2,2'-Bipyridine Mercury(II) Complexes [Hg(bpy)(NO₂)X] (X = NO₂⁻, SCN⁻, CH₃COO⁻); π - π Stacking in the Crystal Structure of [Hg(bpy)(NO₂)₂]

Ali Ramazani^{a, b}, Ali Morsali^c, Leila Dolatyari^a, and Bijan Ganjeie^a

^a Department of Chemistry, Islamic Azad University of Zanjan, P.O. Box 49195-467, Zanjan, Iran

^b Department of Chemistry, University of Zanjan, P.O. Box 45195-313, Zanjan, Iran

^c Department of Chemistry, School of Sciences, Tarbiat Modarres University,

P.O. Box 14155-4838, Tehran, Iran

Reprint requests to Dr. A. Morsali. Fax: +98 21 8006544. E-mail: morsali_a@yahoo.com

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The mercury(II) complexes of 2,2'-bipyridine (bpy), [Hg(bpy)(NO₂)₂], [Hg(bpy)(NO₂) (CH₃COO)], and [Hg(bpy)(NO₂)(NCS)] have been synthesized and characterized by elemental analysis, IR, ¹H NMR and ¹³C NMR spectroscopy. The structure of [Hg(bpy)(NO₂)₂] has been confirmed by X-ray crystallography. The complex is a monomer and the Hg atom has an unsymmetrical six-coordinate geometry, formed by two nitrogen atoms of the bpy ligand and four oxygen atoms of the two nitrite anions. There is a short intermolecular π - π stacking interaction between parallel aromatic rings.

Key words: Mercury(II) Complexes, Crystal Structure, Mixed-Anion Complexes, Nitrite Ligand

Introduction

In our attempts to synthesize mixed-anion complexes of different metal ions [1-4], we have recently become interested in mercury(II) complexes [5]. In this paper, we report the synthesis of some mixed-anion complexes containing nitrite anion, Hg(bpy)(NO₂)X (X=NO₂⁻, CH₃COO⁻, and SCN⁻), differing only in part of the coordination sphere.

The nitrite ion can coordinate to metal ions in a variety of ways, *via* both the N and O atoms. In the monodentate coordination this may occur either through oxygen to give a nitrito complex **1**, or through nitrogen to give a nitro complex **2**. Bidentate coordination is known to take place either by chelation **3**, or by forming a brigde, as in **4** and **5**, [6-10].

It is well known that the coordination mode of the nitrite ion is influenced by the steric nature of neighboring ligands and also by the nature of the metal center [11-14]. It is perceptible that there is a general trend for the nitrite to coordinate *via* nitrogen when little inter-ligand steric crowding is expected, but *via* oxygen when the ligands carry bulky substituents [11-15]. On the other hand, despite the wellestablished coordination chemistry of the nitrite ligand with various transition metals [11, 16], the structural



information available about O-nitrito complexes with the mercury(II) ion is relatively scarce. Building new molecular species of the mercury(II) containing the nitrite ligand and modifying their architecture in order to control their physical properties is therefore of interest.

Experimental Section

Physical measurements

IR spectra were recorded as nujol mulls using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. Microanalyses were carried out using a Heraeus CHN-O- Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected.

Preparation of [Hg(bpy)(NO₂)₂]

The complex was prepared by dissolving mercury(II) acetate (0.318 g, 1 mmol) and sodium nitrite (0.138 g, 2 mmol) in distilled water and adding an alcoholic solution of 2,2'bipyridine (0.312 g, 2 mmol). The resulting solution was

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Table	1.	Crystal	data	and	structure	refinement	for
[Hg(bp	oy)(l	$NO_2)_2].$					

Empirical formula	C ₁₀ H ₈ HgN ₄ O ₄
Formula weight	488.79
Temperature	120(2) K
Wavelength	0.71073 [Å]
Crystal system	monoclinic
Space group	C2/c
Unit cell dimensions	a = 11.6983(15) Å
	b = 14.2382(18) Å
	$\beta = 123.895(4)^{\circ}$
	c = 7.7692(9) Å
Volume	1189.5(3) Å ³
Ζ	4
Density (calculated)	2.506 g/cm ³
Absorption coefficient	12.956 mm^{-1}
F(000)	832
Crystal size	$0.48 \times 0.34 \times 0.22 \text{ mm}^3$
θ Range for data collection	2.37 to 28.06°.
Index ranges	-15 < h < 15,
0	$-18 \leq k \leq 18$,
	$-7 \le l \le 10$
Reflections collected	3919
Independent reflections	1402 [R(int) = 0.0495]
Completeness to $\theta = 28.06^{\circ}$	96.7%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7412 and 0.5246
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1402 / 0 / 87
Goodness-of-fit on F^2	1.043
Final R indices	
[for 1244 refl. With $I > 2\sigma(I)$]	R1 = 0.0399, wR2 = 0.0958
R Indices (all data)	R1 = 0.0451, wR2 = 0.0984
Largest diff. peak and hole	2.278 and −1.701 e·Å ⁻³

