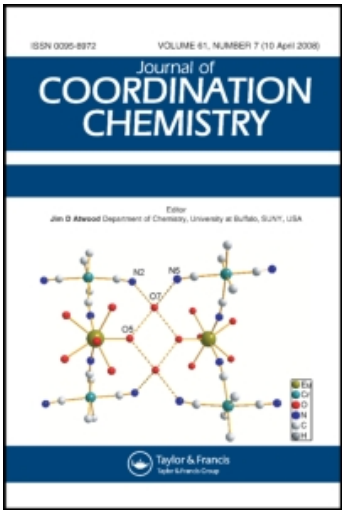

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New mixed-anion mercury(II) complex, spectroscopic, thermal and structural studies of $[Hg(bipy)_2(CH_3COO)]_2(SO_4)\cdot 0.5NaCl$

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New mixed-anion mercury(II) complex, spectroscopic, thermal and structural studies of $[Hg(bipy)_2(CH_3COO)]_2(SO_4)\cdot 0.5NaCl$

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A mixed-anion mercury(II) complex of 2,2′-bipyridine (bipy), $[Hg(bipy)_2(CH_3COO)]_2(SO_4)\cdot 0.5NaCl$ has been synthesized and characterized by elemental analysis, IR-, ^1H NMR- and ^{13}C NMR spectroscopy and the structure of this compound determined by single-crystal X-ray diffraction. The thermal stability of this compound was studied by thermal gravimetric (TG) and differential thermal analyses (DTA). The complex is a monomer and there are two different Hg atoms with unsymmetrical six-coordinate geometry, formed by four nitrogen atoms of the bipy ligands and two oxygen atoms of the acetate anion. There are short intermolecular C–H···O interactions in the packing of this compound.

Keywords: Mercury(II); Crystal structure; Mixed-anion complex; 2,2′-bipyridine; Thermal stability

1. Introduction

The coordination chemistry of mercury(II) with N-donor ligands is a topic of current research, largely because of its importance in solid-state materials [1–5]. Hg(II) complexes with bidentate and tridentate ligands have been obtained in which Hg(II) adopts higher coordination number such as complex with a series of 2,2′-bipyridine [6], 1,10-phenanthroline [7], N-substituted pyrazole [8] and tripod ligands containing pyridine and N-methylimidazole [9–10].

In this article, we report the synthesis, characterization, thermal and structural study of a mixed-anion complex formed between the 2,2′-bipyridine and mercury(II) acetate and sodium sulphate, $[Hg(bipy)_2(CH_3COO)]_2(SO_4)\cdot 0.5NaCl$.

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2. Experimental section

2.1. *Material and physical measurements*

Mercury(II) acetate, 2,2′-bipyridine and sodium sulphate were used as received from Aldrich. IR spectra were obtained from KBr pellets in the range 450–4000 cm^{-1} with 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 and are uncorrected. ^{1}H and ^{13}C NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500 and 125 MHz, respectively. The thermal measurements were performed using a simultaneous TGA-DTA analyzer. Determination of sodium content used the ICP method. Crystallographic measurements were made at 298(2) K using a Bruker APEX area-detector diffractometer. The intensity data were collected within the range of $1.41 \leq \theta \leq 25.02^{\circ}$ using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Accurate unit cell parameters and orientation matrix for data collection was obtained from least-squares refinement. Intensities of 8022 unique reflections were measured, from which 5395 with $I > 2\sigma(I)$ were used in the refinement. The structure has been solved by direct method and refined by full-matrix least-squares techniques on F^2. The molecular structure plots were prepared by using ORTEPIII [11]. Crystal data and structure refinement are given in table 1. Selected bond lengths and angles are given in table 2. Anisotropic thermal

Table 1. Crystal data and structure refinement for $[Hg(bipy)_2(CH_3COO)]_2(SO_4) \cdot 0.5NaCl$.

Empirical formula	$C_{88}H_{76}ClHg_4N_{16}NaO_{16}S_2$
Formula weight	2538.57
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions (Å, °)	
a	10.2903(10)
b	24.762(2)
c	18.0286(17)
β	97.791(2)
Volume ($Å^3$)	4551.5(7)
Z	2
Density (calculated) ($g\,cm^{-3}$)	1.852
Absorption coefficient (mm^{-1})	6.879
$F(000)$	2448
Crystal size (mm^3)	$0.37 \times 0.23 \times 0.13$
θ range for data collection (°)	1.41–25.02
Index ranges	$-12 \leq h \leq 7$, $-29 \leq k \leq 28$, $-21 \leq l \leq 21$
Reflections collected	23747
Independent reflections	8022 [R(int) = 0.0312]
Completeness to $\theta = 25.02^{\circ}$	99.9%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.4183 and 0.1651
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8022/0/582
Goodness-of-fit on F^2	1.040
Final R indices [for 5395 refl. With $I > 2\sigma(I)$]	$R_1 = 0.0497$, $wR_2 = 0.1601$
R Indices (all data)	$R_1 = 0.0744$, $wR_2 = 0.1894$
Largest diff. peak and hole ($e\,Å^{-3}$)	2.414 and −0.993

Table 2. Bond lengths (Å) and angles (°) for $[Hg(bipy)_2(CH_3COO)]_2(SO_4)\cdot 0.5NaCl$.

