

КРАТКИЕ СООБЩЕНИЯ

UDC 541.6:547.13:546.48

STRUCTURAL CHARACTERIZATION OF TETRAKIS(1,3-DIAZINANE-2-THIONE)CADMIUM(II) SULFATE

R. Mahmood¹, S.G. Hussain², A.A. Isab³, M. Fettouhi³,
A. Fazal⁴, S. Ahmad²

¹Department of Chemistry, University of Azad Jammu and Kashmir, Chela Campus, Muzaffarabad, Pakistan

²Department of Chemistry, University of Engineering and Technology, Lahore, Pakistan

E-mail: saeed_a786@hotmail.com

³Department of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia

⁴Center of Research Excellence in Petroleum Refining and Petrochemicals, Research Institute, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia

Received October, 31, 2013

A cadmium(II) complex tetrakis(1,3-diazinane-2-thione)cadmium(II) sulfate $[\text{Cd}(\text{Diaz})_4]\text{SO}_4$ (**1**) is prepared and its crystal structure is determined by X-ray crystallography. The crystal structure of **1** consists of $[\text{Cd}(\text{Diaz})_4]^{2+}$ and SO_4^{2-} ions. In the complex ion, the central cadmium atom is coordinated by four Diaz molecules through sulfur atoms adopting a distorted tetrahedral geometry. The molecular structure is stabilized by N—H...O and N—H...S hydrogen bonding interactions. The complex is also characterized by IR and NMR spectroscopy and the spectroscopic data are discussed in terms of the nature of bonding.

DOI: 10.15372/JSC20150309

Keywords: cadmium sulfate, 1,3-diazinane-2-thione, crystal structure.

In recent years, considerable research efforts have been devoted to the structural characterization of cadmium(II) complexes of thioamides [1—22] because of their applications in biological systems [23, 24], in analytical chemistry [25, 26], in environmental toxicology [27], and as precursors for the preparation of CdS nanoparticles [28—30]. These structural reports describe that in most of the cases, cadmium(II) complexes exist as neutral monomeric [3—16] or polymeric [17—19] molecules of the general formula $[\text{CdL}_2\text{X}_2]$ with the cadmium atom possessing a tetrahedral or distorted octahedral coordination environment respectively. In some cases, ionic complexes of the type $[\text{CdL}_4]\text{X}_2$ (X = nitrate or sulfonate) are also formed [21, 22]. Recently, we have reported the crystal structures of two new complexes $[\text{Cd}(\text{Detu})_4(\text{SO}_4)]$ (Detu = N,N'-diethylthiourea) [1] and $[\text{Cd}(\text{Diaz})_2(\text{CH}_3\text{COO})_2]$ (Diaz = 1,3-diazinane-2-thione) [2] in which cadmium(II) shows severe distortions from the octahedral geometry. In view of our continued interest in the structural chemistry of cadmium(II) complexes with thiones [1—10], we report here the synthesis and crystal structure of a cadmium(II) complex of the heterocyclic ligand 1,3-diazinane-2-thione (3,4,5,6-tetrahydropyrimidine), $[\text{Cd}(\text{Diaz})_4]\text{SO}_4$.

Experimental. Materials. Cadmium sulfate ($\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$) was obtained from Merck Chemical Company, Germany. Diazinane-2-thione (Diaz) was prepared according to the procedure published in the literature [31].

Synthesis of $[\text{Cd}(\text{Diaz})_4]\text{SO}_4$ (1**).** The title complex was prepared by adding 0.24 g (2.0 mmol) of Diaz in 15 ml of methanol to an aqueous solution (5 ml) of cadmium sulfate (1.0 mmol, 0.26 g) and

stirring the mixture for 30 min. The very light yellow cloudy solution was filtered and the filtrate was kept at room temperature for crystallization. As a result, the off-white crystalline product was obtained, which was washed with methanol and dried.

