the uncomplexed host to its $AgNO_3$ complex [6, 7].

The present examination was undertaken to learn the potential structural changes occurring for the host molecule **1** on complexation with two $HgCl_2$ guests and to study the coordination chemistry of this complex. It may help to explain the particular solvent extraction property of **1** for Hg^{2+} (and Ag^+) [8]. This is relevant if one considers the importance of Hg as a polluting agent and its toxicologic aspects for living creatures [9].

Experimental

Sample preparation and data collection

The title complex was obtained as described [5]. Recrystallization from methanol yielded suitable crystals for X-ray crystallography. A colourless crystal of the dimensions 0.2×0.26×0.5 mm was used and the preliminary unit cell parameters of the complex were determined by photographic methods. Accurate cell parameters were obtained using an Enraf-Nonius CAD4 diffractometer equipped with monochromated Mo Kα radiation ($\lambda=0.7107$ Å) by least-squares analysis of 2θ values of 25 general reflections $20°<2\theta<40°$.

Crystal data

$C_{11}H_{15}NS_3\cdot 2(HgCl_2)$, $M_w=804.44$, monoclinic, $P2_1/n$, $a=13.455(5)$, $b=15.627(2)$, $c=8.933(2)$ Å, $\beta=93.42(2)°$, $V=1874.8(9)$ Å^3, $Z=4$, $\mu=17.25$ mm^{-1}, $F(000)=1456$, $T=288$ K, $D_c=2.844$ g cm^{-3}. Three dimensional data of 3480 reflections were collected, out of which 2225 reflections were considered observed

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0020-1693/92/$5.00

with $I > 3\sigma(I)$, Mo Kα radiation, max. $-2\theta = 50$, ω–2θ scan, data collected range $h = 0$ to 16, $k = 0$ to 18, $l = -11$ to 11. Lp^{-1} corrections were applied along with absorption corrections [10]. The relative transmission coefficients for psi scan ranged from 0.5825 to 1.5027 with an average value of 0.9983.

Structure determination and refinement

The structure was solved by the 'heavy atom' method using SHELX-86 [11]. It gave most of the non-hydrogen atoms and the remaining non-hydrogen atoms were located from difference Fourier map. The structure was refined with isotropic temperature factors to R of 0.13. Refinement was carried out by full matrix least-squares (SDP/VAX computer system). All the non-hydrogen atoms were refined anisotropically and all the hydrogen atoms were fixed initially by stereochemical considerations. Hydrogen atoms were included in the structure factor calculations in the final stage. The refinement converged at $R = 0.044$, $R_w = 0.051$, $S = 1.664$, $(\Delta/\sigma)_{\max} = 0.03$, $R = [\Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, the quantity minimized was $\Sigma w[|F_o|^2 - (1/K)|F_c|^2]^2$, where the weight $w = 4|F_o|^2/\sigma|F_c|^2$ and $(\sigma|F_o|^2) = [\sigma^2(I) + (0.05I)^2/Lp$, where K is the scale factor and $\sigma(I)$ is the standard deviation in the intensity based on counting statistics. Maximum and minimum peak heights in the final difference Fourier map are 0.60 and −0.56 e Å^{-3}, respectively. All calculations were performed on a VAX-11/730 computer using SDP/VAX [12]. Anomalous dispersion correction terms were taken from ref. 13 and atomic scattering factors were taken from ref. 14.

Results and discussion

The final atomic coordinates of the non-hydrogen atoms are listed in Table 1; atom labelling is in accordance with Fig. 1. Table 2 shows bond distances and angles of the macroring. Table 3 gives a selection of torsion angles including a comparison of torsion angles of **1** between **1**·$(HgCl_2)_2$, **1**·$AgNO_3$ and uncomplexed **1**. Non-bonding contacts and bond distances and angles involving Hg are shown in Table 4. The molecular structure of the complex is shown in Fig. 1 and the packing diagram is illustrated in Fig. 2.

Structure of the macroring 1

Ring conformation

The host molecule shows an approximate non-crystallographic mirror symmetry passing through the N(1), S(7) and C(14) atoms (Fig. 1(a)). The pyridine ring is coplanar to within ±0.008(13) Å and the basal plane formed by the hetero atoms N(1), S(4), S(7) and S(10) is distorted with N(1) and S(7) lying above the plane and S(4) and S(10) lying below the plane.