Hg(1)–O(2)	2.337(8)	Hg(2)–O(4)	2.351(7)
Hg(1)–N(1)	2.378(8)	Hg(2)–N(7)	2.368(8)
Hg(1)–N(3)	2.386(8)	Hg(2)–N(5)	2.371(7)
Hg(1)–N(4)	2.403(7)	Hg(2)–N(6)	2.383(7)
Hg(1)–N(2)	2.390(7)	Hg(2)–N(8)	2.401(7)
Hg(1)–O(1)	2.438(8)	Hg(2)–O(3)	2.470(7)
O(2)–Hg(1)–N(1)	100.7(3)	O(4)–Hg(2)–N(7)	96.0(3)
O(2)–Hg(1)–N(3)	125.6(3)	O(4)–Hg(2)–N(5)	128.8(3)
N(1)–Hg(1)–N(3)	130.8(3)	N(7)–Hg(2)–N(5)	133.8(3)
O(2)–Hg(1)–N(2)	124.8(3)	O(4)–Hg(2)–N(6)	101.7(3)
N(1)–Hg(1)–N(2)	68.1(3)	N(7)–Hg(2)–N(6)	93.4(3)
N(3)–Hg(1)–N(2)	94.1(3)	N(5)–Hg(2)–N(6)	69.2(3)
O(2)–Hg(1)–N(4)	93.5(3)	O(4)–Hg(2)–N(8)	119.8(3)
N(1)–Hg(1)–N(4)	95.2(3)	N(7)–Hg(2)–N(8)	68.9(3)
N(3)–Hg(1)–N(4)	68.8(3)	N(5)–Hg(2)–N(8)	93.6(2)
N(2)–Hg(1)–N(4)	139.7(3)	N(6)–Hg(2)–N(8)	135.6(3)
O(2)–Hg(1)–O(1)	52.7(3)	O(4)–Hg(2)–O(3)	53.8(3)
N(1)–Hg(1)–O(1)	126.4(3)	N(7)–Hg(2)–O(3)	129.9(3)
N(3)–Hg(1)–O(1)	97.4(3)	N(5)–Hg(2)–O(3)	91.2(2)
N(2)–Hg(1)–O(1)	89.6(3)	N(6)–Hg(2)–O(3)	128.1(3)
N(4)–Hg(1)–O(1)	127.5(3)	N(8)–Hg(2)–O(3)	91.3(3)
O(2)–Hg(1)–C(21)	26.4(3)	O(4)–Hg(2)–C(44)	26.5(3)
N(1)–Hg(1)–C(21)	116.1(4)	N(7)–Hg(2)–C(44)	114.2(3)
N(3)–Hg(1)–C(21)	113.0(4)	N(5)–Hg(2)–C(44)	111.8(3)
N(2)–Hg(1)–C(21)	108.6(3)	N(6)–Hg(2)–C(44)	117.4(3)
N(4)–Hg(1)–C(21)	111.7(3)	N(8)–Hg(2)–C(44)	106.9(3)
O(1)–Hg(1)–C(21)	26.3(3)	O(3)–Hg(2)–C(44)	27.3(3)

parameters, observed and calculated structure factors, full lists of bond distances, bond angles and torsion angles are given in the supplementary material. ORTEP diagram and perspective view of the packing are shown in figures 2 and 3.

2.2. *Preparation of $[Hg(bipy)_2(CH_3COO)]_2(SO_4)\cdot 0.5NaCl$*

A methanolic solution (25 mL) of 2,2′-bipyridine (1 mmol, 0.156 g) was added dropwise over 2 h to a stirred methanolic solution (35 mL) of $Hg(CH_3COO)_2$ (1 mmol) and Na_2SO_4 (2 mmol) and the mixture was refluxed with stirring at 75°C for 4 h. The solution became clear, was cooled, filtered and left for evaporation which yielded crystals after two weeks. (0.2 g, yield 54%), m.p. 243°C. Found C, 41.25; H, 2.50; N, 8.70; Na, 1.10: calculated for $C_{88}H_{76}ClHg_4N_{16}NaO_{16}S_2$; C, 41.60; H, 2.30; N, 8.82; Na, 0.91%. IR (cm^{-1}) selected bound: 617(m), 754(s), 1004(w), 1085(s), 1397(m), 1426(s), 1550(s), 2980(w), 3095(w). ^{1}H-NMR (DMSO, δ): 2.10(s), 7.70(m, 3H), 8.20(m, 4H), 8.64(m, 4H), 8.80(m, 4H), 8.90(m, 4H). ^{13}C-{^{1}H}NMR (DMSO, δ): 22.7, 122.7, 126.5, 140.3, and 150.6 182.3.