IR and NMR measurements. The IR spectra were recorded on a Perkin—Elmer FTIR 180 spectrophotometer using KBr pellets over the range 4000—400 cm^{-1} . The ^1H and ^{13}C $\{^1\text{H}\}$ NMR spectra in $\text{DMSO-}d_6$ were obtained on a Jeol JNM-LA 500 NMR spectrometer operating at frequencies of 500.00 MHz and 125.65 MHz respectively at 297 K. The ^{13}C chemical shifts were measured relative to TMS.

X-ray structure determination. The single crystal data collection for complex **1** was performed at 294 K on a Bruker-Axs Smart Apex system equipped with graphite monochromatized MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$). The data were collected using SMART [32]. The data integration was performed using SAINT [32]. An empirical absorption correction was carried out using SADABS [33]. The structures were solved by direct methods with SHELXS-97 [34] and refined by full-matrix least squares procedures on F^2 using the SHELXL-97 program [34]. All non-hydrogen atoms were refined anisotropically. N—H hydrogen atoms were located in a difference Fourier map and refined isotropically with a bond distance restrained to be 0.86(2) \AA . All other H atoms were placed at calculated positions and allowed to ride with a C—H distance of 0.97 \AA and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The C7 (C7A) and C8 (C8A) atoms in one ligand molecule and C14 (C14A), C15 (C15A), and C16 (C16A) in the second ligand molecule were constrained to double site partial occupancies which were refined to 0.58(2) and 0.55(2) respectively for the two ligands. The thermal displacement parameters of atoms involved in disorder are: C6, C7, C7A, C8, C8A, N4, N7, C14, C14A, C15, C15A, C16, C16A, and N8 were re-

Table 1

Crystal data and refinement details for compound **1**

Formula	$\text{C}_{16}\text{H}_{32}\text{CdN}_8\text{S}_5\text{O}_4$
Formula weight	673.20
Crystal system	Triclinic
Space group	$P1$
$a, b, c, \text{\AA}$	9.250(2), 9.313(3), 9.618(2)
$\alpha, \beta, \gamma, \text{deg.}$	62.737(4), 68.645(4), 76.257(4)
$V, \text{\AA}^3$	683.4(3)
Z	1
$\rho_{\text{calc}}, \text{g/cm}^3$	1.636
$\mu(\text{MoK}_\alpha), \text{mm}^{-1}$	1.219
$F(000)$	344
Crystal size, mm	0.36×0.23×0.18
Temperature, K	294(2)
$\lambda \text{ MoK}_\alpha, \text{\AA}$	0.71073
2θ range, deg.	2.37—28.38
h, k, l limits	−12:12, −12:12, −12:12
Reflections; collected / uniq.	9278 / 6685 [$R(\text{int}) = 0.0186$]
Reflections: observed [$I > 2\sigma(I)$]	6270
$T_{\text{min}}, T_{\text{max}}$	0.6680, 0.8104
Data / restraints / parameters	6685 / 185 / 378
Goodness-of-fit on F^2	1.061
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0271, wR_2 = 0.0625$
R indices (all data)	$R_1 = 0.0302, wR_2 = 0.0662$
Largest diff. peak, hole, e/\AA^3	0.482, −0.567
Flack parameter	−0.009(13)

strained with DELU and SIMU commands [35]. Crystal data and details of the data collection are summarized in Table 1.

Results and discussion. IR and NMR studies. The reaction of CdSO_4 with Diaz in a 1:2 molar ratio resulted in a product of the empirical composition $[\text{Cd}(\text{Diaz})_4]\text{SO}_4$. In the IR spectrum of the complex, the characteristic bands observed were $\nu(\text{C}=\text{S})$ at 512 cm^{-1} and $\nu(\text{N}-\text{H})$ at 3217 cm^{-1} . For free Diaz, these bands were observed at 510 cm^{-1} and 3200 cm^{-1} respectively. The presence of these bands is consistent with the coordination of Diaz to cadmium(II) in the solid state. Sharp bands at 1038 cm^{-1} , 978 cm^{-1} , and 608 cm^{-1} indicate the presence of the SO_4^{2-} ion.

