

КРАТКИЕ СООБЩЕНИЯ

UDC 548.73:546.443

STRUCTURAL CHARACTERIZATION OF A CADMIUM(II)-SULFATO COMPLEX,
[Cd(*N,N'*-DIETHYL THIOUREA)₄(SO₄)]© 2011 М. Altaf¹, Н. Stoeckli-Evans¹, G. Murtaza², А.А. Isab³,
S. Ahmad^{2*}, М.А. Shaheen⁴¹*Institute of Physics, University of Neuchâtel, CH-2009 Neuchâtel, Switzerland*²*Department of Chemistry, University of Engineering and Technology, Lahore 54890, Pakistan*³*Department of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia*⁴*Department of Chemistry, University of Sargodha, Sargodha, Pakistan*

Received March, 30, 2009

A cadmium(II) complex, tetrakis(*N,N'*-diethylthiourea)sulfatocadmium(II), [Cd(Detu)₄SO₄] (**1**) was prepared and its crystal structure was determined by X-ray crystallography. The crystal structure of the complex consists of an independent molecule with the central cadmium atom coordinated to four thione sulfur atoms of Detu and two oxygen atoms of the sulfate ligand. The Cd atom has a pseudo-octahedral coordination environment with the *cis* angles varying from 57.68 to 126.57°, while the *trans* angles fall in the range of 142 to 169°. The new complex was also characterized by IR and NMR spectroscopy and the spectroscopic data are discussed in terms of the nature of bonding.

Keywords: cadmium sulfate, *N,N'*-diethylthiourea, crystal structure.

We have been interested in the spectroscopic and structural studies of d¹⁰ metal ions with thioamide ligands in an attempt to assess their modes of binding and related structural, spectral, and biological properties [1–10]. The study of the coordination behavior of thiones is of considerable interest due to their variable binding modes and because of the relevance of their binding sites to those in living systems [9–20]. The complexes of zinc(II) and cadmium(II) are particularly important in this regard because they act as structural models for metal binding sites in metallothioneins and metalloregulatory proteins [21–23]. Cadmium(II) complexes with thiones possess a variety of structures ranging from four- to six-coordinate species with tetrahedral and octahedral Cd(II) respectively [24–37]. These studies further reveal the monodentate thione sulfur donating character of the ligands. In some cases, these units further aggregate to form the polymeric structures [28–31], such as [Cd(Metu)₂Cl₂]_n [28]. The present report describes the crystal structure of a cadmium(II) complex with *N,N'*-diethylthiourea, tetrakis(*N,N'*-diethylthiourea)sulfatocadmium(II) [Cd(Detu)₄SO₄] (**1**), which shows significant distortions from the octahedral geometry.

Experimental. Materials. Cadmium sulfate (CdSO₄·8/3H₂O) was obtained from Merck Chemical Company, Germany and *N,N'*-diethylthiourea (Detu) was purchased from Acros Organics, Belgium.

Synthesis of 1. Complex **1** was prepared by adding 2 mmolar methanolic solution of Detu to an aqueous solution of cadmium sulfate (1 mmol, 0.26 g). The reaction mixture was stirred for 30 minutes. The solution was filtered and the filtrate was kept at room temperature for crystallization. As a result, a white crystalline product was obtained that was washed with methanol and dried. Yield = 30 %; Melting point = 171–172 °C.

