

Syntheses and Characterization of New Mixed-Ligand Mercury(II) Complexes, $\text{Hg}(\text{bpy})_n(\text{SCN})\text{X}$ ($\text{X} = \text{CH}_3\text{COO}^-$, NO_3^- and ClO_4^-), Crystal Structure of $[\text{Hg}(\text{bpy})_2(\text{SCN})]\text{NO}_3$

Ali Reza Mahjoub, Ali Morsali, and Ramin Ebrahim Nejad

Department of Chemistry, School of Science, Tarbiat Modarres University,
P. O. Box 14155-4838 Tehran, I.R. Iran

Reprint requests to Dr. A. Morsali or Dr. A. R. Mahjoub. Fax: +98 21 8006544.
E-mail: morsali-a@yahoo.com or almahjoub@yahoo.de

Z. Naturforsch. **59b**, 1109 – 1113 (2004); received April 26, 2004

The 1:2 and 1:1 mixed-ligand mercury(II) complexes with 2,2'-bipyridine (bpy) containing two different anions, $\text{Hg}(\text{bpy})_n(\text{SCN})\text{X}$ ($\text{X} = \text{CH}_3\text{COO}^-$, NO_3^- and ClO_4^-), have been synthesized and characterized by elemental analysis, and IR, ^1H and ^{13}C NMR spectroscopy. The structure of $[\text{Hg}(\text{bpy})_2(\text{SCN})]\text{NO}_3$ was confirmed by X-ray crystallography. The complex is 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. This is in contrast to lead(II) complexes, $[\text{Pb}(\text{phen})_2(\text{NO}_3)(\text{NCS})]$, $[\text{Pb}(\text{phen})(\text{O}_2\text{CCH}_3)(\text{NCS})]$ where the thiocyanate ligands are coordinated to the lead atom *via* the nitrogen atom. There is a $\pi - \pi$ stacking interaction between the parallel aromatic rings.

Key words: Mercury(II) Complexes, Crystal Structure, Mixed-Anions Complexes, Thiocyanate Ligand

Introduction

Building new molecular species and modifying their architectures in order to control their physical properties has been a topic for many research groups. The ability of mercury(II) salts to form a wide variety of 1:1 and 1:2 complexes with neutral ligands is well documented [1–5]. Different ligands have been used to study such mercury(II) complexes. The most common neutral donors are phosphines and amines. Most of these complexes contain halide ions, in contrast the thiocyanate ion was rarely employed [6–8]. This ion is an ambidentate ligand and can be coordinated via both its N and S atom. The coordination mode depends on the nature of the metal center, hence N-donor atoms are found in hard acid complexes such as Zn^{2+} , while in soft acid complexes such as Hg^{2+} the S atom is undoubtedly the expected ligating site [9]. This matter becomes acute in complexes of the mixed-ligands type. The mercury(II) complexes containing mixed anions including thiocyanate are interesting not only because of the structural chemistry of multifunction coordination modes of the this ligand, but also they can show the competition of ligands for coordinating to mer-

cury atom in a single complex system, in which case the main section of the coordination sphere remain the same. We synthesized some of mixed-anion complexes $\text{Hg}(\text{bpy})_n(\text{SCN})\text{X}$ ($\text{X} = \text{CH}_3\text{COO}^-$, NO_3^- and ClO_4^-), differing only in one part of the coordination sphere.

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 $[\text{Hg}(\text{bpy})_2(\text{SCN})](\text{NO}_3)$

The complex was prepared by dissolving mercury(II) nitrate (0.649 g, 2 mmol) and potassium thiocyanate (0.194 g, 2 mmol) in distilled water and adding an alcoholic solution of 2,2'-bipyridine (0.312 g, 2 mmol). The resulting solution was stirred for 5 h at room temperature, and then it was allowed to stand for 2–3 d in a refrigerator (*ca.* 6 °C). White crystals of the product precipitated, which were filtered off, washed with acetone and ether and air dried (0.380 g,

Table 1. Crystal data and structure refinement for [Hg(bpy)₂(SCN)]NO₃.

