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Synthesis and Properties of Dimercury(I) Crystal Network Constructed with Functionalized Pyrazine Sulfonate and Nitrate Linkers

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Abstract—Coordination nature in the structures between the heterocyclic sulfonic acid group and heavy metal atoms, structural optimization, their physical and chemical properties have been studied. Herein, a new compound $[Hg_2(P–SO_3)(NO_3)]_n$ (**1**) has been synthesized via solvent volatilization method, according to which pyrazine sulfonic acid ($P–SO_3H$) has been used as the major ligand, and nitrate has been used as the precursor. X-Ray single-crystal diffraction analysis demonstrates that **1** belongs to the *Pca21* space group. Both pyrazine sulfonate and nitrate serve as chelate bridging linkers for the dimercury(I) ions (Hg_2^{2+}or $Hg^I–Hg^I$) forming the 2D layer coordination polymer involved in further construction of the stable 3D network through the π–π stacking of pyrazine rings. Thermal stability and fluorescence properties of **1** have been closely studied.

Keywords: pyrazine sulfonic acid; coordination polymer; weak interaction; crystal structure; luminescence property

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INTRODUCTION

Nowadays, design, synthesis and investigation of the coordination polymers (CPs) attract considerable attention due to the progress of coordination chemistry and crystal engineering because of their diverse topological structures [1–3] and potential applications in such areas as magnetic materials [4–6], biomedicine [7], catalysis [8, 9], luminescence [10–12], chemical sensing [13–15], and more.

Some researchers hypothesized that possible coordination of mercury ions with ligands could form stable coordination polymers that reduce toxicity of mercury [16,17]. For instance, Suresh et al. [18] reported that a dual detection probe developed from an adenine-based luminescent coordination polymer for the selective sensing of mercury ions in an aqueous phase, identified mercury ions in lethal environments. Recently, Huang et al. [19] prepared triazine-based porous organic polymers with high BET surface area to remove mercury ions from aqueous solutions due to the strong chelating effect of oxygen and nitrogen with mercury ions.

On the other hand, nitrogen-containing heterocyclic sulfonic acid coordination polymers attracted close attention due to their unique physicochemical properties [19, 20]. Nitrogen atoms can act as σ-electron donors or π-electron acceptors in the course of coordination process, and sulfonates tend to form intramolecular or intermolecular hydrogen bonds, that are beneficial in assembling extended high-dimensional structures [21]. In our previous research one nitrogen-containing heterocyclic 2-pyridine-sulfonic acid was selected for the synthesis of Cu-based 3D supramolecular polymer with the multiple interpenetration structure [22]. Lately, nitrogen-containing heterocyclic pyrazine sulfonic acid ($P–SO_3H$) has been used in constructing two Ag and one Na–Cu CPs [23, 24]. However, lack of extensive investigations on the mercury compounds containing N-heterocyclic sulfonic acid limited their application unlike those of transition metal CPs. Therefore, we designed and synthesized a new dimercury(I)-based pyrazine sulfonate polymer $[Hg_2(P–SO_3)(NO_3)]_n$[1] (**1**) via the solvent evaporation method. The compound **1** has

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[1] Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Center with CCDC 1995512 for $[Hg_2(P–SO_3)(NO_3)]_n$ ($P–SO_3$=pyrazine sulfonic acid). Copies of this information may be obtained free of charge from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

Table 1. Crystal data and structure refinement for $[Hg_2(P–SO_3)(NO_3)]_n$

Parameter	Value
Empirical formula	$C_4H_3Hg_2N_3O_6S$
Formula weight	622.33
Crystal system	Orthorhombic
Space group	$Pca2_1$
a, Å	10.5680(2)
b, Å	6.23262(11)
c, Å	14.8569(3)
α, deg	90.00
β, deg	90.00
γ, deg	90.00
V, Å^3, z	978.56(3), 4
F(000)	1088.0
2θ, deg	6.54–52.74
Reflections collected	7299
Unique data	1997
R_{int}	0.0504
Completeness to θ, %	99.9
Data/restraints/parameters	1997/1/133
Goodness-of-fit on F^2	1.179
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0962$, $wR_2 = 0.2522$
R indices (all data)	$R_1 = 0.0971$, $wR_2 = 0.2553$
Largest diff. peak/hole, e/Å^3	10.08/–10.33