TABLE 1. Final fractional coordinates and equivalent thermal parameters for the non-hydrogen atoms of **1**·$(HgCl_2)_2$ (e.s.d.s are in parentheses)

Atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{eq} (Å^2)
N(1)	0.4334(7)	0.8938(6)	0.594(1)	1.7(2)
C(2)	0.4939(9)	0.8258(7)	0.605(1)	1.9(3)
C(3)	0.530(1)	0.7944(8)	0.761(2)	2.5(3)
S(4)	0.4491(3)	0.8030(2)	0.9111(4)	2.7(8)
C(5)	0.363(1)	0.7170(9)	0.878(2)	3.6(4)
C(6)	0.296(1)	0.7200(9)	0.741(2)	4.3(4)
S(7)	0.2088(3)	0.8113(2)	0.7380(4)	3.25(8)
C(8)	0.191(1)	0.8315(9)	0.538(2)	3.7(4)
C(9)	0.152(1)	0.921(1)	0.507(2)	3.4(3)
S(10)	0.2363(3)	1.0068(2)	0.5691(4)	2.83(8)
C(11)	0.336(1)	1.0045(8)	0.443(2)	2.6(3)
C(12)	0.406(1)	0.9255(8)	0.455(1)	2.2(3)
C(13)	0.440(1)	0.8901(9)	0.328(1)	2.4(3)
C(14)	0.501(1)	0.8202(9)	0.340(2)	3.2(3)
C(15)	0.527(1)	0.7861(9)	0.479(2)	3.1(3)
Hg(1)	0.33500(4)	0.93292(3)	0.81137(6)	2.64(1)
Hg(2)	0.13750(6)	1.02323(4)	1.07836(8)	4.23(2)
Cl(1)	0.3645(3)	1.0570(2)	0.9638(5)	3.56(8)
Cl(2)	0.0534(3)	1.0292(3)	0.8211(5)	4.8(1)
Cl(3)	0.1705(4)	1.1512(3)	1.2149(6)	6.3(1)
Cl(4)	0.2084(3)	0.8813(2)	1.1166(4)	3.13(8)

Making reference to a previous study [15], the C–S–C–C torsion angles are grouped into two classes, those close to ±60° and those close to 180°, i.e. *gauche* and *anti* conformations about S–C are expected. Torsions angles about C–C are expected [15] to be *gauche*. This comes true for **1** in the present complex (Table 3). Starting from the N(1)–C(2) bond, the macrocycle has the conformation $ag^*gg^-g^-aaggg^-g^{-*}a$ ($g^* = \pm 20° \pm 60°$, correspondent to a distorted *gauche* conformation. Thus, the host molecule exists in an alternative form of 'dentist chair' conformation (Fig. 1(b)) as seen in the minor component of the uncomplexed host structure [6]. By way of contrast, the major component of the uncomplexed host structure [6] shows *anti* conformation about C–C while in the $AgNO_3$ complex of **1** the C–C bonds adopt nearly *gauche* conformations [7] (see Table 3). It is also interesting to note that the host macroring both in uncomplexed **1** and in **1**·$(HgCl_2)_2$ have mirror symmetry whereas in **1**·$AgNO_3$ the host does not show any mirror symmetry (Table 3). On this account, folding of **1** is different for the $AgNO_3$ and $HgCl_2$ complexes. The distored *gauche* conformations about C(2)–C(3) and C(11)–C(12) (indicated by * in Table 3) in the present complex are due to the bending of the pyridine ring away from Hg^{2+} in order to facilitate the lone pair of electrons pointing towards Hg^{2+}, as observed in the **1**·$AgNO_3$ complex [7]. Slight deviation in the torsion angles about

