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Caffeine Complexes of Mercury(I): Crystal Structure of [$Hg_2(caffeine)_2(NO_3)_2$]

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Abstract

The crystal structure of $Hg_2(caffeine)_2(NO_3)_2$ has been determined by X-ray diffraction methods. It crystallizes in the monoclinic space group *C2/c* with $a = 26.969(4)$, $b = 5.273(1)$, $c = 16.956(4)$ Å, $\beta = 100.89(1)°$, $V = 2368.0(9)$ Å^3, $Z = 4$. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least-squares to $R = 0.028$ for 2404 observed reflections. The crystal contains discrete $[Hg_2(caffeine)_2]^{2+}$ ions in which $-Hg-Hg^{2+}_{-}$ ions are linearly bonded to N9. The structure is stabilized by a number of contacts between mercury and nitrate oxygens.

Introduction

Complexes of mercurous ions are rare; this may in part be due to a low tendency for Hg_2^{2+} to form coordinate bonds. However, some nitrogen ligands of low basicity tend to favour Hg_2^{2+}, and, thus, relatively stable complexes with aniline [1] and 1,10-phenanthroline [2] have been characterized in aqueous solution and studied by X-ray diffraction techniques, respectively.

No crystallographic studies on complexes of Hg(I) with purine bases appear to be described in the literature. However, determinations of crystal structures of Hg(II) purine complexes are numerous, particularly those where the methylmercury cation is involved [3–7].

The present paper reports the crystal structure of the solid compound formed by reaction between $Hg_2(NO_3)_2$ and caffeine in aqueous HNO_3 2.5 N.

Experimental

The complex was prepared using a method described by Colacio *et al.* [8]. A subsequent preparation of the complex using more diluted solutions produced colorless crystalline needles which were chemically analyzed. *Anal.* Calc. for $Hg_2C_{16}H_{20}N_{10}O_{10}$: C, 21.02; H, 2.19; N, 15.32. Found: C, 21.63; H, 2.06; N, 15.14%. IR $\nu(NO_3^-)$ 1380 and 810 cm^{-1}.

X-ray Study

The diffraction data were obtained from a single crystal of dimensions 0.80 × 0.38 × 0.32 mm. Crystal data: $M = 913.6$, monoclinic, $a = 26.969(4)$, $b = 5.273(1)$, $c = 16.956(4)$ Å, $\beta = 100.89(1)°$, $V = 2368.0(9)$ Å^3, $Z = 4$, $D_c = 2.56$ g cm^{-3}, $F(000) = 1704$, Mo Kα radiation, $\lambda = 0.7107$ Å, μ(Mo Kα) = 130.22 cm^{-1}. Space group *C2/c* from systematic absences.

Cell parameters were determined from 21 high-angle reflections using the Philips LAT routine.

Intensities were collected on Philips PW 1100 four-circle diffractometer of the Centro di Studio per la Cristallografia Strutturale of the Universitá di Pavia (Italy), using Mo Kα radiation, with the ω scan mode. All the reflections in the range $2 < \theta < 30°$ were collected. Of the 3473 independent measured reflections, 2404 having $I > 5\sigma(I)$ were considered observed and used in the analysis. The intensity data were corrected for Lorentz and polarization factors, and then for absorption following the semi-emperical method of North *et al.* [9] (maximum and minimum absorption corrections 1.8603 and 0.5932).

The structure was solved by Patterson and Fourier methods. The positions of the Hg_2^{2+} ion was determined from a sharpened Patterson function. The remaining non-hydrogen atoms were located in the ensuing Fourier map. The atomic parameters were refined by least-squares methods. The positions of the hydrogen atoms of the three methyl groups and of C(8) were then calculated on the basis of geometrical considerations (XANADU) [10] and checked on a difference Fourier map. All hydrogen atoms were included as fixed contributions in the final anisotropic refinements.

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The final agreement indices, based on 2404 observed reflections, where $R = 0.028$ and $R_w = 0.031$. Scattering factors were from ref. 11. The Parst program [12] was used for calculating molecular parameters; figures were drawn with Ortep II [13]. The final positional and isotropic thermal parameters appear in Table I.