Table 2. Bond distances and bond angles for $[Hg_2(P–SO_3)(NO_3)]_n$[a]

Bond	d, Å	Angle	φ, deg	Angle	φ, deg
$Hg^1–N^1$	2.325(13)	$N^1Hg^1Hg^2$	161.2(5)	$N^1Hg^1Hg^2$	161.2(5)
$Hg^1–Hg^2$	2.5246(16)	$N^1Hg^1O^1$	71.5(7)	$Hg^1Hg^2O^{3\#2}$	98.9(5)
$Hg^1–O^1$	2.54(3)	$Hg^2Hg^1O^1$	121.0(5)	$O^6Hg^2O^{3\#2}$	136.4(9)
$Hg^2–N^{2\#1}$	2.23(2)	$N^{2\#1}Hg^2Hg^1$	176(2)	$S^1O^1Hg^1$	118.8(12)
$Hg^2–O^6$	2.63(3)	$N^{2\#1}Hg^2O^6$	77(2)	$S^1O^3Hg^{2\#3}$	134.5(16)
$Hg^2–O^{3\#2}$	2.65(3)	$Hg^1Hg^2O^6$	102.0(6)	$N^3O^6Hg^2$	111(2)
$N^2–Hg^{2\#4}$	2.234(14)	$N^{2\#1}Hg^2O^{3\#2}$	80(2)	$C^1N^1Hg^1$	121.6(9)
		$C^3N^2Hg^{2\#4}$	123.5(9)	$C^4N^1Hg^1$	118.4(9)
		$C^2N^2Hg^{2\#4}$	116.5(9)		

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x+1/2, y, z+1/2$; #2 $-x+1/2, y, z+1/2$; #3 $-x+1/2, y, z-1/2$; #4 $-x+1/2, y+1, z-1/2$.

been characterized by single crystal X-ray diffraction, IR and fluorescence spectroscopy, and thermal analysis.

EXPERIMENTAL

All reagents were of analytical grade and used without additional purification. FT-IR spectra (KBr discs) were recorded on a PE Spectrum One spectrophotometer. Solid-state fluorescence spectra were recorded on a HORIBA JOBIN JVON fluorescence spectrophotometer, FL3-P-TCSPC, France. Thermogravimetric analysis was performed on a Labsys Evo-TGA, France.

The ligand was prepared in accordance with the developed earlier method [25]. Pyrazine sulfonic acid ($P–SO_3H$, 0.3 mmol) and $Hg(NO_3)_2·0.5H_2O$ (0.5 mmol)