In the ^1H NMR spectrum of the title complex, a small downfield shift in the N—H resonance (7.89 ppm vs 7.81 ppm) was observed as compared to uncomplexed Diaz. In ^{13}C NMR, the $>\text{C}=\text{S}$, C—N and C—C resonances of Diaz in the complex are observed at 173.25 ppm, 40.20 ppm, and 19.11 ppm respectively (175.62 ppm, 39.76 ppm, 19.19 ppm for free Diaz). The upfield shift of 2.4 ppm in the $>\text{C}=\text{S}$ resonance is in accordance with the data observed for other cadmium(II) complexes [1, 3, 4, 10].

X-ray structure description. Fig. 1 shows a perspective view of the molecular structure of **1** along with the atom labeling scheme. Selected bond distances and angles are given in Table 2. The structure is ionic and consists of $[\text{Cd}(\text{Diaz})_4]^{2+}$ cationic units and SO_4^{2-} counter ions. The cadmium ion in the cationic complex is coordinated by four Diaz ligands adopting a distorted tetrahedral geometry with the bond angles at Cd(II) varying from $95.38(3)^\circ$ to $119.48(3)^\circ$. The deviation from the tetrahedral geometry is apparently due to the steric interactions between the bulky Diaz molecules which coordinate through the sulfur atom in a monodentate fashion. The relative orientation of the $[\text{SCN}_2]$ mean planes of the four Diaz ligands, characterizing the conformation of the complex molecule, is superimposed by two different hydrogen bonding interactions of the type: $[\text{N}-\text{H}\cdots\text{O}\cdots\text{H}-\text{N}]$ and $[\text{N}-\text{H}\cdots\text{O}-\text{SO}_2-\text{O}\cdots\text{H}-\text{N}]$. The six-membered Diaz ring adopts a *half-chair* conformation with two or three out of plane carbon atoms disordered on two sites each. The Cd—S bond distances ($2.5032(9)$ – $2.5713(10)\text{ \AA}$) and the other bond lengths are in agreement with those reported for the related compounds, *e.g.*, $[\text{Cd}(\text{Diaz})_2(\text{acetate})_2]$ [2], $[\text{Cd}(\text{Diaz})_2\text{I}_2]$ [3], and $[\text{Cd}(\text{2-mercaptopyridine})_4](\text{NO}_3)_2$ [21]. The bond lengths and bond angles around the sulfate sulfur atom are in normal ranges (Table 2). Several examples are also known in which the sulfate ion acts as a monodentate

