



**2D polymeric cadmium(II) complexes containing
1,3-imidazolidine-2-thione (Imt) ligand,
[Cd(Imt)(H₂O)₂(SO₄)]_n and [Cd(Imt)₂(N₃)₂]_n**

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2D Polymeric cadmium(II) complexes containing 1,3-imidazolidine-2-thione (Imt) ligand, $[\text{Cd}(\text{Imt})(\text{H}_2\text{O})_2(\text{SO}_4)]_n$ and $[\text{Cd}(\text{Imt})_2(\text{N}_3)_2]_n$

Rashid Mahmood^{a*}, Saeed Ahmad^{b*}, Mohammed Fettouhi^c, Thierry Roisnel^d,
Mazhar Amjad Gilani^e, Kashif Mehmood^f, Ghulam Murtaza^f, Anvarhusein A. Isab^c

^aDepartment of Chemistry, University of Azad Jammu and Kashmir, Chela Campus, Muzaffarabad, Pakistan

^bDepartment of Chemistry, College of Sciences and Humanities, Prince Sattam bin Abdulaziz University, Al-Kharj 11942, Saudi Arabia

^cDepartment of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

^dCentre de Diffractométrie X (CDIFX), Institut des Sciences Chimiques de Rennes UMR6226 CNRS - Université de Rennes 1 35042 Rennes Cedex, France

^eDepartment of Chemistry, COMSATS Institute of Information Technology, Lahore, Pakistan

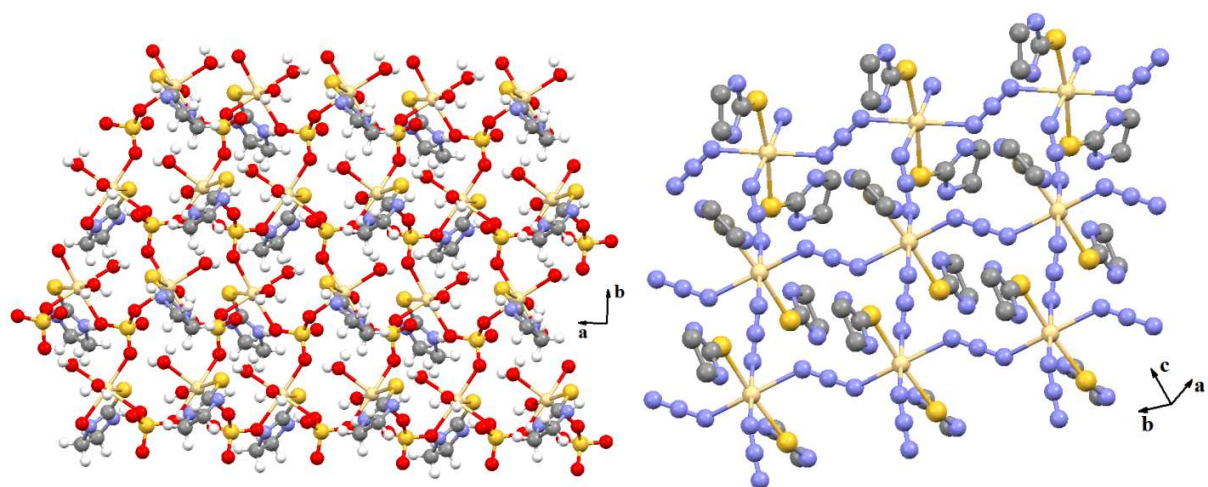
^fDepartment of Chemistry, University of Engineering and Technology, Lahore 54890, Pakistan

*Corresponding authors (E-mail: rashid_meh786@yahoo.com, saeed_a786@hotmail.com)

Abstract

The present study aims at preparing and carrying out the structural investigation of two polymeric cadmium(II) complexes of imidazolidine-2-thione (Imt) based on sulfate or azide ions, $[\text{Cd}(\text{Imt})(\text{H}_2\text{O})_2(\text{SO}_4)]_n$ (**1**) and $[\text{Cd}(\text{Imt})_2(\text{N}_3)_2]_n$ (**2**). The structures of the complexes were determined by single crystal X-ray analysis. Both compounds, **1** and **2** crystallize in the form of 2D coordination polymers and the cadmium(II) ion is six-coordinate having a distorted octahedral geometry in each compound. In **1**, the metal ion is bonded to one sulfur atom of Imt and five oxygen atoms with two from water and three of bridging sulfate ions. In **2**, the cadmium coordination sphere is completed by two Imt molecules binding through the sulfur atoms and four nitrogen atoms of bridging azide ions. The crystal structures are stabilized by intra and intermolecular hydrogen bonding interactions. The complexes were also characterized by IR and NMR spectroscopy and the spectroscopic data is consistent with the binding of the ligands.