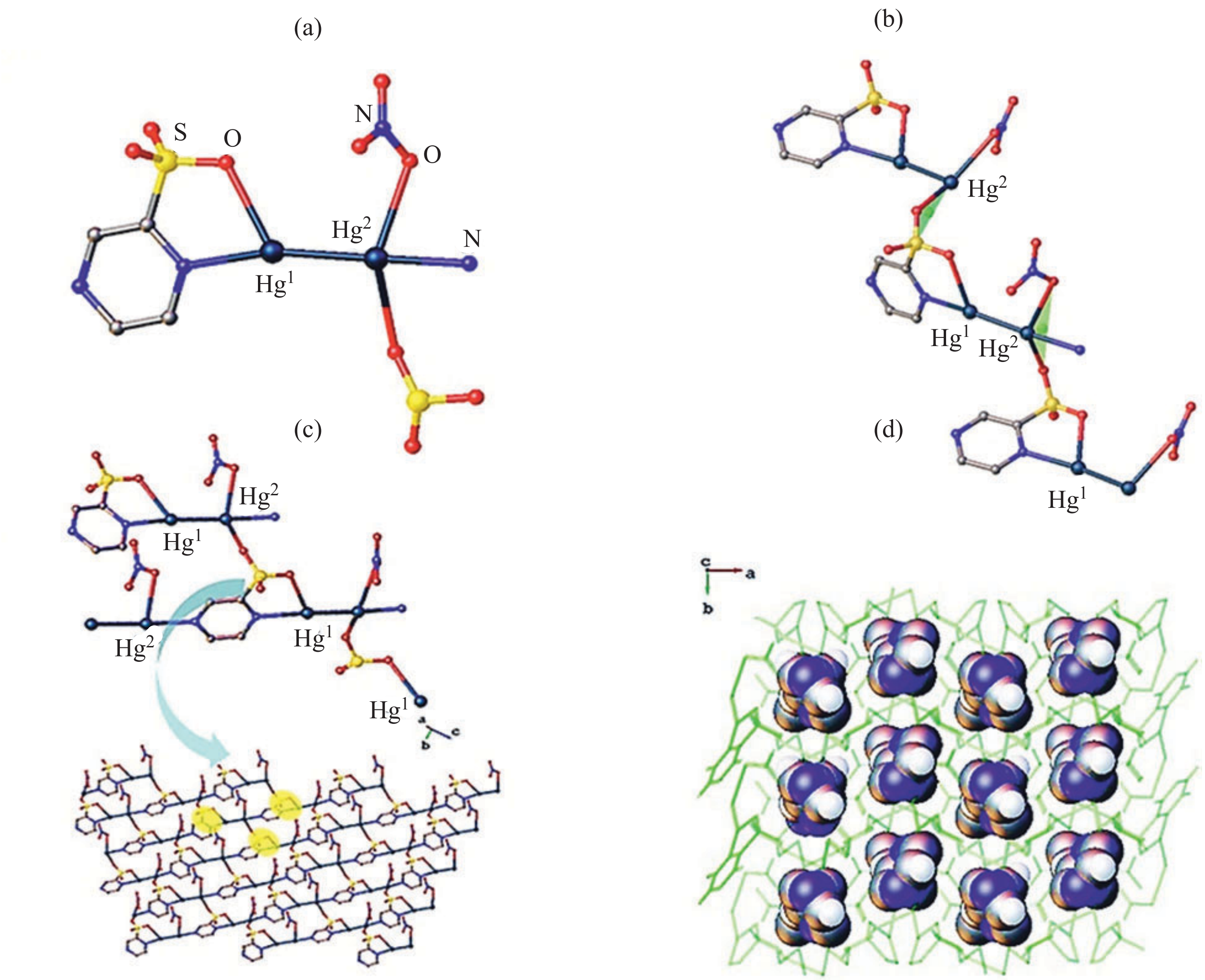

Fig. 1. (a) The coordination structure of dimercury(I) ions (Hg^I–Hg^I); (b, c) the 2D module constructed by nitrate and the break angle; (d) 3D network of the polymer **1** constructed by the weak π–π stacking effect.

were added to a mixture of ethanol and acetonitrile (2 : 3 ratio) of the certain volume. The mixture was placed in a dark container and stirred at 60°C for 5 h, then filtered, and the filtrate was volatilized at room temperature giving a yellow flake-like crystal after 8 days of storage, yield 12.5% (based on Hg). IR spectrum, ν, cm^{-1}: 3434 (OH), 1632 (C=C), 1384 (C=N), 1237 (S=O), 1208 (S=O), 645 (C–S). Found, %: C 7.76; H 0.51; N 6.78. $C_3H_4Hg_2N_3O_6S$. Calculated, %: C 7.72; H 0.49; N 6.75. *M* 622.