* E-mail: saeed_a786@hotmail.com

Table 1

Summary of the crystal data and structure determination details

| | |
|--|--|
| <i>Crystal data</i> | |
| Formula | C ₂₀ H ₄₈ CdN ₈ O ₄ S ₅ |
| Formula weight | 737.36 |
| Crystal system | Orthorhombic |
| Space group | <i>Pbca</i> |
| <i>a</i> , <i>b</i> , <i>c</i> (Å) | 16.5358(10), 16.9877(13), 23.6281(17) |
| <i>V</i> (Å ³) | 6637.3(8) |
| <i>Z</i> | 8 |
| ρ _{calc} (g/cm ³) | 1.476 |
| μ (MoK _α) (mm ⁻¹) | 1.011 |
| <i>F</i> (000) | 3072 |
| Crystal size (mm) | 0.49×0.30×0.19 |
| <i>Data collection</i> | |
| Temperature (K) | 173(2) |
| λ MoK _α (Å) | 0.71073 |
| θ Min—Max (deg.) | 2.05—26.00 |
| <i>h</i> , <i>k</i> , <i>l</i> limits | −20:18, −20:20, −29:28 |
| Reflns: Total, Uniq. Data, <i>R</i> _{int} | 42243, 6477, 0.0506 |
| Observed data [<i>I</i> > 2σ(<i>I</i>)] | 4551 |
| Absorption: <i>T</i> _{min} / <i>T</i> _{max} | 0.97083/1.02374 |
| <i>Refinement</i> | |
| <i>N</i> _{ref} , <i>N</i> _{par} | 6477, 349 |
| <i>R</i> , <i>wR</i> ² , <i>S</i> [<i>I</i> > 2σ(<i>I</i>)] | 0.0307, 0.0680, 0.902 |
| <i>w</i> = [σ ² (<i>F</i> _o ²) + (0.0242 <i>P</i>) ² + 1.6454 <i>P</i>] ⁻¹ where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3 | |
| Goodness-of-fit on <i>F</i> ² | 0.902 |
| Min. and Max. Resd. Dens. [e/Å ³] | −0.852, 0.710 |

IR and NMR Measurements. The IR spectrum of complex **1** was recorded as KBr pellets on a Perkin Elmer Spectrum One FTIR spectrophotometer in the 4000—450 cm⁻¹ range. The ¹H and ¹³C NMR spectra were recorded on Bruker AMX 350 MHz using MeOD as solvent. TMS was used as an internal standard.

X-ray Structure Determination. Single crystal data collection for complex **1** was performed at 173K (−100 °C) on a Stoe Mark I-Image Plate Diffraction System [38] equipped with a one-circle goniometer and using MoK_α graphite monochromated radiation. Image plate distance 70 mm, φ rotation scans 0—165°, step Δω = 1.0°, exposures of 2 min per image, 2θ range 4.10—52.00°, *d*_{min} − *d*_{max} = 0.716—17.779 Å. The structure was solved by direct methods using the SHELXS-97 program [39]. The refinement and all further calculations were carried out using SHELXL-97 [23]. The H atoms were included in calculated positions and treated as riding atoms: N—H = 0.88 Å, C—H = 0.98—0.99 Å and *U*_{iso}(H) = 1.2*U*_{eq} (parent N or C atom). The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on *F*². An empirical absorption correction was applied using the MULscanABS routine in PLATON [40]; transmission factors: *T*_{min}/*T*_{max} = 0.97083/1.02374. Crystal data and details of the data collection are summarized in Table 1.

Results and Discussion. IR and NMR Studies. The reaction of CdSO₄ with Detu in a 1:2 molar ratio resulted in a product of empirical composition [Cd(Detu)₄SO₄]₄. In the IR spectrum of **1**, the characteristic bands observed due to Detu were: ν(C=S) at 616 cm⁻¹ and ν(N—H) at 3218 cm⁻¹. For

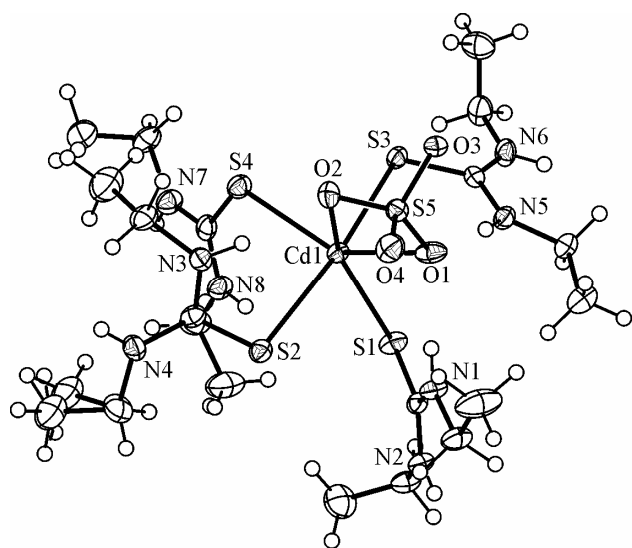


Fig. 1. View of the molecular structure of **1** with complete atom labeling scheme. Displacement ellipsoids are drawn at the 50 % probability level

NMR, the appearance of CH₂ and CH₃ resonances at 39.96 ppm and 14.57 ppm respectively indicated the presence of Detu ligand. However, the >C=S resonance of Detu (which for free Detu appears at 182.07 ppm) was not observed.

