J. Iran. Chem. Soc., Vol. 5, No. 4, December 2008, pp. 574-578.

JOURNAL OF THE
Iranian
Chemical Society

Spectroscopic, Thermal and Structural Studies of a New Mercury(II) Complex of 4'-(4-Pyridyl)-2,2':6',2''-terpyridine (Pyterpy) Ligand, $[Hg(Hpyterpy)(SCN)_2]_2(MeSO_4)_2$

G. Mahmoudi[a], A. Morsali[a,*] and M. Zeller[b]

[a]*Department of Chemistry, Faculty of Sciences, Tarbiat Modarres University, P.O. Box 14155-4838, Tehran/I. R. Iran*

[b]*Department of Chemistry, Youngstown State University, One University Plaza, P.O. Box 44555-3663, Youngstown, Ohio, USA*

(Received 5 November 2007, Accepted 16 December 2007)

A new mercury(II) complex $[Hg(Hpyterpy)(SCN)_2]_2(MeSO_4)_2$ was prepared from the reaction of 4'-(4-pyridyl)-2,2':6',2''-terpyridine (pyterpy), as a polypyridyl ligand, with mercury(II) thiocyanate. The compound was characterized by elemental analysis, IR, ^1H NMR and ^{13}C NMR spectroscopy and its structure was determined by X-ray single-crystal diffraction. The thermal stability of compound was studied by thermogravimetric (TG) and differential thermal analyses (DTA).

Keywords: Mercury(II), 4'-(4-Pyridyl)-2,2':6',2''-terpyridine, Complex, Crystal structure

INTRODUCTION

Crystal engineering of metal-organic frameworks has been of great interest due to preparation of new coordination polymers exhibiting specific topology [1-8]. It is possible to build crystalline metal complexes with one, two or three dimensions, and the key factor in designing such metal complexes is to use polyfunctional ligands capable to bridge metal centres to form polymeric structures [2]. The construction of coordination polymers has achieved great progress in forming interesting architectures with novel properties such as magnetism [3], electrical conductivity [4], non-linear optical behaviour [5], luminescence [6] and porosity [7].

The ligand 4'-(4-pyridyl)-2,2':6',2''-terpyridine (pyterpy) is known to form polynuclear complexes with transition metals [9-10]. This ligand is able to form both complexes bridged by the 4-pyridyl group and chelated by terpyridine moiety. Since the architectures of coordination polymers or supramolecular compounds constructed from mercury(II) ions and the ligand pyterpy have not been reported so far, in this paper we report the preparations and crystal structure of a new mercury(II) complex $[Hg(Hpyterpy)(SCN)_2]_2(MeSO_4)_2$.

The general structure of this ligand and its possible coordination modes are shown in Fig. 1. The structural chemistry of this ligand is especially interesting because of its multifunctional coordination modes, as it can bind to a metal ion in a tridentate fashion forming two five-membered chelate rings (Fig. 1a), in a unidentate mode (Fig. 1b), or, even in a tetradentate way to two metal centers so that it might form polymeric structures.

EXPERIMENTAL

Physical Measurements

IR spectra were recorded using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. Microanalyses were carried out using a Heraeus CHN-O- Rapid analyzer. Melting points

*Corresponding author. E-mail: morsali_a@modares.ac.ir

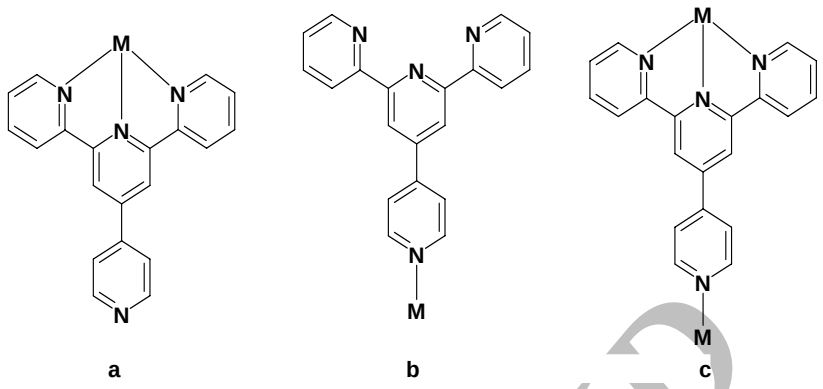

Fig. 1. The general structure of the 4'-(4-pyridyl)-2,2':6',2"-terpyridine (pyterpy) ligand and the possible modes of its coordination.

were measured on an Electrothermal 9100 apparatus and are uncorrected. The thermal behavior was measured with a PL-STA 1500 apparatus. ^{1}H and ^{13}C NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer, at 500 MHz for ^{1}H NMR and at 125 MHz for ^{13}C NMR; all chemical shifts are reported in δ units downfield from Me_4Si.