Diffraction data were collected on an Agilent SuperNova diffractometer at 298 K (MoK_α, $\lambda = 0.71073$ Å) and analyzed by Olex2 [26]. All the non-hydrogen atoms were refined by the SHELXTL program package using the full matrix least square method [27]. The accumulated crystallographic data, and the selected bond distances and angles determined for **1** are listed in Tables 1 and 2, respectively.

RESULTS AND DISCUSSION

According to the single-crystal X-ray crystallography (Fig. 1a) Hg^1 exhibited a distorted pentagonal geometry when coordinated with nitrogen and oxygen atoms of the deprotonated pyrazine sulfonic acid ligand (P–SO_3). The bond distances Hg^1–N^1 [2.325(13) Å] and Hg^1–O^1 [2.54(3) Å] were shorter than those reported earlier [28]. The metal-metal bond was formed upon coordination of dimercury(I) ion (Hg^I–Hg^I), Hg^2 and Hg^1, and then linked by oxygen of the nitrate and two P–SO_3 ligands. The bond distances Hg^1–Hg^2 [2.5246(16) Å], Hg^2–O^6 [2.63(3) Å] and Hg^2–$O^{3\#1}$ [2.65(3) Å] were in agreement with those determined for the mercury polymers [29].

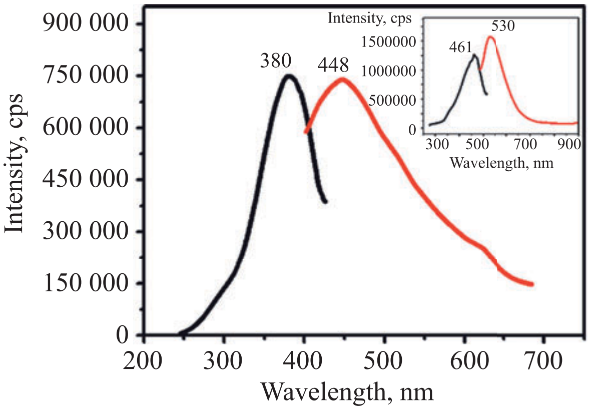

Fig. 2. Solid-state photoluminescent spectra of polymer **1** and free P–SO_3H ligand (the inner figure).

The structural unit could extend into the 2D network via sharing oxygen atoms of the P–SO_3 ligand being coordinated with dimercury(I) ion. The contact angles of two sulfonate anions $O^6Hg^2O^{3\#1}$ and $S^1O^3Hg^{2\#3}$ were determined to be 136.4° and 134.5°, respectively (Figs. 1b, 1c). The 3D network could be constructed from the 2D structure via the weak π–π stacking of pyrazine rings (Fig. 1d).

According to TGA analysis weight loss of polymer **1** proceeded in three steps. In the range of room temperature to 218°C the first step of mass loss was due to gradual release of the guest nitrate linkers (Obs. 5.2%, Calcd 9.8%). Then, the rapid decomposition was recorded at ~358°C, and the maximum weight loss could be attributed to the loss of mercury pyrazine sulfonate species (Obs. 43.7%, Calcd 42.3%). Finally, the TGA curve decreased slowly upon further heating which led to pyrolysis and formation of mercury oxide at ~800°C (Obs. 35.8%, Calcd 34.9%).

To date, only limited data are available for luminescent properties of dimercury(I) based pyrazine sulfonate complexes. In order to fill in this gap, solid state luminescence was studied by scanning the polymer **1** and free P–SO_3H at room temperature (Fig. 2).

The maximum emission signal for **1** was recorded at 448 nm (λ_{ex} = 380 nm). The fluorescent intensity of polymer **1** was weaker than that of P–SO_3H and demonstrated blue shift at 82 nm (λ_{ex} = 461 nm, λ_{em} = 530 nm) which could be attributed to the heavy atom effect and electron transfer from the excited state (π orbital) of the ligand to the vacant ^6s orbital of mercurous ion upon coordination [30]. Regarding the above, we presume that some of the ligand's fluorescence energy might be transferred to the dimercury(I) ion (Hg^I–Hg^I) via the sulfonate moiety, resulting in the increase in the fluorescence quenching effect of **1**. Nevertheless, the authenticity of this phenomenon should be scrutinized further.