TABLE I. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters for the Non-hydrogen Atoms with e.s.d.s in Parentheses

Atom	x/a	y/b	z/c	B (Å^2)
Hg	4731.9(2)	4519.1(4)	8032.3(2)	3.221(11)
N1	2990(2)	−1265(11)	8590(3)	3.74(13)
C1	2573(3)	−3031(15)	8577(5)	5.26(23)
C2	3225(2)	−1307(13)	7928(4)	3.57(15)
O2	3107(2)	−2848(10)	7396(3)	5.02(15)
N3	3593(2)	502(11)	7902(3)	3.29(11)
C3	3801(2)	680(16)	7172(4)	4.53(18)
C4	3725(2)	2167(11)	8530(3)	2.87(12)
C5	3487(2)	2133(12)	9172(3)	3.16(14)
C6	3097(2)	408(14)	9257(4)	3.75(15)
O6	2874(2)	256(11)	9811(3)	5.70(16)
N7	3703(2)	4067(9)	9668(3)	3.24(14)
C7	3581(3)	4806(16)	10449(4)	4.79(21)
C8	4057(2)	5120(12)	9327(3)	3.28(17)
N9	4079(2)	4013(9)	8616(3)	2.97(12)
N1A	5147(2)	9287(13)	9033(4)	4.41(16)
O1A	4730(2)	9420(11)	8544(3)	5.86(17)
O1B	5390(3)	11188(15)	9230(4)	8.95(26)
O1C	5270(3)	7123(13)	9274(4)	7.44(22)
H8	4270	6670	9550	
H1A	2610	−4760	8400	
H1B	2260	−2240	8250	
H1C	2480	−3810	9080	
H3A	4140	430	7250	
H3B	3550	100	6760	
H3C	3880	2620	7130	
H7A	3220	4670	10370	
H7B	3720	6630	10540	
H7C	3690	3413	10900	

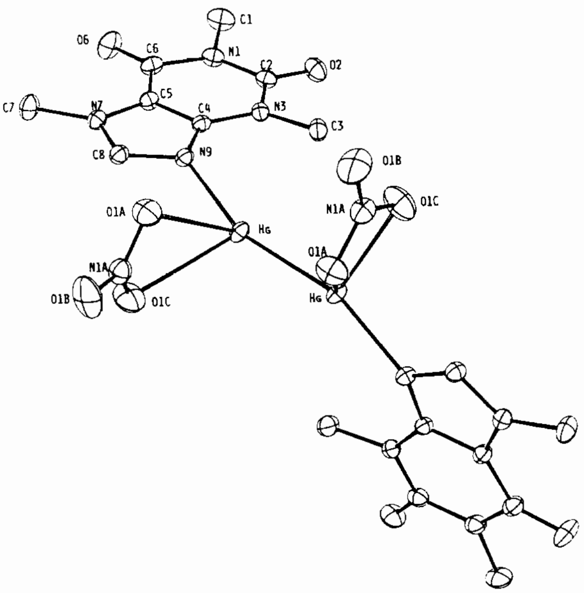

Fig. 1. Perspective view of the $Hg_2(caffeine)_2(NO_3)_2$ unit.

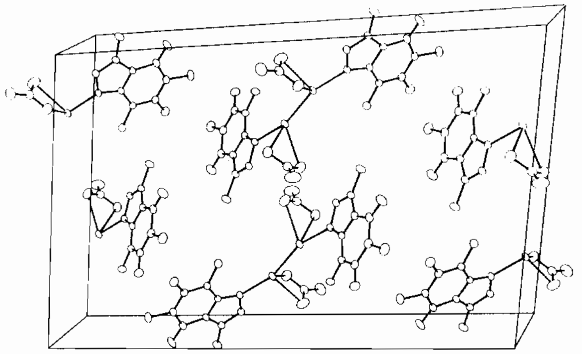

Fig. 2. Stereoview of the contents of a single unit cell of $Hg_2(caffeine)_2(NO_3)_2$.

Description of the Structure and Discussion

Figure 1 shows a view of the structure, which consists of discrete $[Hg_2(caffeine)_2]^{2+}$ ions separated by layers of nitrate ions. A drawing of the contents of a unit cell is shown in Fig. 2. Bond distances and angles are listed in Table II.