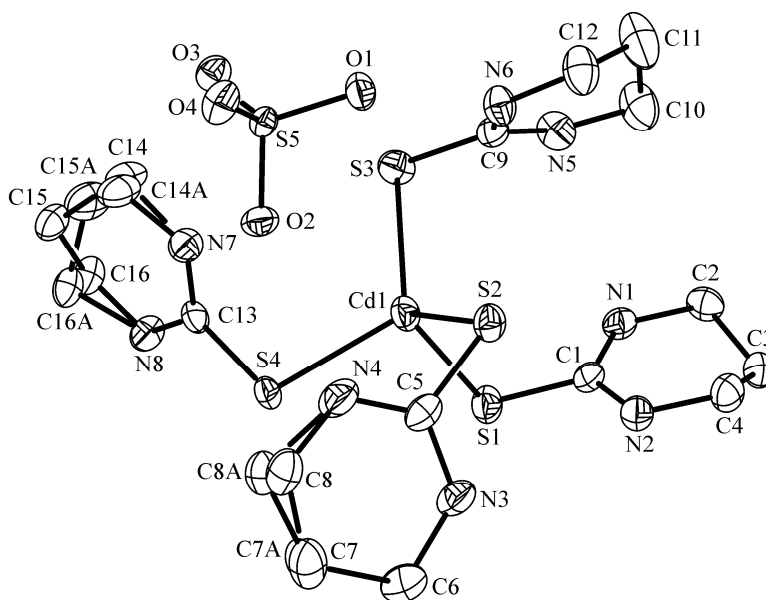


Fig. 1. ORTEP view of compound **1**, including the atomic numbering scheme

Table 2

Selected bond distances (Å) and bond angles (deg.) for 1

Bond distance		Bond angles	
Cd(1)—S(1)	2.5713(10)	S(1)—Cd(1)—S(2)	105.18(3)
Cd(1)—S(2)	2.5262(8)	S(1)—Cd(1)—S(3)	112.36(4)
Cd(1)—S(3)	2.5210(8)	S(1)—Cd(1)—S(4)	95.38(3)
Cd(1)—S(4)	2.5032(9)	S(2)—Cd(1)—S(3)	110.43(3)
C(1)—S(1)	1.738(3)	S(2)—Cd(1)—S(4)	119.48(3)
C(1)—N(1)	1.312(4)	S(3)—Cd(1)—S(4)	112.74(3)
C(2)—N(1)	1.466(5)	Cd(1)—S(1)—C(1)	104.48(10)
S(5)—O(1)	1.474(2)	N(1)—C(1)—S(1)	119.5(2)
S(5)—O(2)	1.481(2)	N(1)—C(1)—N(2)	119.7(3)
S(5)—O(4)	1.467(2)	O(1)—S(5)—O(2)	109.64(13)

or bidentate ligand [1, 36]. The $[\text{Cd}(\text{Diaz})_4]^{2+}$ complex ions pack along the a axis to form columns hosting the sulfate counter ions. The four oxygen atoms of the tetrahedral anion are engaged in both bridging intra- and inter-column $[\text{N}-\text{H}\dots\text{O}-\text{SO}_2-\text{O}\dots\text{H}-\text{N}]$ hydrogen bonding interactions between the adjacent complex molecules generating a three-dimensional hydrogen bonding network (Fig. 2). The details of hydrogen bonds are given in Table 3.

This paper describes the synthesis and crystal structural of the ionic cadmium complex of 1,3-diazinane-2-thione (Diaz). The geometry at cadmium is distorted tetrahedral and the Diaz ligand coordinates through the sulfur atom in a monodentate terminal mode. Different types of $\text{N}-\text{H}\dots\text{O}$ hydrogen bonding interactions between the Diaz ligands and the sulfate anions control the conformation of the complex and extend in a 3D network.

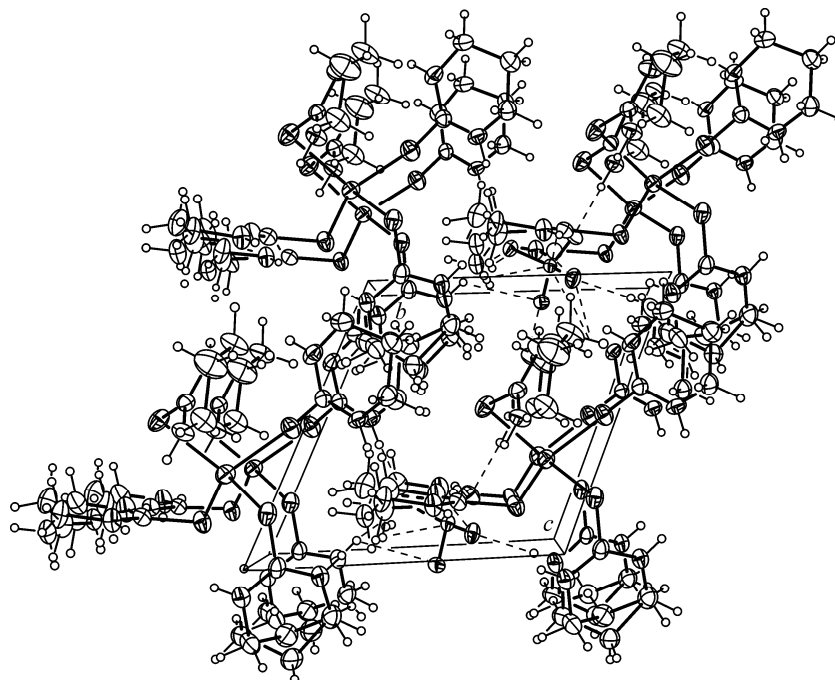


Fig. 2. View of the crystal packing in 1 showing the formation of a 3-dimensional polymeric network

Table 3

Hydrogen bonds in the title complex (Å, deg.)