Preparation of Ligand 4'-(4-Pyridyl)-2,2':6',2''-terpyridine (Pyterpy)

The ligand pyterpy was prepared by a reported method [11], yielding a white powder, m.p.: 227.2-228.1 °C. IR (KBr) (υ_{max}, cm^{-1}): 3053 (C-H, arom); 1476-1584 (C=C, arom); 1392 (C=N). ^{1}H NMR ($CDCl_3$) δ_H: 7.37 (2H, d of d, $^{3}J_{HH}$ = 4.75 Hz, $^{3}J_{HH}$ = 6 Hz, $^{4}J_{HH}$ = 1 Hz, arom); 7.79 (2H, d, $^{3}J_{HH}$ = 4.5 Hz, arom); 8.09 (2H, d of t, $^{3}J_{HH}$ = 6 Hz, $^{3}J_{HH}$ = 8 Hz, $^{4}J_{HH}$ = 1.75 Hz, arom); 8.70 (2H, d,$^{3}J_{HH}$ = 8 Hz, arom); 8.78 (2H, d, $^{3}J_{HH}$ = 4.75 Hz, arom); 8.82 (2H, s, arom); 8.91 (2H, d, $^{3}J_{HH}$ = 4.5 Hz, arom) ppm. ^{13}C NMR ($CDCl_3$) δ_C: 118.6, 121.4, 121.9, 124.1, 136.9, 149.2, 150.6 (14CH); 147.5, 150.6, 155.7, 156.4 (6C) ppm.

Preparation of $[Hg(Hpyterpy)(SCN)_2]_2(MeSO_4)_2$

4'-(4-Pyridyl)-2,2':6',2"-terpyridine (pyterpy) (0.154 g, 0.5 mmol) was placed in one arm of a branched tube and mixtures of Mercury(II) thiocyanate (0.158 g, 0.5 mmol) and $HMeSO_4$ in the other. Methanol was carefully added to fill both arms, then the tube was sealed and the ligand-containing arm immersed in a bath at 60 ˚C, while the other was at ambient temperature. After 4 days, yellow crystals were deposited in the cooler arm, which were filtered off, washed with acetone and ether and air dried (0.166 g yield 45%), m.p.: 207 °C. (Found: C, 35.60; H, 2.13; N, 11.40. Calcd. for $C_{23}H_{18}HgN_6O_4S_3$: C, 35.72; H, 2.03; N, 11.37%). IR (KBr) (υ_{max}, cm^{-1}): 574(w), 747(s), 784(s), 1001(m), 1252(s), 1401(s), 1597(m), 2075(vs), 2950(w), 3050(w) and 3475(w). ^{1}H NMR (DMSO) δ_H: 2.70 (3H, s, alip), 7.60 (2H, d of d, $^{3}J_{HH}$ = 4.75 Hz, $^{3}J_{HH}$ = 6 Hz, $^{4}J_{HH}$ = 1 Hz, arom); 8.02 (2H, d, $^{3}J_{HH}$ = 4.5 Hz, arom); 8.11 (2H, d of t, $^{3}J_{HH}$ = 6 Hz, $^{3}J_{HH}$ = 8 Hz, $^{4}J_{HH}$ = 1.75 Hz, arom); 8.73 (2H, d, $^{3}J_{HH}$ = 8Hz, arom); 8.78 (2H, d, $^{3}J_{HH}$ = 4.75 Hz, arom); 8.78 (2H, s, arom); 8.82 (2H, d, $^{3}J_{HH}$ = 4.5 Hz, arom) ppm. ^{13}C NMR (DMSO) δ_C: 27.5, 118.6, 122.2, 122.9, 125.8, 138.9, 149.8, 151.1, 147.9, 151.2, 154.2, 156.6 ppm.