stirred for 3 h at room temperature, and then it was allowed to stand for 2-3 d at *ca*. 25 °C. Colorless crystals of the product precipitated, which were filtered off, washed with acetone and ether and dried in air (0.342 g, yield 70%), m.p. 220 °C. C₁₀H₈HgN₄O₄: calcd. C 24.55, H 1.63, N 11.45; found C 24.30, H 1.50, N 11.30.

IR (cm⁻¹) selected bands: v = 720(s), 1010(s), 1270(vs), 1590(s), 1618(s), 3040(w). ¹H NMR (DMSO): $\delta = 7.80$ (t, 2H), 8.30 (q, 2H), 8.72 (d, 2H), and 7.70 (d, 2H). ¹³C{¹H} NMR (DMSO): $\delta = 117.50$, 124.25, 127.60, 141.65, 149.90, and 150.60.

Preparation of $Hg(bpy)(NO_2)X(X = CH_3COO^- and SCN^-)$

Complexes Hg(bpy)(NO₂)X (X = CH₃COO⁻ and SCN⁻) were prepared *via* the method analogous to that used for $[Hg(bpy)(NO_2)_2]$.

 $Hg(bpy)(NO_2)(CH_3COO)$: Reactant materials: bpy, mercury(II) acetate, sodium nitrite, (1:1:1); white crystals, m.p. = 200 °C. Yield 60%. $C_{12}H_{11}N_3O_4Hg$: calcd. C 28.80, H 2.19, N 8.37; found C 28.50, H 2.30, N 8.55.

Table 2. Selected bond lengths /Å and angles $/^{\circ}$ for $[Hg(bpy)(NO_2)_2]$.

Hg(1)-N(1)	2.292(5)	Hg(1)-N(1) [#]	2.292(5)				
Hg(1)-O(2N)#	2.323(5)	Hg(1)-O(2N)	2.323(5)				
Hg(1)-O(1N) [#]	2.523(5)	Hg(1)-O(1N)	2.523(5)				
N(1)-Hg(1)-N(1) [#]	72.5(2)	N(1)-Hg(1)-O(2N)#	121.83(19)				
N(1)#-Hg(1)-O(2N)#	127.03(18)	N(1)-Hg(1)-O(2N)	127.03(18)				
$N(1)^{\#}-Hg(1)-O(2N)$	121.83(19)	$N(1)^{\#}-Hg(1)-O(2N)^{\#}$	127.03(18)				
O(2N)#-Hg(1)-O(2N)	91.1(3)	$N(1)-Hg(1)-O(1N)^{\#}$	144.20(18)				
N(1)#-Hg(1)-O(1N)#	86.60(18)	O(2N)#-Hg(1)-O(1N)#	51.03(19)				
O(2N)-Hg(1)-O(1N)*	88.63(19)	N(1)-Hg(1)-O(1N)	86.60(18)				
$N(1)^{\#}-Hg(1)-O(1N)$	144.20(18)	$O(2N)^{\#}-Hg(1)-O(1N)$	88.63(19)				
O(2N)-Hg(1)-O(1N)	51.03(19)	$O(1N)^{\#}-Hg(1)-O(1N)$	124.4(3)				
Symmetry transform	nations used	d to generate equiva	lent atoms:				
$x^{\#} - x + 1, y, -z + 1/2.$							

IR (cm⁻¹) selected bands: v = 725(s), 1014(s), 1265(vs), 1420, 1580, 1601(s), and 3020(w). ¹H NMR (DMSO): $\delta =$ 1.62 (s, 3H), 7.80 (t, 2H), 8.25 (q, 2H), 8.75 (d, 2H), 7.80 (d, 2H). ¹³C{¹H} NMR (DMSO): $\delta = 27.30$ (CH₃), 117.65, 124.30, 127.50, 141.78, 149.90, 150.60 and 178.50 (COO).