Keywords: Cadmium; Imidazolidine-2-thione; Sulfate; Azide; Crystal structure



1. Introduction

Cadmium(II) is known to form a wide variety of 1:1 to 1:4 complexes with thiones (L), with the structural arrangements generally based on tetrahedral and octahedral coordination environments. The 1:1 complexes [1-4] for example, $[\text{Cd}(\text{Tu})(\text{H}_2\text{O})_2(\text{SO}_4)]_n$ [2] and $[\text{Cd}(\text{MeImt})(\text{SeCN})_2]_n$ [4] (MeImt = N-methylimidazolidine-2-thione) usually exist in the polymeric form. The structures of the 1:2 complexes such as, $[\text{Cd}(\text{Tu})_2\text{X}_2]$ [5], $[\text{Cd}(\text{Dmtu})_2\text{X}_2]$ [6,7], $[\text{Cd}(\text{Tmtu})_2\text{X}_2]$ [8-10] or $[\text{Cd}(\text{Imt})_2\text{X}_2]$ [11,12] ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) are the most common and often consist of discrete monomeric molecules with a tetrahedrally [5-21] (or octahedrally [22,23]) coordinated Cd(II) ion. In some cases, polymeric species are formed through bridging sulfur or nitrogen atoms [21, 24-29], *e.g.*, $[\text{Cd}(\text{Metu})_2(\text{SCN})_2]_n$ [24] and $[\text{Cd}(\text{Imt})_2(\text{SCN})_2]_n$ [25]. The 1:3 compounds are rare. The crystal structure of $[\text{Cd}(\text{Tu})_3(\text{SO}_4)]$ shows that the molecule is a dimer, and the coordination around the metal atom is intermediate between square pyramidal and trigonal bipyramidal [30]. Another such compound is known in the form of a co-crystal of $[\text{Cd}(\text{Tu})_2(\text{H}_2\text{O})_4]\text{SO}_4$ and $[\text{Cd}(\text{Tu})_3(\text{H}_2\text{O})_3]\text{SO}_4$ [31]. The complexes with a Cd:thione ratio of 1:4 may be ionic or nonionic. In the ionic complexes like $[\text{Cd}(\text{2-mercaptopyridine})_4](\text{NO}_3)_2$ [32] or $[\text{Cd}(\text{Diaz})_4]\text{SO}_4$ (Diaz = 1,3-diazinane-2-thione) [33], the Cd(II) ion possesses a tetrahedral environment. The molecular species for instance, $[\text{Cd}(\text{Diaz})_4\text{Cl}_2]$ [34] display a distorted octahedral geometry around the metal ion [29,34,35]. These structural studies show that thioureas or thiones coordinate to cadmium(II) *via* the sulfur atom. We have reported earlier the crystal structures of several cadmium(II) complexes of heterocyclic thiones [4,5-10,14-17,23,24,33-35]. To investigate further about the structural aspects of such complexes, we report in this work the spectroscopic data and the X-ray structures of two new 2D polymeric cadmium(II) complexes of imidazolidine-2-thione (Imt), $[\text{Cd}(\text{Imt})(\text{H}_2\text{O})_2(\text{SO}_4)]_n$ (**1**) and $[\text{Cd}(\text{Imt})_2(\text{N}_3)_2]_n$ (**2**). The main goal of the present study is to exploit the effect of binding flexibility of sulfate and azide ions for the preparation of Cd-Imt polymers.

2. Experimental

2.1. Materials

Cadmium sulfate ($\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$) and NaN_3 were obtained from Merck Chemical Company, Germany. Imidazolidine-2-thione was prepared according to the method reported in the literature [36].