RESULTS AND DISCUSSION

The IR spectrum of the title compound shows absorption bands resulting from the skeletal vibrations of aromatic rings in the 1400-1600 cm^{-1} range. The relatively weak absorption bands at around 2950 cm^{-1} are due to the C-H modes involving the CH_3- of $MeSO_4^-$ anions in the compound $[Hg(Hpyterpy)(SCN)_2]_2(MeSO_4)_2$, while the relatively weak absorption bands at around 3050 cm^{-1} are due to the C-H modes of aromatic rings. Bands in the region 550-1070 cm^{-1} are due to the bending vibration of C-H group in or out of the aromatic plane, and ring deformation absorptions of “py” of ligands Hpyterpy [12]. The ^{1}H NMR spectrum of the DMSO solution of the compound $[Hg(Hpyterpy)(SCN)_2]_2(MeSO_4)_2$ displays

Table 1. Crystal Data and Structure Refinement for $[Hg(Hpyterpy)(SCN)_2]_2(MeSO_4)_2$

Empirical formula	$C_{23}H_{18}HgN_6O_4S_3$
Formula weight	739.20
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	Pī
Unit cell dimensions	a = 13.202(2) Å
	b =13.666(2) Å
	c =14.471(2) Å
	α =75.435(2)°
	β =79.481(2)°
	γ = 87.476(2)°
Volume	2484.3(5) $Å^3$
Z	4
Density (calculated)	g m^{-3}
F(000)	1432
Crystal size	0.27 × 0.24 × 0.08 mm^3
Index ranges	-16 ≤ h ≤ 16
	-17 ≤ k ≤ 16
	-18 ≤ l ≤ 18
Reflections collected	10165
Independent reflections	9087 (*R*(int) = 0.0313)
Completeness to theta	θ = 1.48° to 26.37°
Absorption correction	multi-scan
Max. and min. transmission	0.595and 0.355
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	10165/27/698
Goodness-of-fit on F^2	1.208
Final R. [I > 2sigma(I)]	R1 = 0.0685, wR2 = 0.1392
R indices (all data)	R1 = 0.0769, wR2 = 0.1429
Largest diff. Peak, hole	6.717 and -3.009 e $Å^{-3}$

six resonance signals assigned to CH protons of "py" groups of the ligands. Another signal at 2.70 ppm has been assigned to methyl protons of $MeSO_4^-$ anions. The ^{13}C NMR spectrum of the DMSO solution of $[Hg(Hpyterpy)(SCN)_2]_2(MeSO_4)_2$ displays eleven distinct resonance signals assigned to the aromatic carbons of "py" groups of the ligand pyterpy. One other signal at 27.5 ($^{13}CH_3$-OSO_3) has been assigned to the carbon of $MeSO_4^-$ anions.

The TG-DTA measurements of complex were determined in the range of 25-700 °C in a static atmosphere of air. To study the thermal stability of compound, thermogravimetric analyses (TGA) were performed on the single crystal samples. TG data showed that $[Hg(Hpyterpy)(SCN)_2]_2(MeSO_4)_2$ is stable up to 207 °C; the weight loses from 210 to 339 °C correspond to decomposition of ligand L, (obs: 39.2%, calcd: 40.2%) and finally weight loses from 339 to 610 °C