3. Results and discussion

Reaction between 2,2′-bipyridine (2,2′-bipy) and mixtures of mercury(II) acetate with sodium sulphate provided crystals analyzed as $[Hg(bipy)_2(CH_3COO)]_2(SO_4)\cdot 0.5NaCl$. The IR spectrum of this compound showed absorption bands resulting from the skeletal

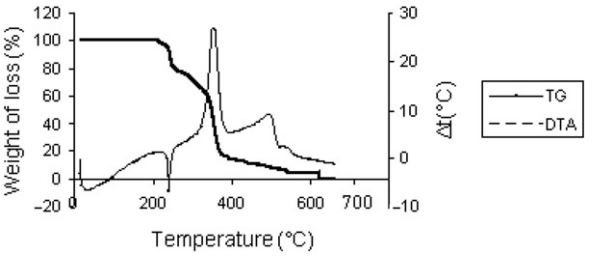

Figure 1. Thermal behaviour of $[Hg(bipy)_2(CH_3COO)]_2(SO_4)\cdot 0.5NaCl$.

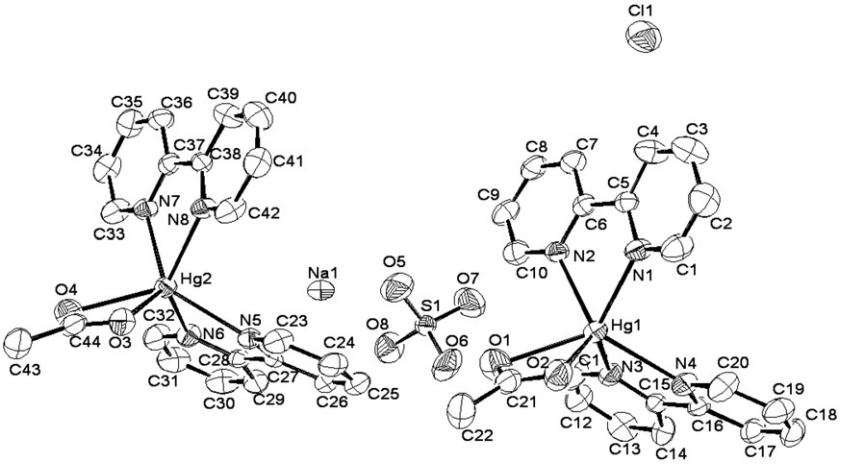

Figure 2. ORTEP diagram of $[Hg(bipy)_2(CH_3COO)]_2(SO_4)\cdot 0.5NaCl$ complex with ellipsoids of 30% probability, H-atoms were omitted for clarity.

vibrations of aromatic rings (1400–1523 cm^{-1}). The relatively weak bands around 2980 and 3095 cm^{-1} are assigned to the ν(CH) mode of acetate anions and "2,2′-bipy" rings, respectively. A very strong band at 1085 cm^{-1} characterizes the ν(S–O) vibrations. The characteristic bands of the carboxylate group appear around 1550 for $\upsilon_{as(C-O)}$ and 1397 for $\upsilon_{sym(C-O)}$. The $\Delta\upsilon$ value ($\upsilon_{as} - \upsilon_{sym}$) of 153 cm^{-1}, indicates that the carboxylate group is bidentate [12–13], as also unambiguously confirmed by the crystal structure of the complex. ^{1}H NMR spectrum of the DMSO solution of this compound displays four signals assigned to protons of aromatic rings of 2,2′-bipy. Another signal at 2.10 ppm has been assigned to methyl protons of acetate. The ^{13}C NMR spectrum of the DMSO solution displays five distinct resonances assigned to the aromatic carbons of bipyridine. Two other signals at 22.7 ($^{13}CH_3$-COO) and 182.3 ppm (CH_3-^{13}COO) have been assigned to carbons of acetate.

The thermal decomposition behavior was investigated in air from ambient to 700°C (figure 1). The compound melts at 243°C with an endothermic effect. Removal of bipyridine molecules and decomposition of mercury salt, occurs at 250°C with three exothermic peaks at 380, 510 and 540°C. The residue formed around 515°C is suggested to be HgO, which is evaporated at higher temperature.