Empirical formula	C ₂₁ H ₁₆ HgN ₆ O ₃ S
Formula weight	633.05
Temperature	140(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	<i>C c</i>
Unit cell dimensions	<i>a</i> = 19.669(5) Å <i>b</i> = 7.566(2) Å; <i>c</i> = 17.121(4) Å <i>β</i> = 123.895(4)°
Volume	2115.0(10) Å ³
<i>Z</i>	4
Density (calculated)	1.988 Mg/m ³
Absorption coefficient	7.413 mm ⁻¹
<i>F</i> (000)	1216
Crystal size	0.27 × 0.25 × 0.22 mm ³
Theta range for data collection	2.49 to 28.06°
Index ranges	−25 ≤ <i>h</i> ≤ 26, −10 ≤ <i>k</i> ≤ 10, −22 ≤ <i>l</i> ≤ 22
Reflections collected	10498
Independent reflections	5012 [<i>R</i> (int) = 0.0905]
Completeness to <i>θ</i> = 28.06°	99.8%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.012760 and 0.036626
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	5012/2/246
Goodness-of-fit on <i>F</i> ²	1.040
Final <i>R</i> indices [for 4677 refl. With <i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0506, <i>wR</i> 2 = 0.1192
<i>R</i> Indices (all data)	<i>R</i> 1 = 0.0537, <i>wR</i> 2 = 0.1228
Absolute structure parameter	0.427(15)
Largest diff. peak and hole	2.381 and −1.244 eÅ ⁻³

yield 60%), m.p. 185 °C. C₂₁H₁₆HgN₆O₃S: calcd. C 39.8, H 2.52, N 13.27; found C 39.65, H 2.56, N 13.50.

IR (cm⁻¹) selected bands: *ν* = 740(s), 1010(s), 1380(vs), 1590(s), 1618(s), 2080(vs), 3040(w).

¹H NMR (DMSO): *δ* = 7.80 (t, 2H), 8.20 (q, 2H), 8.70 (d, 2H), and 7.78 (d, 2H). ¹³C{¹H} NMR (DMSO): *δ* = 117.50, 124.20, 127.62, 1141.65, 149.96, and 150.62.

Preparation of Hg(bpy)(SCN)X (X = CH₃COO⁻ and ClO₄⁻)

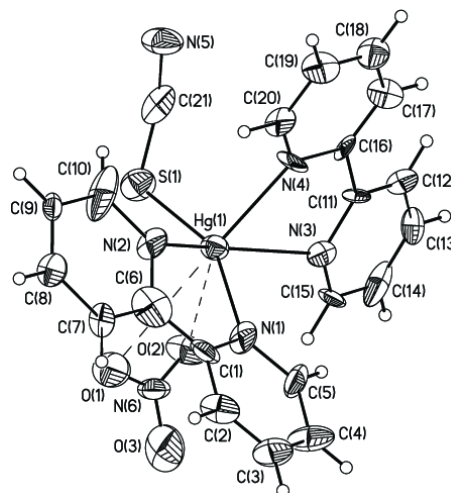
Complexes Hg(bpy)(SCN)X (X = CH₃COO⁻ and ClO₄⁻) were prepared *via* the method analogous to that used for [Hg(bpy)₂(SCN)](NO₃).

Hg(bpy)(SCN)(CH₃COO): Reactant materials: bpy, mercury(II) acetate, potassium thiocyanate, (2:2:2); white crystals, m.p. = 220 °C. Yield 50%. C₁₃H₁₁N₃O₂HgS: calcd. C 35.48, H 2.32, N 8.87; found C 35.40, H 2.43, N 8.90. IR (cm⁻¹) selected bands: *ν* = 720(s), 862(s), 1220(s), 1435(s), 1601(s), 2075(vs), and 3020(w). ¹H NMR (DMSO): *δ* = 1.60 (s, 3H), 7.80 (t, 2H), 8.20 (q, 2H), 8.70 (d, 2H), 7.78 (d, 2H). ¹³C{¹H} NMR (DMSO): *δ* = 27.20 (CH₃),

Table 2. Selected bond lengths /Å and angles /° for [Hg(bpy)₂(SCN)]NO₃.

Hg(1)–N(1)	2.294(11)	Hg(1)–N(4)	2.353(9)
Hg(1)–S(1)	2.452(3)	Hg(1)–N(2)	2.494(10)
Hg(1)–N(3)	2.523(8)	Hg(1)–O(2)	2.729(10)
Hg(1)–O(1)	3.143(9)		
N(1)–Hg(1)–N(4)	103.5(2)	N(1)–Hg(1)–S(1)	153.7(3)
N(4)–Hg(1)–S(1)	101.6(3)	N(1)–Hg(1)–N(2)	68.1(4)
N(4)–Hg(1)–N(2)	93.8(4)	S(1)–Hg(1)–N(2)	102.4(3)
N(1)–Hg(1)–N(3)	95.1(3)	N(4)–Hg(1)–N(3)	69.1(3)
S(1)–Hg(1)–N(3)	101.2(2)	N(2)–Hg(1)–N(3)	153.2(2)
N(1)–Hg(1)–O(2)	82.5(4)	N(4)–Hg(1)–O(2)	145.5(3)
S(1)–Hg(1)–O(2)	81.4(3)	N(2)–Hg(1)–O(2)	119.4(4)
N(3)–Hg(1)–O(2)	76.6(3)		

Symmetry transformations used to generate equivalent atoms.