The coordination environments of each mercury atom are similar, with two close and four more distant neighbors, namely the other mercury atom at a distance of 2.517(1) Å, one nitrogen atom (at 2.192(5) Å) belonging to the caffeine molecule, and four oxygen atoms (O1C, O1A, O1A′ and O1B′) of two nitrate ions, one at x, y, z (unprimed) and the other at $x, y-1, z$ positions (primed), at somewhat greater distances (2.696(6), 2.726(6), 2.826(5) and 3.000(7) Å). The IR spectrum showed the usual IR active bands of nitrate group at 1380 and 810 cm^{-1}.

As commonly observed in mercurous compounds, this complex contains pairs of Hg atoms in linear groups $-Hg-Hg^{2+}_{-}$. The bond angle –Hg–Hg–N9 (160.5°) is similar to that observed for the bond angles Hg–Hg–O in $Hg_2(H_2O)_2(NO_3)_2$ [14], Hg_2SO_4 [15] and $Hg_2(NO_3)_2$(*o*-phenanthroline) [2].

The geoemtry of the Hg(I) coordination sphere is a distorted octahedral group analogous to mercurous halides [15]. The distances between the mercury atom and the oxygen atoms belonging to the nitrate ion are comparable to those found in ref. 2, but are significantly larger than the distances (2.40 and 2.42 Å) found in ref. 14.

TABLE II. Bond Lengths (Å) and Bond Angles (deg) with e.s.d.s in Parentheses

Atoms	Distance	Atoms	Distance	Atoms	Angle	Atoms	Angle
Coordination sphere				Caffeine angles			
Hg–Hg^{i}	2.517(1)	Hg–O1A	2.726(6)	C2–N1–C6	126.7(5)	C4–C5–N7	105.5(5)
Hg–N9	2.192(5)	Hg–O1A^{ii}	2.826(5)	C2–N1–C1	116.5(6)	C4–C5–C6	124.0(5)
Hg–O1C	2.696(6)	Hg–O1B^{ii}	3.000(7)	C6–N1–C1	116.7(5)	N7–C5–C6	130.5(5)
				O2–C2–N3	121.8(6)	O6–C6–N1	121.4(6)
Caffeine				O2–C2–N1	121.1(6)	O6–C6–C5	127.4(6)
				N3–C2–N1	117.1(5)	N1–C6–C5	111.2(5)
N1–C1	1.457(9)	C4–N9	1.353(7)	C4–N3–C2	119.8(5)	C8–N7–C5	107.5(5)
N1–C2	1.390(9)	C5–N7	1.380(7)	C4–N3–C3	122.2(5)	C8–N7–C7	125.6(5)
N1–C6	1.420(9)	C5–C6	1.418(9)	C2–N3–C3	117.8(5)	C5–N7–C7	126.9(5)
C2–O2	1.211(8)	C6–O6	1.209(9)	C5–C4–N3	121.2(5)	N7–C8–N9	111.4(5)
C2–N3	1.384(8)	N7–C8	1.327(8)	C5–C4–N9	110.6(5)	C8–N9–C4	104.9(5)
N3–C4	1.374(7)	N7–C7	1.476(9)	N3–C4–N9	128.1(5)	C8–N9–Hg	121.7(4)
N3–C3	1.454(8)	C8–N9	1.350(8)			C4–N9–Hg	130.5(4)
C4–C5	1.365(8)						
Nitrate				Nitrate angles			
N1A–O1A	1.267(8)	N1A–O1C	1.236(9)	O1B–N1A–O1C	125.1(7)	O1A–N1A–O1B	120.2(7)
N1A–O1B	1.210(10)			O1A–N1A–O1C	114.7(6)		
				Angles about Hg			
				Hg–Hg–N9	160.5(1)	N9–Hg–O1C	94.0(2)
				Hg–Hg–O1A	105.3(1)	O1A–Hg–O1A^{ii}	143.5(2)
				Hg–Hg–O1A^{ii}	104.8(1)	O1A–Hg–O1B^{ii}	112.1(2)
				Hg–Hg–O1B^{ii}	98.0(1)	O1A–Hg–O1C	45.7(2)
				Hg–Hg–O1C	105.2(2)	O1A^{ii}–Hg–O1B^{ii}	43.1(2)
				N9–Hg–O1A	85.5(2)	O1A^{ii}–Hg–O1C	106.1(2)
				N9–Hg–O1A^{ii}	72.4(2)	O1B^{ii}–Hg–O1C	66.9(2)
				N9–Hg–O1B^{ii}	92.6(2)		

(i) $-x, y, -1/2 - z$; (ii) $x, y - 1, z$.