Single X-ray crystal analysis reveals that $[Hg(bipy)_2(CH_3COO)]_2(SO_4)\cdot 0.5NaCl$ complex crystallizes in the monoclinic space group $P2_1/c$. The structure of the complex

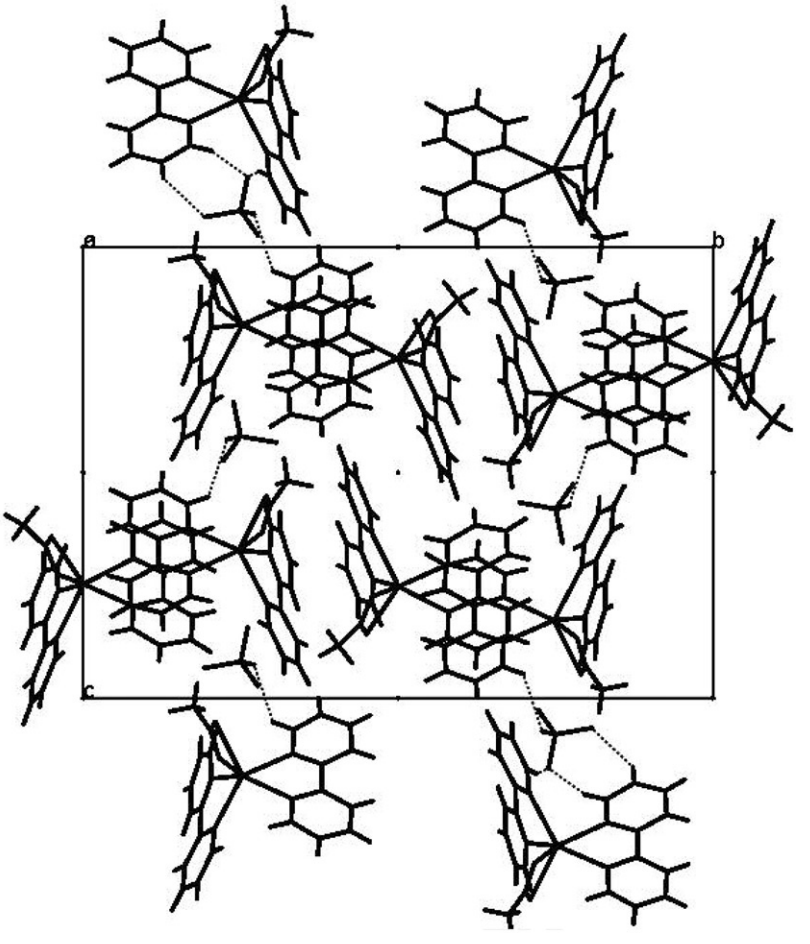

Figure 3. The unit cell and O···HC interactions in the packing of $[Hg(bipy)_2(CH_3COO)]_2(SO_4)\cdot 0.5NaCl$.

consists of two discrete $[Hg(bipy)_2(CH_3COO)]^+$ cations and one SO_4^{2-} anion (figure 2). In the structure of $[Hg(bipy)_2(CH_3COO)]_2(SO_4)\cdot 0.5NaCl$, there are two Hg-atoms with six coordination, HgO_2N_4 units of the same environment. The HgO_2N_4 units have C_2 symmetry, distorted octahedral coordination. Each Hg is chelated by pyridine N-atoms of two "bipy" ligands, as well as by one bidentate acetate anion (figure 2). Two of the four rings have dihedral angles (7.94, 7.58, 4.26 and -1.92°) and are not coplanar (figure 2). The carboxylate group of acetate is a multifunctional ligand that acts with a variety of binding geometries, monodentate, bidentate either by chelation, or by forming a bridge, and tri- and tetradentate by both chelation and bridging [14]. In this complex acetate is bidentate chelation (figure 2). There is half additional free sodium chloride that has been co-crystallized with this complex that may result from impurity in the sodium sulphate.

To study packing factors in this compound, a search was made for non-classical $CH_{py}\cdots O$ approaches. There are $CH\cdots O$ interactions between the oxygen atoms of sulphate with distances of $O\cdots H = 2.56$–$2.70\,\text{Å}$ as shown in figure 3. The weak

CH···O hydrogen bonds grow the monomeric structure into a one-dimensional polymeric unit.

Supplementary material

Crystallographic data for the structure reported in the article has been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-615082 for $[Hg(bipy)_2(CH_3COO)]_2(SO_4)\cdot 0.5NaCl$. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44-1223/336033; Email: deposit@ccdc.cam.ac.uk].

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