Fig. 1. ORTEP diagram of the [Hg(bpy)₂(SCN)]NO₃ complex.

178.58 (COO), 117.60, 124.20, 127.60, 1141.70, 149.96, and 150.62.

Hg(bpy)(SCN)(ClO₄): Reactant materials: bpy, mercury(II) acetate, sodium perchlorate, potassium thiocyanate, (2:2:2); white crystals, (0.476 g yield 65%), m.p. 168 °C. C₁₁H₈N₃O₄HgSCl: calcd. C 25.68, H 1.55, N 8.17; found C 25.22, H 1.72, N 8.43. IR (cm⁻¹) selected bands: *ν* = 720(s), 866(s), 1118(vs), 1445(w), 1591(s), 2075(vs), and 3025(w). ¹H NMR (DMSO): *δ* = 7.82 (t, 2H), 8.20 (q, 2H), 8.70 (d, 2H), and 7.78 (d, 2H). ¹³C{¹H} NMR (DMSO): *δ* = 117.50, 124.20, 127.60, 1141.63, 149.94, and 150.65.

Crystallography

Crystallographic measurements were made at 140(2) K using a Siemens R3m/V diffractometer. The intensity data were collected within the range 2.49 ≤ *θ* ≤ 28.06° using graphite-monochromated Mo-K_α radiation (*λ* =

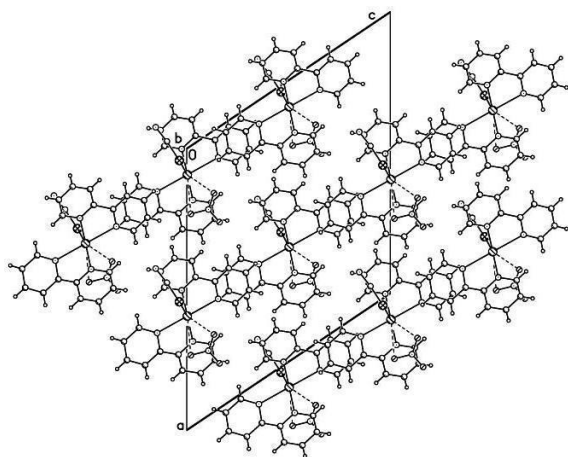


Fig. 2. $\pi - \pi$ Stacking interactions in the unit cell of $[\text{Hg}(\text{bpy})_2(\text{SCN})]\text{NO}_3$.

0.71073 Å). Accurate unit cell parameters and an orientation matrix for data collection were obtained from least-squares refinement. Intensities of 10498 unique reflections were measured, 5012 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 structure-factor calculation as fixed-atom contributions. Corrections for Lorentz and polarization effects as well as the semi-empirical absorption correction were applied. All calculations were carried out with a PDP-11/23+ computer using the SDP-PLUS program package [10–11].

Crystal data and refinement parameters are summarized 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.

Complete list of bond lengths and angles, co-ordinates 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 218814.

Discussion

Synthesis

Reaction between 2,2'-bipyridine (bpy) and mixtures of mercury(II) acetate with potassium thiocyanate, or mercury(II) thiocyanate with sodium perchlorate, and also of mercury(II) nitrate with potassium thiocyanate provided crystalline materials analyzing as $\text{Hg}(\text{bpy})(\text{SCN})(\text{CH}_3\text{COO})$, $\text{Hg}(\text{bpy})(\text{SCN})(\text{ClO}_4)$ and $[\text{Hg}(\text{bpy})_2(\text{SCN})](\text{NO}_3)$, respectively. The IR spec-