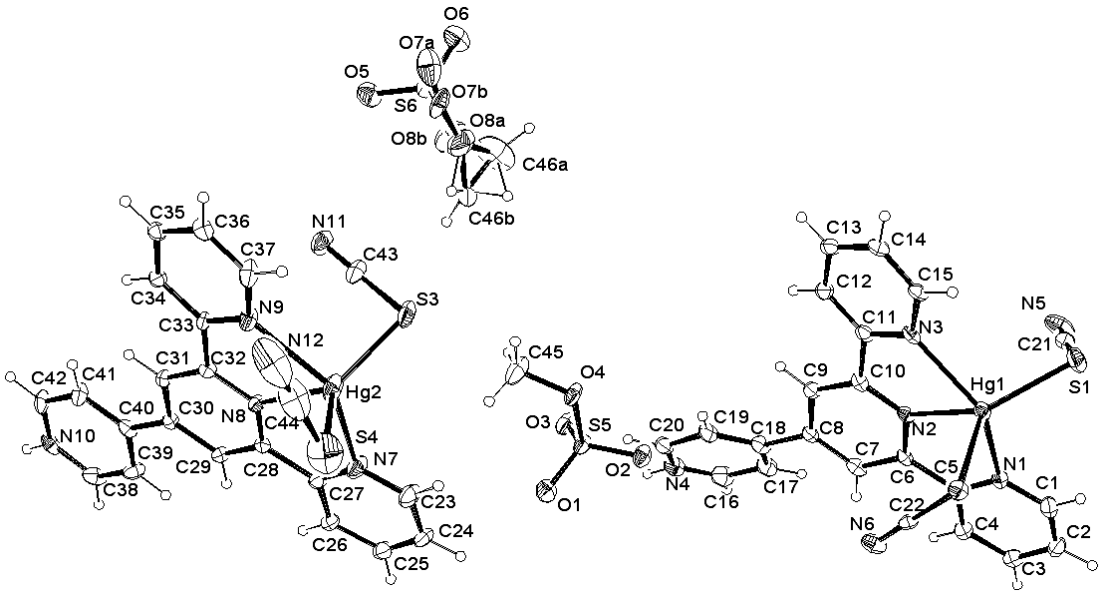

Fig. 2. ORTEP diagram of the $[Hg(Hpyterpy)(SCN)_2]_2(MeSO_4)_2$ complex with ellipsoids of 30% probability. Selected bond lengths (Å) and angles (°) for $[Hg(Hpyterpy)(SCN)_2]_2(MeSO_4)_2$: Hg1-N2 2.409(8), Hg1-N3 2.411(9), Hg1-S1 2.472(3), Hg1-N1 2.479(9), Hg1-S2 2.505(3), Hg2-N9 2.406(9), Hg2-N8 2.427(8), Hg2-N7 2.460(10), Hg2-S4 2.478(5) Hg2-S3 2.491(4), N2-Hg1-N3 68.0(3), N2-Hg1-S1 126.4(2), N3-Hg1-S1 104.9(2), N2-Hg1-N1 66.4(3), N3-Hg1-N1 133.6(3), S1-Hg1-N1 95.0(2), N2-Hg1-S2 104.94(19), N3-Hg1-S2 105.9(2), S1-Hg1-S2 126.99(9), N1-Hg1-S2 93.87(19), N9-Hg2-N8 68.0(3), N9-Hg2-N7 134.5(3), N8-Hg2-N7 66.5(3), N9-Hg2-S4 102.2(3), N8-Hg2-S4 116.3(2), N7-Hg2-S4 98.3(3), N9-Hg2-S3 97.4(2), N8-Hg2-S3 108.7(2), N7-Hg2-S3 96.0(3), S4-Hg2-S3 134.92(16).

correspond to the losses of $Hg(SCN)_2$.

Single X-ray crystal analysis revealed that $[Hg(Hpyterpy)(SCN)_2]_2(MeSO_4)_2$ complex crystallize in triclinic with space group of Pī. The structure of the complex consists of two discrete $[Hg(Hpyterpy)(SCN)_2]^+$ cations and two $MeSO_4^-$ anions (Fig. 2). In the structure of $[Hg(Hpyterpy)(SCN)_2]_2(MeSO_4)_2$, there are two Hg-atoms with coordination number five, *i.e.*, HgS_2N_3 units. Thereby, the environment of the two Hg-atoms is same and the HgS_2N_3 units represent distorted trigonal bipyramid coordination geometry. Each of these Hg-atoms is chelated by the three pyridine N-atoms of one Hpyterpy ligand, as well as by one of two thiocynate anions (Fig. 2). In this compound the potentially tetradentate ligand pyterpy acts as a tridentate ligand in which the 4-pyridyl ring is not coordinated. One of the $MeSO_4^-$ anion is disordered.

For the study of packing controller factors in this compound, a search was also generally made for non-classical $NH_{py}\cdots O$, $O\cdots O$ approaches and π-π stacking interactions. The interesting feature of the complex is that, there are both $NH\cdots O$ and $O\cdots O$ interactions. There are N-H···O hydrogen bondings between the hydrogen atoms of the pyridinium group of Hpyterpy ligand and oxygen atoms of carbonyl groups of $MeSO_4^-$ belonging to adjacent molecules. In $[Hg(Hpyterpy)(SCN)_2]_2(MeSO_4)_2$, there are also close intermolecular contacts between the oxygen atoms of the $MeSO_4^-$ anions of neighboring molecules. The lattice of this complex shows distances of O···O = 3.038 Å, possibly indicating the donor···acceptor interactions [13] (Fig. 3). Consequently, the N-H···O hydrogen bonding and O···O interactions grow the structure into a hybrid two-dimensional network (see Fig. 3).