X-Ray Structure Description. The molecular structure of **1**, along with the crystallographic numbering scheme, is shown in Fig. 1. The selected bond distances and bond angles are given in Table 2. The structure is based on monomeric molecules. In the monomeric unit, the coordination polyhedra around the cadmium ion is a distorted octahedron constituted by four Detu and one SO₄²⁻ ligands. Diethylthiourea ligands behave as S-donors and are binding in a terminal mode, although the bridging mode has also been observed in some other Cd-thiourea systems, for example, in [Cd(Metu)₂Cl₂]_n (Metu = *N*-methylthiourea) [29]. The sulfate ion acts as a bidentate ligand with two oxygen atoms oriented in *cis* position. The sulfate ion has also been reported as coordinating to transition metals through one, two or three O atoms, giving rise to monomeric, dimeric or polymeric structures [44–48]. However, the presence of the terminal bidentate sulfate ion in the coordination sphere

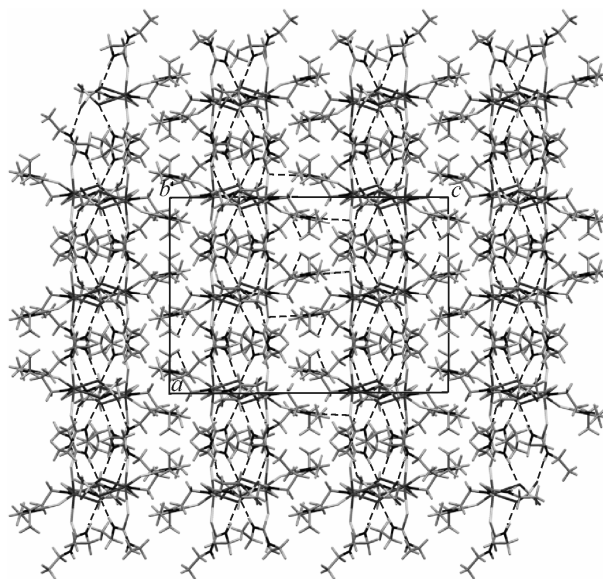
free Detu these bands are observed at 642 and 3215 cm⁻¹ respectively. A low frequency shift in the ν(C=S) band and a high frequency shift in ν(N—H) indicate the existence of the thione form of Detu in the solid state. Sharp bands at 1108, 961, and 598 cm⁻¹ indicate the presence of the coordinated SO₄²⁻ ion [41–43]. In the ¹H NMR spectrum of the complex, the CH₃ and CH₂ signals of Detu are observed at 1.20 ppm and 3.31 ppm respectively (1.07 ppm and 3.35 ppm for the free ligand), while the N—H resonance could not be detected. In the ¹³C