trum of the $\text{Hg}(\text{bpy})(\text{SCN})(\text{CH}_3\text{COO})$ shows $\nu(\text{SCN})$ at *ca.* 2075 cm^{-1} , and $\nu(\text{COO})$ at *ca.* 1435 and 1601 cm^{-1} . $[\text{Hg}(\text{bpy})_2(\text{SCN})](\text{NO}_3)$ exhibits $\nu(\text{NO}_3)$ at *ca.* 1380 cm^{-1} and $\nu(\text{SCN})$ at *ca.* 2080 cm^{-1} . The IR spectrum of the $\text{Hg}(\text{bpy})(\text{SCN})(\text{ClO}_4)$ shows $\nu(\text{ClO}_4)$ at *ca.* 1118 cm^{-1} , and $\nu(\text{SCN})$ at *ca.* 2075 cm^{-1} . The IR spectra of these complexes show $\nu(\text{SCN})$ at *ca.* 2075–2080 cm^{-1} , a significant change compound to data for lead(II) complexes, for example $[\text{Pb}(\text{phen})_2(\text{NO}_3)(\text{NCS})]$ (2020 cm^{-1}) [12], $[\text{Pb}(\text{phen})(\text{O}_2\text{CCH}_3)(\text{NCS})]$ (2040 cm^{-1}) [13] and $[\text{Pb}(\text{phen})_2(\text{O}_2\text{CCH}_3)](\text{NCS})$ (2040 cm^{-1}) [14] complexes. This suggested that the thiocyanate anion may be coordinated differently in the lead(II) and mercury(II) complexes.

Crystal structure of $[\text{Hg}(\text{bpy})_2(\text{SCN})](\text{NO}_3)$

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 $[\text{Hg}(\text{bpy})_2(\text{SCN})](\text{NO}_3)$. Each mercury atom is chelated by the nitrogen atoms of 2,2'-bipyridine with Hg–N distances of 2.294, 2.353, 2.494 and 2.523 Å, and bonded to the sulfur atom of the thiocyanate ligand with a Hg–S distance of 2.452 Å. The coordination number in this complex is five. There is a weak interaction of the mercury(II) atom with oxygen atoms of nitrate anion with a Hg–O distances of 2.729 and 3.143 Å (Table 2). In fact each Hg atom in this structure along with five normal bonds forms two “weak” Hg...O bonds.

The structure of this complex is closely related to that of complex $[\text{Hg}(\text{phen})_2(\text{SCN})_2]$, (phen=1,10-phenanthroline) [15]. In $[\text{Hg}(\text{phen})_2(\text{SCN})_2]$, the crystal structure contains discrete molecules, in which mercury is coordinated to four nitrogen atoms from two 1,10-phenanthroline molecules and to two sulfur atoms from thiocyanate groups. These donor atoms define a distorted octahedral geometry around mercury.

There are some evident similarities in the two mercury(II) complexes. In both complexes, the thiocyanate anions are coordinated *via* the sulfur atoms and both 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 $\pi - \pi$ stacking interactions [16, 17] between “phen” and “bpy” rings of adjacent chains, as shown in Fig. 2. As planar species in which the mean molecular planes are close to parallel and separated by a distance of

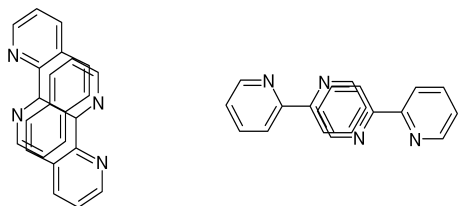
[Hg(phen)₂(SCN)₂][Hgb(bpy)₂(SCN)](NO₃)

Fig. 3. Projection of nearest neighbour pairs in the $\pi - \pi$ stacks of heteroaromatic bases in [Hg(phen)₂(SCN)₂] and [Hgb(bpy)₂(SCN)](NO₃) complexes.

~ 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 [18–21]. Projection of the structure perpendicular to the ring plane shows the overall form of “slipped” stacking [18–22], which is at least qualitatively understandable in terms of optimizing approaches between atoms of opposite charges [23].

It has been shown that electron-poor aromatic groups interact most strongly with electron-rich aromatic groups [24, 25]. Hence, it can 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 favoured. Since in the molecules of [Hgb(bpy)₂(SCN)](NO₃) both ligands are equal or almost equal, it can be expected that model face-to-face π -stacking interactions should be disfavoured due to the dominance of $\pi - \pi$ repulsion.

In lead(II) complexes the thiocyanate ion is coordinated *via* its N atom [25–27], as for example in the recently reported crystal structures of Pb(phen)₂(NO₃)(NCS) and [Pb(phen)(O₂CCH₃)(NCS)]. By contrast, in the mercury complexes Hg(phen)₂(SCN)₂ [15], [Hg(DPBTZ)(SCN)₂] (DPBTZ = 2,2'-diphenyl-4,4'-bithiazole) [26], [Hg(DABTZ)(SCN)₂] (DABTZ = 2,2'-diamino-4,4'-bithiazole) [27], [Hg(L)(SCN)₂] (L = N-(2-pyridyl)carbonylaniline) [28] and [Hg(bq)(SCN)₂] (2,2'-biquinoline) [29], the thiocyanate ions are coordinated *via* their S atom. This shows that Hg⁺² ion is “softer” than Pb⁺² ion.