 $Hg(bpy)(SCN)(NO_2)$: Reactant materials: bpy, mercury(II) acetate, sodium nitrite, potassium thiocyanate, (1:1:2:2), white crystals, (0.310 g, yield 62%), m.p. 186 °C. $C_{11}H_8N_4O_2HgS$: calcd. C 26.35, H 1.59, N 11.18; found C 26.20, H 1.80, N 11.80.

IR (cm⁻¹) selected bands: v = 720(s), 1010(s), 1275(vs), 1591(s), 2075(vs), and 3025(w). ¹H NMR (DMSO): $\delta =$ 7.80 (t, 2H), 8.25 (q, 2H), 8.80 (d, 2H), and 7.75 (d, 2H). ¹³C{¹H} NMR (DMSO): $\delta =$ 117.50, 124.25, 127.60, 141.60, 149.90, and 150.60.

X-ray crystallography

X-ray measurements were made at 120(2) K using a Siemens R3m/V diffractometer. The intensity data were collected within the range $2.37 \le \theta \le 28.06^{\circ}$ using graphite-monochromated Mo-K_{α} radiation ($\lambda = 0.71073$ Å). Accurate unit cell parameters and an orientation matrix for data collection were obtained from least-squares refinement. Intensities of 3919 unique reflections were measured, 1244 of which were unique. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2 .

The positions of hydrogen atoms were calculated at idealized geometrical position and included in the structurefactor calculation as fixed-atom contributions. Corrections for Lorentz and polarization effects as well as a semiempirical absorption correction were applied. All calculations were carried out with a PDP-11/23+ computer using the SDP-PLUS program package [17–18].

Crystal data and refinement parameters are given in Table 1. Selected bond lengths and angles are given in Table 2. ORTEP diagrams and a perspective view of the packing in the unit cells are shown in Figures 1 and 2.



Fig. 1. ORTEP diagram of the [Hg(bpy)(NO₂)₂] complex.



Fig. 2. π - π Stacking interactions in the unit cell of [Hg(bpy)(NO₂)₂].

Discussion

Synthesis

The reactions between 2, 2'-bipyridine (bpy) and mixtures of mercury(II) acetate with sodium nitrite (1:2), mercury(II) acetate with sodium nitrite (1:1) and mercury(II) acetate with sodium nitrite and potassium thiocyanate (1:2:2) provided crystalline materials analyzing as Hg(bpy)(NO₂)₂, Hg(bpy)(NO₂)(CH₃COO) and Hg(bpy)(SCN)(NO₂), respectively. The IR spectra of all three complexes show absorption bands resulting from the skeletal vibrations of aromatic rings in the 1400–1600 cm⁻¹ range. The IR spectrum of the Hg(bpy)(SCN)(NO₂) shows v(SCN) at *ca*. 2075 cm⁻¹, and v(NO₂) at *ca*. 1275 cm⁻¹. Hg(bpy)(NO₂)₂ ex-

hibits $v(NO_2)$ at *ca.* 1270 cm⁻¹. The IR spectrum of the Hg(bpy)(NO₂)(CH₃COO) shows v(COO) at *ca*. 1420 and 1580 cm⁻¹, and $v(NO_2)$ ca. 1265 cm⁻¹. The characteristic bands of the acetate anion in the Hg(bpy)(NO₂)(CH₃COO) complex appear at about 1640 v_{as} (C-O) and 1430 v_{svm} (C-O) cm⁻¹. The Δ value $(v_{as}-v_{sym})$ indicates that the acetate anions coordinate to the M^{II} center in a bridging mode [19-21]. The IR spectra of the Hg(bpy)(SCN)(NO₂) complex show v(SCN) at *ca.* 2080 cm⁻¹, a significant change relative to data for lead(II) complexes, for example [Pb(phen)₂(NO₃)(NCS)] (2020 cm⁻¹) [22], $[Pb(phen)(O_2CCH_3)(NCS)]$ (2040 cm⁻¹) [23] and $[Pb(phen)_2(O_2CCH_3)](NCS)$ (2040 cm⁻¹) [24]. This suggested that the thiocyanate anion may be coordinated differently in the lead(II) and mercury(II) complexes, and in this complex is coordinated via the sulfur atom to the mercury(II) ion. Shifting of both v_{as} and v_s of the nitrite ligand to lower frequencies compared with the free nitrite ion indicates that this anion is coordinated as a chelating unit (form 3) [14-15].