Table 2

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

| Bond distances | | | | | |
|-----------------|-----------|-----------------|-----------|-----------------|------------|
| Cd(1)—S(1) | 2.6337(7) | S(2)—C(6) | 1.727(3) | N(3)—C(6) | 1.330(3) |
| Cd(1)—S(2) | 2.6830(8) | S(3)—C(11) | 1.722(3) | N(3)—C(7) | 1.463(3) |
| Cd(1)—S(3) | 2.6702(7) | S(4)—C(16) | 1.703(3) | S(5)—O(4) | 1.452(2) |
| Cd(1)—S(4) | 2.6390(7) | N(1)—C(1) | 1.326(3) | S(5)—O(3) | 1.464(2) |
| Cd(1)—O(1) | 2.508(2) | N(1)—C(2) | 1.457(3) | S(5)—O(2) | 1.489(2) |
| Cd(1)—O(2) | 2.413(2) | N(1)—C(1) | 1.326(3) | S(5)—O(1) | 1.4910(19) |
| S(1)—C(1) | 1.727(3) | N(1)—C(2) | 1.457(3) | | |
| Bond angles | | | | | |
| O(2)—Cd(1)—O(1) | 57.62(6) | O(1)—Cd(1)—S(3) | 87.63(5) | S(3)—Cd(1)—S(2) | 169.22(2) |
| O(2)—Cd(1)—S(1) | 145.79(5) | S(1)—Cd(1)—S(3) | 96.71(2) | C(1)—S(1)—Cd(1) | 106.55(9) |
| O(1)—Cd(1)—S(1) | 90.51(4) | S(4)—Cd(1)—S(3) | 80.49(2) | S(5)—O(1)—Cd(1) | 96.34(10) |
| O(2)—Cd(1)—S(4) | 87.19(5) | O(2)—Cd(1)—S(2) | 92.20(5) | S(5)—O(2)—Cd(1) | 100.46(10) |
| O(1)—Cd(1)—S(4) | 141.96(4) | O(1)—Cd(1)—S(2) | 103.12(5) | O(3)—S(5)—O(1) | 109.00(12) |
| S(1)—Cd(1)—S(4) | 126.56(2) | S(1)—Cd(1)—S(2) | 82.67(2) | O(2)—S(5)—O(1) | 105.58(12) |
| O(2)—Cd(1)—S(3) | 94.22(5) | S(4)—Cd(1)—S(2) | 91.20(2) | | |

Fig. 2. View of the polymeric chain structure of **1** with NH...O hydrogen bonding interactions along the *b* axis



is rare. The *cis* O—Cd—O angle is considerably smaller than the expected 90° { $57.62(6)^\circ$ }, which is probably a result of the ring strain created by the 4-membered Cd—O—S—O ring. The opposite *cis* S—Cd—S angle is consequently increased from 90° . The *trans* angles are also much smaller than 180° (Table 2). The values are indicative of a significant distortion of the CdS₄O₂ octahedra. The Cd—S—C bond angles varying from $106.55(9)$ — $109.76(10)^\circ$ are nearly equal to the tetrahedral value. The carbon atoms in N—C=S moieties of the ligands are *sp*²-hybridized. The Cd—S distances of $2.6337(7)$ — $2.6830(8)$ Å (Table 2) and other bond lengths observed in the title complex are comparable to those in the reported complexes [24—34]. The Cd—S bond lengths are slightly longer than those observed for a tetrahedral Cd(II) complex of the same ligand, [Cd(Detu)₂Cl₂] ($2.497(4)$ & $2.519(3)$ Å [29]) showing that an increase in coordination number lengthens the bond distances. Coordination did not affect the dimensions of the sulfate moiety; no significant differences are observed among the S—O distances involving either coordinated or uncoordinated O atoms. The mean S—O distance $1.474(2)$ Å is similar to that reported for the free anion (a mean value of $1.472(8)$ Å for 118 structures) [47].

Within the crystal there are extensive hydrogen bonds involving N—H of Detu (as donor) and oxygen atoms of sulfate (as acceptor). All N—H bonded hydrogen atoms are involved in hydrogen bonding. Both intermolecular and intramolecular hydrogen bonds are observed in the solid state structure of **1**. These non-covalent intermolecular interactions result in a hydrogen bonded polymeric structure as shown in Fig. 2. Hydrogen bond length details are listed in Table 3.

The present report shows that the interaction of *N,N'*-diethylthiourea with cadmium sulfate results in a highly distorted octahedral complex in which the sulfate ion is coordinated in a bidentate terminal mode.