Donor—H...Acceptor	D—H	H...A	D...A	∠D—H...A
N1—H1...S5	0.860(18)	2.82(3)	3.557(3)	154(4)
N1—H1...O4	0.860(18)	2.10(3)	2.826(3)	142(4)
N2—H2...O3	0.837(19)	2.06(2)	2.869(3)	161(4)
N3—H3...O3	0.833(19)	1.98(2)	2.782(3)	161(4)
N4—H4...O2	0.854(19)	2.06(2)	2.881(4)	162(4)
N5—H5...O4	0.844(19)	2.13(2)	2.959(4)	167(4)
N6—H6...O1	0.844(18)	1.90(2)	2.733(3)	169(4)
N7—H7...O2	0.869(19)	2.01(2)	2.861(3)	165(4)
N8—H8...O1	0.845(19)	1.96(2)	2.756(3)	156(4)

Crystallographic data for compound **1** have been deposited with the Cambridge Crystallographic Data Center via the CCDC Number 795733. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk.

The authors gratefully acknowledge King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia, for the use of the X-ray facility.

REFERENCES

1. *Altaf M., Stoeckli Evans H., Murtaza G., Isab A.A., Ahmad S., Shaheen M.A.* // *J. Struct. Chem.* – 2011. – **52**. – P. 625 – 630.
2. *Mahmood R., Hussain S.G., Fettouhi M., Isab A.A., Ahmad S.* // *Acta Cryst. E.* – 2012. – **68**. – P. m1352 – m1353.
3. *Ahmad S., Amir Q., Naz G., Fettouhi M., Isab A.A., Ruffer T., Lang H.* // *J. Chem. Crystallogr.* – 2012. – **42**. – P. 615 – 620.
4. *Mahmood R., Sadaf S., Isab A.A., Akkurt M., Sharif S., Khan I.U., Tariq J., Ahmad S.* // *Russ. J. Coord. Chem.* – 2012. – **38**. – P. 456 – 460.
5. *Ahmad S., Altaf M., Stoeckli-Evans H., Isab A.A., Malik M.R., Ali S., Shuja S.* // *J. Chem. Crystallogr.* – 2011. – **41**. – P. 1099 – 1104.
6. *Malik M.R., Ali S., Fettouhi M., Isab A.A., Ahmad S.* // *J. Struct. Chem.* – 2010. – **51**. – P. 976 – 979.
7. *Fettouhi M., Malik M.R., Ali S., Isab A.A., Ahmad S.* // *Acta Cryst. E.* – 2010. – **66**. – P. m997.
8. *Nawaz S., Sadaf S., Fettouhi M., Fazal A., Ahmad S.* // *Acta Cryst. E.* – 2010. – **66**. – P. m950.
9. *Nawaz S., Sadaf S., Fettouhi M., Fazal A., Ahmad S.* // *Acta Cryst. E.* – 2010. – **66**. – P. m951.
10. *Wazeer M.I.M., Isab A.A., Fettouhi M.* // *Polyhedron.* – 2007. – **26**. – P. 1725 – 1730.
11. *Marcos C., Alia J.M., Adovasio V., Prieto M., Garcia-Granda S.* // *Acta Cryst. C.* – 1998. – **54**. – P. 1225 – 1229.
12. *Lobana T.S., Sharma R., Sharma R., Sultana R., Butcher R.J.* // *Z. Anorg. Allg. Chem.* – 2008. – **634**. – P. 718 – 723.
13. *Al-Arfaj A.R., Reibenspies J.H., Isab A.A., Hussain M.S.* // *Acta Cryst. C.* – 1998. – **54**. – P. 51 – 53.
14. *Bell N.A., Clegg W., Coles S.J., Constable C.P., Harrington R.W., Hursthouse M.B., Light M.E., Raper E.S., Sammon C., Walker M.R.* // *Inorg. Chim. Acta.* – 2004. – **357**. – P. 2091 – 2099.
15. *Matsunaga Y., Fujisawa K., Amir N., Miyashita Y., Okamoto K.-I.* // *J. Coord. Chem.* – 2005. – **58**. – P. 1047 – 1061.
16. *Beheshti A., Brooks N.R., Clegg W., Hyvadi R.* // *Acta Cryst. E.* – 2005. – **61**. – P. m1383 – m1385.
17. *Moloto M.J., Malik M.A., O'Brien P., Motevalli M., Kolawole G.A.* // *Polyhedron.* – 2003. – **22**. – P. 595 – 603.
18. *Wang X.Q., Yu W.T., Xu D., Lu M.K., Yuan D.R.* // *Acta Cryst. C.* – 2002. – **58**. – P. m336 – m337.
19. *Zhu H.-G., Yang G., Chen X.-M., Ng S.W.* // *Acta Cryst. C.* – 2000. – **56**. – P. e430 – e431.
20. *Rajalingam U., Dean P.W.A., Jenkins H.A.* // *Can. J. Chem.* – 2000. – **78**. – P. 590.
21. *Rajalingam U., Dean P.W.A., Jenkins H.A., Jennings M., Hook J.M.* // *Can. J. Chem.* – 2001. – **79**. – P. 1330.
22. *Yang G., Liu G.-F., Zheng S.-L., Chen X.-M.* // *J. Coord. Chem.* – 2001. – **53**. – P. 269 – 279.