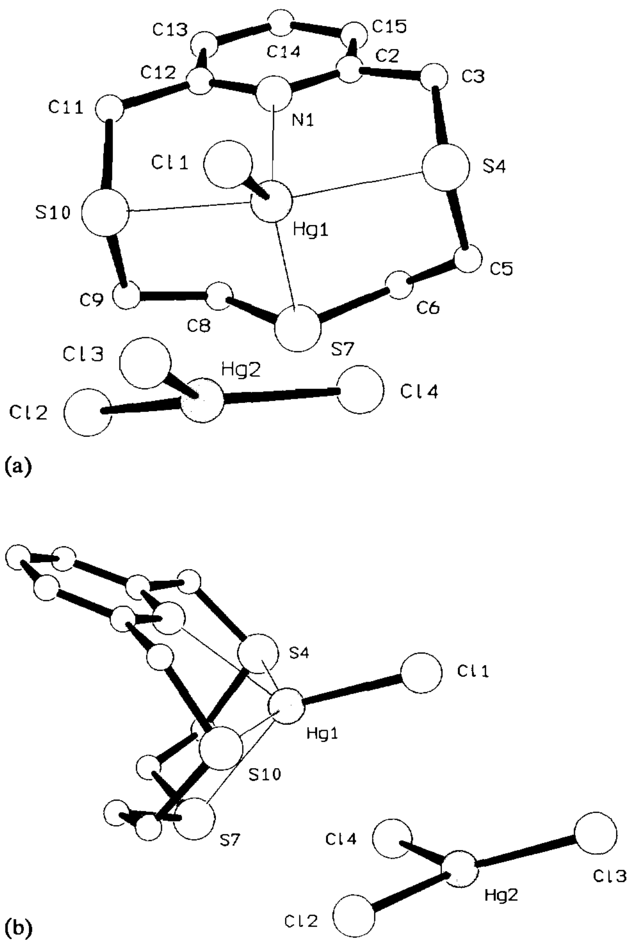

Fig. 1. Structure of the $1\cdot(HgCl_2)_2$ complex (Hg shaded): (a) top view giving indication of the numbering scheme for the atoms; (b) side view showing the conformation of the host molecule.

TABLE 2. Bond distances (Å) and bond angles (°) for $1\cdot(HgCl_2)_2$ (e.s.d.s are in parentheses)

Distances			
N(1)–C(2)	1.34(2)	S(7)–C(8)	1.81(2)
N(1)–C(12)	1.37(2)	C(8)–C(9)	1.52(2)
C(2)–C(3)	1.53(2)	C(9)–S(10)	1.83(2)
C(2)–C(15)	1.38(2)	S(10)–C(11)	1.81(1)
C(3)–S(4)	1.78(1)	C(11)–C(12)	1.55(2)
S(4)–C(5)	1.79(2)	C(12)–C(13)	1.37(2)
C(5)–C(6)	1.47(2)	C(13)–C(14)	1.37(2)
C(6)–S(7)	1.84(2)	C(14)–C(15)	1.38(2)
Angles			
C(2)–N(1)–C(12)	119(1)	C(8)–C(9)–S(10)	115(1)
N(1)–C(2)–C(3)	118(1)	C(9)–S(10)–C(11)	106(1)
N(1)–C(2)–C(15)	122(1)	S(10)–C(11)–C(12)	116(1)
C(3)–C(2)–C(15)	120(1)	N(1)–C(12)–C(11)	119(1)
C(2)–C(3)–S(4)	120(1)	N(1)–C(12)–C(13)	122(1)
C(3)–S(4)–C(5)	104(1)	C(11)–C(12)–C(13)	120(1)
S(4)–C(5)–C(6)	118(1)	C(12)–C(13)–C(14)	119(1)
C(5)–C(6)–S(7)	113(1)	C(13)–C(14)–C(15)	120(1)
C(6)–S(7)–C(8)	101(1)	C(2)–C(15)–C(14)	119(1)
S(7)–C(8)–C(9)	112(1)		

TABLE 3. Selected torsion angles (°) of $1\cdot(HgCl_2)_2$ and of $1\cdot AgNO_3$ as well as of uncomplexed 1 (e.s.d.s are in parentheses)

Atoms	$1\cdot(HgCl_2)_2$	$1\cdot AgNO_3$ [7]	Uncomplexed 1 [6]ᵃ	
C(12)–N(1)–C(2)–C(3)	176	−179	−178	
N(1)–C(2)–C(3)–S(4)	34	−32	109	100*
C(2)–C(3)–S(4)–C(5)	77	76	−51	−70*
C(3)–S(4)–C(5)–C(6)	−65	79	−68	100*
S(4)–C(5)–C(6)–S(7)	−63	66	176	−177*
C(5)–C(6)–S(7)–C(8)	150	168	−91	112*
C(6)–S(7)–C(8)–C(9)	−161	68	92	−103*
S(7)–C(8)–C(9)–S(10)	64	63	−177	−179*
C(8)–C(9)–S(10)–C(11)	71	−157	67	−110*
C(9)–S(10)–C(11)–C(12)	−68	53	49	66*
S(10)–C(11)–C(12)–N(1)	−40	45	−105	−95*
C(11)–C(12)–N(1)–C(2)	−180	−179	178	

ᵃUnstarred values refer to the major component, starred values refer to the minor component of the structure.