Supplementary data. Crystallographic data (excluding structure factors) for structure **1** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 719644 CCDC (**1**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 3

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

| Donor—H...Acceptor | D—H | D...A | H...A | D—H...A | Donor—H...Acceptor | D—H | D...A | H...A | D—H...A |
|---------------------------|------|-------|----------|---------|----------------------------|------|-------|----------|---------|
| N1—H1N...O1 | 0.88 | 1.97 | 2.848(3) | 176 | N5—H5N...O1 | 0.88 | 2.06 | 2.933(3) | 174 |
| N2—H2N...O3 ⁱ | 0.88 | 2.05 | 2.860(3) | 152 | N6—H6N...O4 ⁱⁱⁱ | 0.88 | 2.01 | 2.805(3) | 150 |
| N3—H3N...O2 | 0.88 | 1.96 | 2.823(3) | 166 | N7—H7N...S3 ^{iv} | 0.88 | 2.56 | 3.349(2) | 150 |
| N4—H4N...O3 ⁱⁱ | 0.88 | 2.07 | 2.902(3) | 158 | N8—H8N...S2 | 0.88 | 2.74 | 3.490(2) | 144 |

Symmetry codes: ⁱ $-x, y-1/2, -z+1/2$; ⁱⁱ $x+1/2, y, -z+1/2$; ⁱⁱⁱ $x-1/2, y, -z+1/2$; ^{iv} $-x, y-1/2, -z+1$.