The Hg–Hg bond length (2.517 Å) in Hg_2(caffeine)$_2$(NO_3)$_2$ is the same as that observed in ref. 2 (2.516 Å) and is in the range of Hg–Hg bond lengths reported for several mercurous compounds [15].

In the isolated complex, the caffeine acts as a monodentate ligand. The binding of Hg(I) to N9 has no appreciable effect on the ligand geometry. A comparison of the dimensions of the caffeine ligand in this complex with those reported for caffeine [16], [H(caffeine)]$^+$ [17], $CuCl_2$(caffeine)(H_2O) [18], [Cu(NO_3)(caffeine)(H_2O)$_3$]$^+$ [19], [RuCl_2(caffeine)(NH_3)$_3$]$^+$ [20], [Rh_2(acetato)$_4$(caffeine)$_2$ [21], [$PtCl_3$(caffeine)]$^-$ [22] (caffeine)$_2$Mg(OH_2)$_6Br_2$, (caffeine)$_2$Mn(OH_2)$_6$I•I_3 [23] and [Pt(caffeine)$_2Cl_2$] [24] reveals no significant differences except in the Ru complex, where the metal ion is bound at atom C8. Comparison of structural data for caffeine hexaaquamagnesium(II)bromide [23] and the present complex reveals a very slight effect on the bonds adjacent to the coordination site N9. The lengthening is only 0.001 Å in N9–C8 and 0.002 Å in N9–C4 bond without the expected opening of the C4–N9–C8 angle. The values observed for this angle in the present complex are in close agreement with those found for the $PtCl_3$-(caffeine)$^-$ and [(Cu(NO_3)(caffeine)(H_2O)$_3$]$^+$ (104.7-(4) and 104.6(2)°, respectively).

The imidazole ring is planar (plane 2, Table III) with a maximum deviation from the least-squares plane of −0.008(6) Å for C8; the Hg(I) ion is displaced from this plane by −0.531 Å. The pyrimidine ring (plane 1) shows a larger deviation from planarity, with N3 and C2 displaced 0.011(5) and −0.013(6) Å, respectively, from the plane. Likewise, there is a characteristic [18–24] non-zero dihedral angle between the imidazole and pyrimidine rings of 0.5°.

On the other hand, nitrate ions have the expected regular planar configurations (plane 3) with three normal N–O bond lengths. The crystal packing of the unit cell is shown in Fig. 2. The complex cations are grouped as dimeric units. The caffeine molecules have the barycentres at $x \simeq 1/6$, 1/3, 2/3 and 5/6. The nitrate ions interpose at $x \simeq 1/2$, 0. An important contribution to crystal stabilization results from mercury–nitrate interactions. There are three Hg–O contacts shorther than 2.9 Å, the sum of the admitted van der Waals radii of mercury (1.5 Å) and oxygen (1.4 Å) [25]; the other Hg–O bond length is 3 Å. These interactions probably have a determining effect on molecular packing.

TABLE III. Parameters Defining Planes[a]

	Plane 1	Plane 2	Plane 3
M_1	−0.608(2)	−0.601(2)	0.634(3)
M_2	0.642(2)	0.644(2)	−0.125(5)
M_3	−0.466(2)	−0.472(2)	−0.763(3)
D	−10.332(28)	−10.374(39)	−5.135(84)

Best weighted least-squares planes

Plane 1		Plane 2		Plane 3	
Atom	Deviation (Å)	Atom	Deviation (Å)	Atom	Deviation (Å)
N1	0.002(5)	N9	0.002(5)	N1A	0.001(6)
C2	−0.013(6)	C8	−0.008(6)	O1A	−0.000(6)
N3	0.011(5)	N7	0.006(5)	O1B	−0.001(7)
C4	−0.007(5)	C4	0.001(5)	O1C	−0.000(7)
C5	−0.002(6)	C5	−0.006(6)		
C6	0.005(7)	Hg	−0.531		
O2	−0.026[b]				
O6	0.003				

Dihedral angles (deg) between planes

Plane 1–Plane 2	0.53(17)	Plane 2–Plane 3	95.80(28)

[a] The equation of the plane is $M_1x + M_2y + M_3z = D$. [b] If no error is given, the atom was not used in the calculation of the plane.

Supplementary Material

A listing of the observed and calculated structure factors and anisotropic thermal parameters are available from the Editor-in-Chief.

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