Crystal structure of $[Hg(bpy)(NO_2)_2]$

The ORTEP diagram is shown in Fig. 1 and selected bond lengths and angles are given in Table 2. The crystal structure of this compound consists of monomeric units of [Hg(bpy)(NO₂)₂. Each mercury atom is chelated by the nitrogen atoms of 2, 2'bipyridine with Hg–N distances of 2.292 Å, and by the oxygen atoms of the nitrite ligands with Hg(1)-O(1N) = Hg(1) - O(1N) #1 = 2.523(5) Å and Hg(1)-O(2N) = Hg(1) - O(2N) #1 = 2.323 Å. It is to be noted that the two Hg-O distances trans to Hg-N bonds are appreciably (~ 0.2 Å) longer than the two Hg-O distances cis to Hg-N bonds in this complex. The angles N(1)-Hg(1)-O(1N)#1 = $144.20(18)^{\circ}$ and N(1)#1- $Hg(1)-O(2N) = 121.83(19)^{\circ}$ are different. The coordination number in this complex is six and the geometry is distorted octahedral.

The structure of this complex is closely related to that of $[Hg(phen)_2(SCN)_2]$, (phen = 1,10phenanthroline) [25] and $[Hg(bpy)_2(SCN)](NO_3)$ [5]. In $[Hg(phen)_2(SCN)_2]$, the structure contains discrete molecules, in which mercury is coordinated to four nitrogen atoms of two 1,10-phenanthroline molecules and to two sulfur atoms of thiocyanate groups. These donor atoms define a distorted octahedral geometry around mercury. The $[Hg(bpy)_2(SCN)](NO_3)$ complex



 $\begin{array}{ll} [Hg(phen)_2(SCN)_2] & [Hg(bpy)_2(SCN)](NO_3) & [Hg(bpy)(NO_2)_2] \\ Fig. 3. Projection of nearest neighbour pairs in the <math>\pi$ - π stacks of heteroaromatic bases in [Hg(bpy)_2(SCN)](NO_3), [Hg(phen)_2(SCN)_2] and [Hg(bpy)(NO_2)_2] complexes. \end{array}

is also monomeric and the Hg atom has an unsymmetrical five-coordinate geometry, with four nitrogen atoms of two bpy ligands and one sulfur atom of the thiocyanate ligand as donor atoms.

There are some evident similarities in the three mercury(II) complexes. The compounds are packed in layers that are held together by normal van der Waals interactions. Within the layers, the packing of the complexes is characterized by π - π stacking interactions [26–27] between "phen" and "bpy" rings of adjacent chains, as shown in Fig. 3. With the mean molecular planes close to parallel and separated by a distance of ~ 3.5 Å, this resembles the planes in graphite. Parallel arrays of the planes of the aromatic moieties indicate that these interactions are of the " π -stacking" type, rather than "edge-to-face" or "vertex-to-face" types [28–30]. Projection of the structure perpendicular to the ring plane shows the overall form of "slipped"

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stacking [28-30], which is at least qualitatively understandable in terms of optimizing approaches between atoms of opposite charges [31]. Such a paralleldisplaced structure also has a contribution from π - σ attraction, the more so with increasing offset. In the crystal reported here, the interplanar distance is 3.43 Å, appreciably shorter than the normal π - π stacking [32-33].

It has been shown that electron-poor aromatic groups interact most strongly with electron-rich aromatic groups [34–35]. The order of stability in the interaction of two π system is π -deficient- π -deficient> π -deficient- π -rich> π - rich- π -rich. Hence, it *ca*. be expected that within the [Hg(phen)₂(SCN)₂] complex, interaction of the electron-poor pyridyl rings with less electron-poor phenyl groups should be favored. Since in the molecules of [Hg(bpy)₂(SCN)](NO₃) and [Hg(bpy)(NO₂)₂] both ligands are equal or almost equal, it *ca*. be expected that face-to-face π -stacking interactions should be disfavored due to the dominance of π - π repulsion.

Complete lists of bond lengths and angles, coordinates and displacement parameters have been deposited at Cambridge Crystallography Data Centre. Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number 242751.

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