CONCLUSIONS

A new dimercury(I) based pyrazine sulfonate polymer **1** has been synthesized using the solvent volatilization method. The single-crystal structure, thermal stability and fluorescence properties of it have been studied, and have indicated that the heterocyclic sulfonic acid ligand could acted as a bridging linker in coordination with different mercury(I) ions with different coordination environments, and form 3D network via π–π stacking.

AUTHOR CONTRIBUTIONS

Haojin Hu (undergraduate student) and Jinli Quan (undergraduate student) contributed equally to this work. Zhuojie Tan and Jun-Hong Fu participate in data analysis and results discussion; Dr. Yi-Jun Liang and Dr. Jun-xia Li: conceived the central idea, manuscript written, revised, and supervision. All authors have given approval to the final version of the manuscript.

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

REFERENCES

1. Li, J.-X., Du, Z.-X., Zhang, L.-L., Liu, D.-L., and Pan, Q.-Y., *Inorg. Chim. Acta*, 2020, vol. 512, p. 119890. https://doi.org/10.1016/j.ica.2020.119890
2. Li, J.-X., Du, Z.-X., and Huang, W.-P., *Synth. React. Inorg. Met.-Org. Chem*., 2014, vol. 44, p. 352. https://doi.org/10.1080/15533174.2013.769588
3. Li, J.-X. and Du, Z.-X., *Z. Naturforsch. B*, 2015, vol. 70, p. 505. https://doi.org/10.1515/znb-2015-0010
4. Li, J.-X., Du, Z.-X., Xiong, L.-Y., Fu, L.-L., and Bo, W.-B., *J. Solid State Chem*., 2021, vol. 293, p.121799. https://doi.org/10.1016/j.jssc.2020.121799
5. Du, Z.-X. and Li, J.-X., *Z. Naturforsch. B*, 2020, vol. 75,