REFERENCES

1. Ahmad S., Isab A.A., Arab M. // Polyhedron. – 2002. – **21**. – P. 1267 – 1271.
2. Ahmad S., Isab A.A., Ashraf W. // Inorg. Chem. Comm. – 2002. – **5**. – P. 816 – 816.
3. Ahmad S., Isab A.A., Perzanowski H.P. // Transition Met. Chem. – 2002. – **27**. – P. 782 – 785.
4. Ahmad S., Isab A.A., Perzanowski H.P. // Can. J. Chem. – 2002. – **80**. – P. 1279 – 1284.
5. Isab A.A., Fettouhi M.B., Ahmad S., Ouahab L. // Polyhedron. – 2003. – **22**. – P. 1349 – 1354.
6. Ashraf W., Ahmad S., Isab A.A. // Transition Met. Chem. – 2002. – **29**. – P. 400 – 404.
7. Al-Maythalony B.A., Wazeer M.I.M., Isab A.A. et al. // Spectroscopy. – 2008. – **22**. – P. 361 – 370.
8. Ali S., Malik M.R., Isab A.A., Ahmad S. // J. Coord. Chem. – 2009. – **62**. – P. 475 – 480.
9. Zoufalá P., Rüffer T., Lang H. et al. // Anal. Sci.: X-ray Structure Analysis Online. – 2007. – **23**. – P. x219 – x220.
10. Hanif M., Ahmad S., Altaf M., Stoeckli-Evans H. // Acta Crystallogr. – 2007. – **E63**. – P. m2594.
11. Nadeem S., Rauf M.K., Ahmad S. et al. // Transition Met. Chem. – 2009. – **34**. – P. 197 – 202.
12. Serrano J.L., Perez J., Sanchez G. et al. // Transition Met. Chem. – 2002. – **27**. – P. 105 – 109.
13. Raper E.S. // Coord. Chem. Rev. – 1985. – **61**. – P. 115 – 184.
14. Raper E.S. // Coord. Chem. Rev. – 1994. – **129**. – P. 91 – 156.
15. Raper E.S. // Coord. Chem. Rev. – 1996. – **153**. – P. 199 – 255.
16. Akrivos P.D. // Coord. Chem. Rev. – 2001. – **213**. – P. 181 – 210.
17. del Campo R., Criado J.J., Gheorghe R. et al. // J. Inorg. Biochem. – 2004. – **98**. – P. 1307 – 1314.
18. Rodríguez-Fernández E., Manzano J.L., Benito J.J. et al. // J. Inorg. Biochem. – 2005. – **99**. – P. 1558 – 1572.
19. Lobana T.S., Khanna S., Butcher R.J. et al. // Polyhedron. – 2006. – **25**. – P. 2755 – 2763.
20. Marverti G., Cusumano M., Ligabue A. et al. // J. Inorg. Biochem. – 2008. – **102**. – P. 699 – 712.
21. Baggio R., Gerland M.T., Percec M. // J. Chem. Soc., Dalton Trans. – 1993. – P. 3367 – 3372.
22. Kaim W., Schwederski B. Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life. – New York: John Wiley and Sons Inc., 1994. – P. 367.
23. Stillman M.J., Shaw III C.F., Suzuki K.T. / Metallothionein. – New York: VCH Publishers Inc., 1992.
24. Tadjarodi, Adhami F., Gharehdaghi Z. // Anal. Sci.: X-ray Structure Analysis Online. – 2007. – **23**. – P. x35 – x36.
25. Wazeer M.I.M., Isab A.A., Fettouhi M. // Polyhedron. – 2007. – **26**. – P. 1725 – 1730.
26. Beheshit A., Brooks N.R., Clegg W., Hyvadi R. // Acta Crystallogr. – 2005. – **E61**. – P. m1383 – m1385.
27. Matsunaga Y., Fujisawa K., Amir N. et al. // Coord. Chem. – 2005. – **58**. – P. 1047 – 1061.
28. Moloto M.J., Malik M.A., O'Brien P. et al. // Polyhedron. – 2003. – **22**. – P. 595 – 603.
29. Wang X.Q., Yu W.T., Xu D. et al. // Acta Crystallogr. – 2002. – **C58**. – P. m336 – m337.
30. Yang G., Liu G.-F., Zheng S.-L., Chen X.-M. // J. Coord. Chem. – 2001. – **53**. – P. 269 – 279.
31. Zhu H.-G., Yang G., Chen X.-M., Ng S.W. // Acta Crystallogr. – 2000. – **C56**. – P. e430 – e431.
32. Al-Arfaj A.R., Reibenspies J.H., Isab A.A., Hussain M.S. // Acta Crystallogr. – 1998. – **C54**. – P. 51 – 53.
33. Corao E., Baggio S. // Inorg. Chim. Acta. – 1969. – **3**. – P. 617 – 622.
34. Fettouhi M., Wazeer M.I.M., Isab A.A. // Inorg. Chem. Commun. – 2008. – **11**. – P. 252 – 255.
35. Rajalingam U., Dean P.W.A., Jenkins H.A. et al. // Can. J. Chem. – 2001. – **79**. – P. 1330 – 1337.
36. Rajalingam U., Dean P.W.A., Jenkins H.A. // Can. J. Chem. – 2000. – **78**. – P. 590 – 597.
37. Bell N.A., Clegg W., Coles S.J. et al. // Inorg. Chim. Acta. – 2004. – **357**. – P. 2091 – 2099.
38. Stoe & Cie, X-Area V1.26 & X-RED32 V1.26 Software, Stoe & Cie GmbH, Darmstadt, Germany, 2005.
39. Sheldrick G.M. // Acta Crystallogr. – 2008. – **A64**. – P. 112.
40. Spek A.L. // J. Appl. Crystallogr. – 2003. – **36**. – P. 7 – 13.
41. Zalkind O.A., Makarov D.V., Makarov V.N. // J. Anal. Chem. – 2004. – **59**. – P. 722 – 723.
42. Shagabutdinova S.N., Fedotov M.A., Belyaev A.V. // Russ. J. Coord. Chem. – 2007. – **33**. – P. 140 – 144.
43. Chumakov Y.M., Janneau E., Bezhenari N.P. et al. // Russ. J. Coord. Chem. – 2008. – **34**. – P. 44 – 52.
44. Zhao W., Fan J., Song Y. et al. // Dalton Tran. – 2005. – P. 1509 – 1517.
45. Sofetis A., Papaefstathiou G.S., Terzis A. et al. // Z. Naturforsch. – 2004. – **59B**. – P. 291 – 297.
46. Harvey M., Baggio S., Mombro A., Baggio R. // Acta Crystallogr. – 2000. – **C56**. – P. 771 – 774.
47. Harvey M., Baggio S., Mombro A., Baggio R. // Acta Crystallogr. – 2003. – **C59**. – P. m171 – m174.
48. Coxall R.A., Lindoy L.F., Miller H.A. et al. // Dalton Trans. – 2003. – P. 55 – 64.