23. *Akrivos P.D.* // *Coord. Chem. Rev.* – 2001. – **213**. – P. 181.
24. *Kaim W., Schwederski B.* *Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life*, John Wiley and Sons Inc, New York, 1994. – P. 335.
25. *Otazo-Sanchez E., Perez-Marin L., Estevez-Hernandez O., Rojas-Lima S., Alonso-Chamarro J.* // *J. Chem. Soc., Perkin Trans. 2.* – 2001. – P. 2211 – 2218.
26. *Sandhya D., Subramanian M.S., Radioanal J.* // *Nuc. Chem.* – 1997. – **224**. – P. 53 – 57.
27. *Lokeshwari H., Chandarapa G.T., Enviro J.* // *Sci. Eng.* – 2006. – **48**. – P. 183 – 188.
28. *Stoev M., Ruseva S., Keremidchieva B.* // *Monatsh. Chem.* – 1994. – **125**. – P. 1215.
29. *Yao J., Zhao G., Han G.* // *J. Mater. Sci. Lett.* – 2003. – **22**. – P. 1491 – 1493.
30. *Mandal T., Stavila V., Rusakova I., Ghosh S., Whitmire K.H.* // *Chem. Mater.* – 2009. – **21**. – P. 5617 – 5626.
31. *Ahmad S., Isab A.A., Perzanowski H.P.* // *Can. J. Chem.* – 2002. – **80**. – P. 1279 – 1284.
32. *Bruker.* SMART and SAINT, Bruker Axs Inc. Madison. Wisconsin, USA, 2008.
33. *Sheldrick G.M.* SADABS. Program for Empirical Absorption correction of Area detector Data. University of Gottingen, Germany, 1996.
34. *Sheldrick G.M.* // *Acta Crystallogr.* – 2008. – **A64**. – P. 112 – 122.
35. *Muller P.* // *Cryst. Rev.* – 2009. – **15**. – P. 57 – 83.
36. *Harvey M., Baggio S., Russi S., Baggio R.* // *Acta Crystallogr.* – 2003. – **C59**. – P. m171 – m174.