nos. 6–7, p. 577. https://doi.org/10.1515/znb-2020-0042

6. Li, J.-X., Du, Z.-X., Pan, Q.-Y., Zhang, L.-L., and Liu, D.-L., *Inorg. Chim. Acta*., 2020, vol. 509, p. 119677. https://doi.org/10.1016/j.ica.2020.119677
7. Wang, D.-D., Jana, D.-L., and Zhao, Y.-L., *Acc. Chem. Res*., 2020, vol. 53, p. 1389. https://doi.org/10.1021/acs.accounts.0c00268
8. Bavykina, A., Kolobov, N., Khan, I.S., Bau, J.A., Ramirez, A., and Gascon, J., *Chem. Rev*., 2020, vol. 120, p. 8468. https://doi.org/10.1021/acs.chemrev.9b00685
9. Du, Z.-X. and Li, J.-X., *Inorg. Chim. Acta*., 2015, vol. 436, p. 159. https://doi.org/10.1016/j.ica.2015.07.036
10. Li, J.-X. and Du, Z.-X., *J. Clust. Sci*., 2020, vol. 31, p. 507. https://doi.org/10.1007/s10876-019-01666-w
11. Li, J.-X., Du, Z.-X., Wang, J., and Feng, X., *Z. Naturforsch. B*, 2019, vol. 74, nos. 11–12, p. 839. https://doi.org/10.1515/znb-2019-0147
12. Li, J.-X. and Du, Z.-X., *J. Coord. Chem*., 2016, vol. 69, p. 2563. https://doi.org/10.1080/00958972.2016.1216106
13. Yi, F.-Y., Chen, D., Wu, M.-K., Han, L., and Jiang, H.-L., *ChemPlusChem*., 2016, vol. 81, p. 675. https://doi.org/10.1002/cplu.201600137
14. Li, J.-X., Du, Z.-X., and Feng, X., *Z. Naturforsch. B*, 2019, vol. 74, nos. 11–12, p. 833. https://doi.org/10.1515/znb-2019-0128
15. Du, Z.-X., Li, J.-X., Liu, S.-J., Wang, Z.-Q., and Pan, Q.-J., *Z. Naturforsch. B*, 2020 , vol. 75, nos. 6–7, p. 567. https://doi.org/10.1515/znb-2020-0036
16. Pletz, J., Sánchez-Bayo, F., and Tennekes, H.-A., *Toxicology*, 2016, vol. 347, p. 1. https://doi.org/10.1016/j.tox.2016.02.006
17. Ding, S.-Y., Dong, M., Wang, Y.-W., Chen, Y.-T., Wang, H.-Z., Su, C.-Y., and Wang, W., *J. Am. Chem. Soc*., 2016, vol. 138, p. 3031. https://doi.org/10.1021/jacs.5b10754
18. Rachuri, Y., Parmar, B., Bisht, K.-K., and Suresh, E., *Cryst. Growth Des*., 2017, vol. 17, p. 1363. https://doi.org/10.1021/acs.cgd.6b01755
19. Peng, R.-X., Chen, G., Zhou, F., Man, R.-L., and Huang, J.-H., *Chem. Eng. J*., 2019, vol. 371, p. 260. https://doi.org/10.1016/j.cej.2019.04.063
20. Neelakandan, S., Ramachandran, R., Fang, M.L., and Wang, L., *Int. J. Energ. Res*., 2020, vol. 44, p. 1673. https://doi.org/10.1002/er.4981
21. Maity, D.-K., Otake, K., Ghosh, S., Kitagawa, H., and Ghoshal, D., *Inorg. Chem*., 2017, vol. 56, p.1581. https://doi.org/10.1021/acs.inorgchem.6b02674
22. Jiang, Y.M., Yin, Z., He, K.H., Zeng, M.H., and Kurmoo, M., *Inorg. Chem*., 2011, vol. 50, p. 2329. https://doi.org/10.1021/ic102020g
23. Liang, Y.-J., Feng, G., Zhang, X., Li, J.-X., and Jiang, Y., *J. Struct. Chem*., 2021, vol. 62, p. 300. https://doi.org/10.1134/S0022476621020153
24. Zheng, Z., Xu, P., Jiang, Y., Liang, Y.-J., and Li, J.-X., *J. Struct. Chem*. 2021, vol. 62, p. 292. https://doi.org/10.1134/S0022476621020141
25. Hort, E. and Spoerri, P.E., *J. Am. Chem. Soc*., 1948, vol. 70, p. 1657. https://doi.org/10.1021/ja01184a507
26. Dolomanov, O.-V., Bourhis, L.-J., Gildea, R.-J., Howard, J.A.K., and Puschmann, H., *J. Appl. Crystallogr*., 2009, vol. 42, p. 339. https://doi.org/10.1107/S0021889808042726
27. Sheldrick, G.M., *SHELXS-97*, Program for Crystal Structure Solution, Göttingen: Göttingen University, 1997.
28. Lo, H.-C., Chen, H., and Fish, R.-H., *Eur. J. Inorg. Chem*., 2001, vol. 2001, p. 2217. https://doi.org/10.1002/1099-0682(200109)2001:9<2217::AID-EJIC2217>3.0.CO;2-L
29. Brodersen, K., *Comment Inorg. Chem*., 1981, vol. 1, p. 207. https://doi.org/10.1080/02603598108078093
30. Li, F., Hong, Y.-S., Zuo, K.-X., Sun, Q., and Gao, E.-Q., *J. Solid State Chem*., 2019, vol. 270, p. 509. https://doi.org/10.1016/j.jssc.2018.12.025