TABLE 4. Non-bonding contacts and bond distances (Å) and angles (°) involving Hg for $1\cdot(HgCl_2)_2$ (e.s.d.s are in parentheses)

Distances			
N(1)· · ·S(4)	3.163(10)	S(7)· · ·S(10)	3.437(5)
S(4)· · ·S(7)	3.503(5)	N(1)· · ·S(10)	3.182(10)
Hg(1)–N(1)	2.488(10)	Hg(2)–Cl(2)	2.503(4)
Hg(1)–S(4)	2.667(4)	Hg(2)–Cl(3)	2.371(5)
Hg(1)–S(7)	2.607(4)	Hg(2)–Cl(4)	2.431(4)
Hg(1)–S(10)	2.728(4)	Hg(2)· · ·Cl(1)	3.320(4)
HG(1)–Cl(1)	2.389(4)	Hg(2)· · ·Cl(2ⁱ)	2.889(4)
Hg(1)· · ·Cl(4)	3.397(4)		
Angles			
N(1)–Hg(1)–S(4)	75.6(2)	Cl(2)–Hg(2)–Cl(3)	120(1)
S(4)–Hg(1)–S(7)	83.3(1)	Cl(2)–Hg(2)–Cl(4)	108(1)
S(7)–Hg(1)–S(10)	80.2(1)	Cl(3)–Hg(2)–Cl(4)	130(1)
S(10)–Hg(1)–N(1)	75.0(2)		

ⁱ = −x, −y, −z.

C–S bonds in $1\cdot(HgCl_2)_2$ may arise from the small ring as compared to the large diameter of S atoms [15] while the pyridine moiety does not introduce any irregularities [16]. The non-bonding contacts between hetero atoms are: N(1)· · ·S(4) = 3.163(10), N(1)· · ·S(10) = 3.182(10), S(4)· · ·S(7) = 3.503(5), S(7)· · ·S(10) = 3.437(5) Å (Table 4).

Bond distances and angles (Table 2)

The mean $C(sp^3)$–$C(sp^3)$ bond length of the present complex amounts to 1.495 Å, which is shorter than the normal value of 1.537 Å but is rather frequently seen in crown complexes [17]. The mean C–S bond length (1.81(2) Å) is normal compared with other macrocyclic thioethers [18] and considering 1 in its uncomplexed [6] and $AgNO_3$-complexed [7] states. The mean

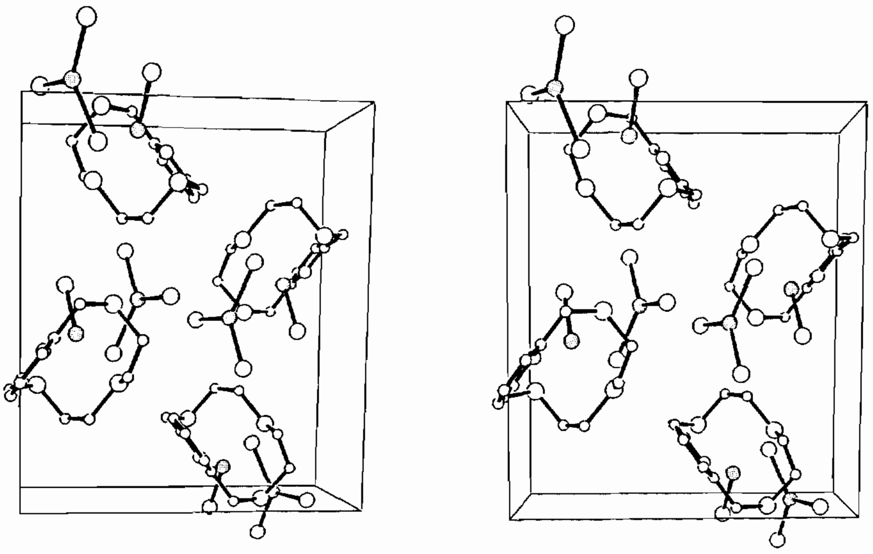

Fig. 2. Crystal packing of the $1\cdot(HgCl_2)_2$ complex (stereoview, Hg shaded).