Supplementary material: Crystallographic data for the structure reported in the paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary

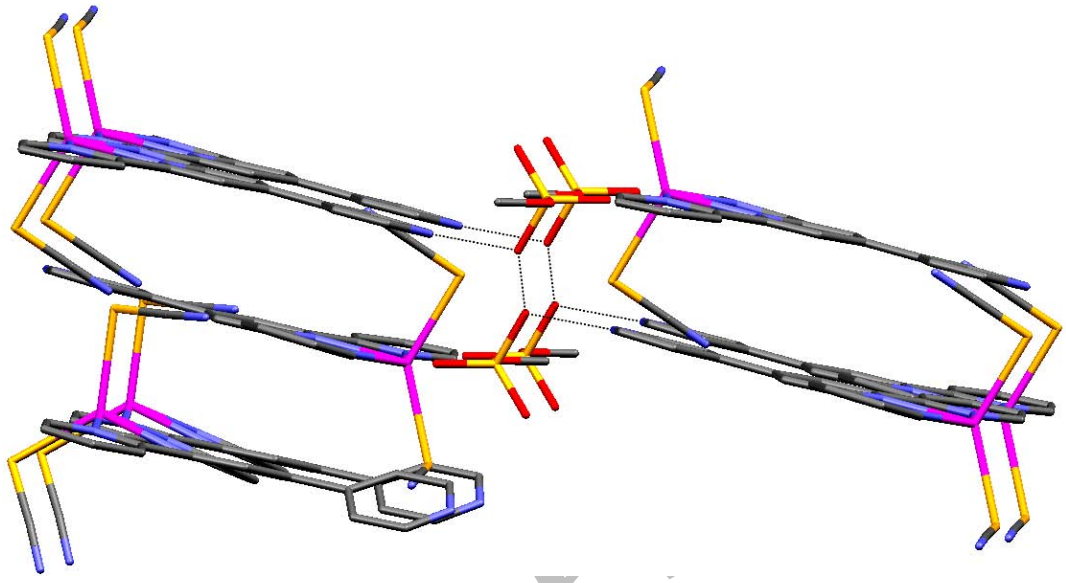

Fig. 3. The packing and showing of the O···HN and O···O interactions in $[Hg(Hpyterpy)(SCN)_2]_2(MeSO_4)_2$.

publication no, CCDC-647037. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: + 44–1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

ACKNOWLEDGEMENTS

The support of this investigation by Iran National Science Foundation, INSF (Project Number 84118) is gratefully acknowledged. The Smart Apex diffractometer was funded by NSF grant 0087210, by Ohio Board of Regents grant CAP-491, and by YSU.

REFERENCES

[1] H.K. Chae, D.Y. Siberio-Perez, J. Kim, Y. Go, M. Eddaoudi, A.J. Matzger, M. O'Keeffe, O.M. Yaghi, Nature 427 (2004) 523.

[2] Y. Kim, M. Suh, D.Y. Jung, Inorg. Chem. 43 (2004) 245.

[3] P.J. Hagrman, D. Hagrman, J. Zubieta, Angew. Chem., Int. Ed. Engl. 38 (1999) 2638.

[4] M. Eddaoudi, J. Kim, D. Vodak, A. Sudik, J. Wachter, M. O'Keeffe, O.M. Yaghi, PNAS 99 (2002) 4900.

[5] L. Carlucci, G. Ciani, D. Proserpio, Coord. Chem. Rev. 246 (2003) 247.

[6] B. Moulton, M.J. Zaworotko, Chem. Rev. 101 (2001) 1629.

[7] D. Braga, F. Grepioni, G.R. Desiraju, Chem. Rev. 98 (1998) 1375.

[8] a) A. Askarinejad, A. Morsali, Helv. Chim. Acta 89 (2006) 265; b) A. Askarinejad, A. Morsali, Inorg. Chem. Commun. 9 (2006) 143; c) A. Morsali, J. Abedini, Inorg. Chem. Commun. 8 (2005) 460; d) A. Morsali, Solid State Sci. 8 (2006) 82; e) N. Atoub, G. Mahmoudi, A. Morsali, Inorg. Chem. Commun. 10 (2007) 166; g) K. Akhbari, A. Morsali, A.D. Hunter, M. Zeller, Inorg. Chem. Commun. 10 (2007) 178.

[9] E.C. Constable, A.M.W. Cargill Thompson, J. Chem. Soc., Dalton Trans. (1994) 1409.

[10] S.-S. Sun, A.J. Lees**,** Inorg. Chem. 40 (2001) 3154.

[11] E.C. Constable, A.M.W.C. Thompson, J. Chem. Soc., Dalton Trans. (1992) 2947.

[12] J.G. Contreras, C.J. Diz, J. Coord. Chem. 16 (1997) 245.

[13] J. Syssa-Magale, K. Boubekeur, B. Schollhorn, J. Molecular Structure 737 (2005) 103.