Another notable difference between the Pb(phen)₂(NO₃)(NCS) and Hg(bpy)₂(SCN)(NO₃) complexes is that the nitrate anion is strongly coordinated to lead in the former, but weakly coordinated to mercury atom in the complex reported here.

Acknowledgements

To the Tarbiat Modarres University Research Council that supported this work.

- [1] P. A. W. Dean, In S. J. Lippard, (Ed), Progress in Inorganic Chemistry, Vol. **24**, p. 109, Wiley, New York (1978).
- [2] C. E. Holloway and M. Melnik, Main Group Met. Chem. **17**, 799 (1994).
- [3] F. Y. Kulba, Zhur. Neorg. Khim. **4**, 1393 (1959).
- [4] D. K. Demertzi, J. R. Miller, N. Kourkoulis, S. K. Hadjikakou, and M. A. Demertzis, Polyhedron, **18**, 1005 (1999).
- [5] D. K. Demertzi, A. Domopoulou, M. A. Demertzis, J. Valle, and A. Papageorgiou, J. Inorg. Biochem. **68**, 147 (1997).
- [6] S. Trofimenko, Chem. Rev. **93**, 943 (1993).
- [7] W. R. McWhinnie and J. D. Miller, Adv. Inorg. Chem. Radiochem. **12**, 135 (1969).
- [8] S. Trofimenko, J. Am. Chem. Soc. **88**, 1842 (1966).
- [9] G. Pavlovic, Z. Popovic, Z. Soldin, and D. M. Calogovic, Acta Crystallogr. C **56**, 61 (2000).
- [10] G. Ferguson, C. Glidewell and E. S. Lavender, Acta Crystallogr. **B55**, 591. (1999)
- [11] G. M. Sheldrick, SHLXTL-97 V5.10, 1997, Bruker AXS Inc., Madison, WI- 53719, USA.
- [12] A. R. Mahjoub and A. Morsali, Z. Kristallogr. NCS **216**, 601 (2001).
- [13] A. R. Mahjoub and A. Morsali, Polyhedron **21**, 1223 (2002).
- [14] A. Morsali, A. R. Mahjoub, S. Janitabar Darzi, and M. J. Soltanian, Z. Anorg. Allg. Chem. **629**, 2599 (2003).
- [15] A. L. Beauchamp, B. Saperas, and R. Rivest, Can. J. Chem. **52**, 2923 (1974).
- [16] N. N. Greenwood and A. Earnshaw, Chemistry of the Elements, pp. 235–236, Pergamon Press, Oxford (1986).
- [17] Molecular Complexes, ed. R. Foster and Paul Elek (Scientific Books) Ltd., London (1973).
- [18] V. Russell, M. L. Scudder, and I. G. Dance, J. Chem. Soc. Dalton Trans. 789 (2001) and references therein.
- [19] I. G. Dance and M. L. Scudder, J. Chem. Soc. Dalton Trans. 3755 (1996).
- [20] C. Janiak, J. Chem. Soc. Dalton Trans. 3885 (2000).
- [21] Z.-H. Liu, C.-Y. Duan, J.-H. Li, Y.-J. Liu, Y.-H. Mei, and X.-Z. You, New J. Chem. **24**, 1057 (2000).
- [22] T. M. Barclay, A. W. Cordes, J. R. Mingie, R. T. Oakley, and K. E. Preuss, Cryst. Eng. Comm. **80** (2000) (No15).
- [23] C. A. Hunter and J. K. M. Sanders, J. Am. Chem. Soc. **112**, 5525 (1990).

- [24] J. M. Steed, T. A. Dixon and W. Klemperer, *J. Chem. Phys.* **70**, 4940 (1979).
- [25] J. C. Collings, K. P. Roscoe, E. G. Robins, A. S. Bat-sanov, L. M. Stimson, J. A. K. Howard, S. J. Clark, and T. B. Marder, *New J. Chem.* **26**, 1740 (2002).
- [26] A. Morsali and A. R. Mahjoub, *J. Coord. Chem.* **56**, 779 (2003).
- [27] A. Morsali, M. Payheghader, M. R. Poorheravi, and F. Jamali, *Z. Anorg. Allg. Chem.* **629**, 1627 (2003).
- [28] A. Morsali, A. Ramazani, A. R. Mahjoub, and A. A. Soudi, *Z. Anorg. Allg. Chem.* **629**, 2058 (2003).
- [29] A. Morsali, A. R. Mahjoub, and A. Ramazani, *J. Coord. Chem.* **57**, 347 (2004).