C(sp^2)-N distance (1.35(2) Å) differs slightly compared with other crown compounds [19]; mean C–C of the pyridine ring is found to be 1.37(2) Å.

The mean value of the bond angles for C–S–C is 104(2)°; C–N–C of the pyridine ring is 119(1)°. The C–C–S angles (mean 116(2)°) differ considerably from the tetrahedral value. A similar deviation is observed in the $1\cdot AgNO_3$ complex [7] which can be attributed to the sulfur–sulfur interactions of the S–C–C–S groups. On the whole, there is a good agreement of bond lengths and angles with that of previously studied species [6, 7, 15–19].

Structure of the complex $1\cdot(HgCl_2)_2$

The most remarkable facts of the present complex is that the structure contains mercury in two very different environments (Fig. 1). Out of the two mercury atoms per asymmetric unit, one, Hg^{2+} cation (1), is fivefold coordinated and the geometry around this cation can be best described as a highly distorted square pyramid with the four hetero atoms of the macrocycle **1** forming the basal plane and one chloro atom (Cl(1)) occupying the apical position. Although this Hg^{2+} is definitely related to the host macroring (or its donor atoms), it does not occupy the ligand cavity, instead it is displaced considerably (−1.284 Å) from the basal plane of the ring hetero atoms (see 'Supplementary material') which is to be explained by the small ring size and the close proximity of large sulfur atoms. Consequently, there is not sufficient space for $Hg^{2+}(1)$ to occupy the host cavity. Nevertheless, the distances between $Hg^{2+}(1)$ and the ring hetero atoms are normal compared with other Hg^{2+} complexes of thia-/aza-macrocycles [20, 21]. Namely, Hg(1)···S range from 2.607(4) to 2.728(4) Å; Hg(1)···N=2.488(10) Å; Hg(1)···Cl(1)=2.389(4) Å (Table 4). Both the Hg(1)···N and the Hg(1)···S bonds show covalent character [22, 23]. Also the Hg(1)–Cl(1) bond suggests covalent character. By way of contrast, the other cation of the asymmetric unit $Hg^{2+}(2)$, does not contact to the host macroring. Instead it is surrounded by three chloro atoms (Cl(2), Cl(3) and Cl(4)) in a trigonal-planar geometry [24] (see Fig. 1(b)) with the Hg(2) being slightly (0.192 Å) out of the plane defined by the three chloro atoms (see 'Supplementary material'); Hg(2)–Cl distances range from 2.371(5) to 2.503(4) Å. The trigonal-planar coordination of Hg(2) is completed by an additional intermolecular contact to Cl(2^i)(i = $-x$, $-y$, $-z$) of 2.889(4) Å which is closer than the sum of the van der Waals radii to give a distorted trigonal-pyramidal coordination. Apart form these covalent bonds, Hg(2) maintains a weak interaction with Cl(1) and similarly Hg(1) with Cl(4). The respective distances are 3.320(4) and 3.397(4) Å, just within the sum of the van der Waals radii (3.3 Å).

Therefore, the structure of this complex can be best described as comprising discrete $[\text{crown-HgCl}]^{\oplus}$ and $[HgCl_3]^{\ominus}$ species packed in a van der Waals mode (Fig. 2). There is no other noticeable packing feature in the crystal lattice such as stacking of the pyridine rings which is frequently seen for pyridino crowns [19, 25].

A previous crystal structure of a $HgCl_2$ complex of dithia-18-crown-6 [20] also contains two Hg in different environments, but not identical with the present case, since one Hg is associated with the two sulfur atoms of the macroring and with two Cl atoms in a distorted tetrahedral geometry while the second Hg is bound to two Cl atoms in a largely linear fashion and shows an additional weaker contact to a Cl atom of the first Hg. Consequently, this latter structure reveals still usual coordination geometries of Hg^{2+} [26] whereas the present complex with fivefold coordination of Hg^{2+} is more unique.

Supplementary material

Least-squares planes through various groups of atoms, thermal parameters, hydrogen positions, bond lengths and angles involving hydrogen atoms, and observed and calculated structure factors are available from the authors on request.

Acknowledgements

E.W. thanks the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

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