2.2. Synthesis of $[\text{Cd}(\text{Imt})(\text{H}_2\text{O})_2(\text{SO}_4)]_n$ (**1**) and $[\text{Cd}(\text{Imt})_2(\text{N}_3)_2]$ (**2**)

Complex **1** was prepared by adding 0.10 g (1.0 mmol) Imt in 15 mL methanol to an aqueous solution (5 mL) of cadmium sulfate (0.26 g, 1.0 mmol) and stirring the mixture for 30 minutes. Mixing resulted in a colorless solution. The clear solution was kept at room temperature for crystallization. As a result, a white crystalline product was obtained, that was washed with methanol and dried. Yield = 65 %, melting point = 275-278 °C. IR (cm^{-1}): ν = 3416 (O-H), 3311 (N-H), 2888 (C-H), 1489 (C-N), 1163 (C=S), 1025, 976 (S-O), δ = 1533, 1521 (N-H) (Imt, ν = 3236, 2882, 1456, 1195; δ = 1515, 1497 cm^{-1}). ^1H NMR (DMSO-d_6), δ (ppm): 3.52, 8.20 (Imt, δ = 3.62, 7.98). ^{13}C NMR (DMSO-d_6), δ (ppm): 45.16, 181.02 (Imt, δ = 44.0, 183.4).

For preparation of **2**, 0.20 g (2.0 mmol) Imt in 15 mL methanol was added to 0.26 g (1 mmol) cadmium sulfate in 5 mL water. On mixing a clear solution was obtained that was stirred for 15 minutes. Then 2 equivalents of NaN_3 (0.135 g) in 10 mL water were added. After stirring for 30 minutes, the colorless solution was filtered and kept at room temperature for crystallization. An off white crystalline product was obtained, that was washed with methanol and dried. Yield = 60 %, melting point = 180-182 °C. IR (cm^{-1}): ν = 3331, 3246 (N-H), 2892 (C-H), 2031 ($\text{N}\equiv\text{N}$), 1470 (N-H), 1196 (C=S), δ = 1509. ^1H NMR (DMSO-d_6), δ (ppm): 3.52, 8.09. ^{13}C NMR (DMSO-d_6), δ (ppm): 44.62, 182.86.

2.3. IR and NMR Measurements

The IR spectra were recorded on a Nicolet iS5 FTIR spectrophotometer using Diamond ATR accessories over the range 4000–500 cm^{-1} with the resolution of 2 cm^{-1} . The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra in DMSO-d_6 were recorded 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.

2.4 X-ray Structure Determination

Single-crystal data collections were performed at 150 K on a Bruker AXS D8 VENTURE diffractometer using a multilayer graphite mono-chromated $MoK\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The data were collected, integrated and reduced using SAINT [37]. An empirical absorption correction was carried out using SADABS [38]. The structure was solved with direct methods using SHELXT [39] and refined by full matrix least square methods based on F^2 , using SHELXTL [40]. Graphics were generated using ORTEP3 [41] and Mercury [42]. All non-hydrogen atoms were refined with anisotropic displacement parameters. For the N-H and O-H hydrogen atoms, coordinates were refined with the U_{iso} values being set to 1.2Ueq of the carrying atoms. The methylene H atoms were included at calculated positions using a riding model with U_{iso} values set to 1.2Ueq of the carbon atoms. Crystal data and details of the data collection are summarized in Table 1.

3. Results and Discussion

3.1. X-ray Structure Studies

The molecular structure of compound **1** is illustrated in Figure 1. Selected bond angles and distances are given in Table 1. The compound crystallizes in *Pbca* space group in the form of a 2D polymer comprising of $[Cd(Imt)(H_2O)_2(SO_4)]$ units (Figure 2). The 2D wavy network is characterized by 12-membered ring motifs $[CdOSO]_3$, where the cadmium ion is hexa-coordinate as $[Cd(Imt)(OH_2)_2(OSO_3)_3]$. It is bonded to two water molecules in a *cis* position, the sulfur atom of the terminal imidazolidine-2-thione ligand, in addition to three meridional oxygen atoms, each belonging to a sulfate anion (Figure 1). Hydrogen bonding interactions of the type $O_{\text{water}} \cdots O_{\text{sulfate}}$ take place. The geometry around the metal ion is distorted octahedral, the *cis* bond angles being in the range $82.68(5) - 103.65(4)^\circ$, while the *trans* angles are between $169.67(5)$ and $170.58(5)^\circ$. The Cd-S bond distance is $2.5354(6) \text{ \AA}$ and the Cd-O bond distances are in the range $2.2737(15) \text{ \AA} - 2.3628(14) \text{ \AA}$. These values are in agreement with those reported for aqua(bipyridine)(imidazolidine-2-thione)sulfatocadmium(II) complex [3] and other Cd-Imt complexes [11,12].

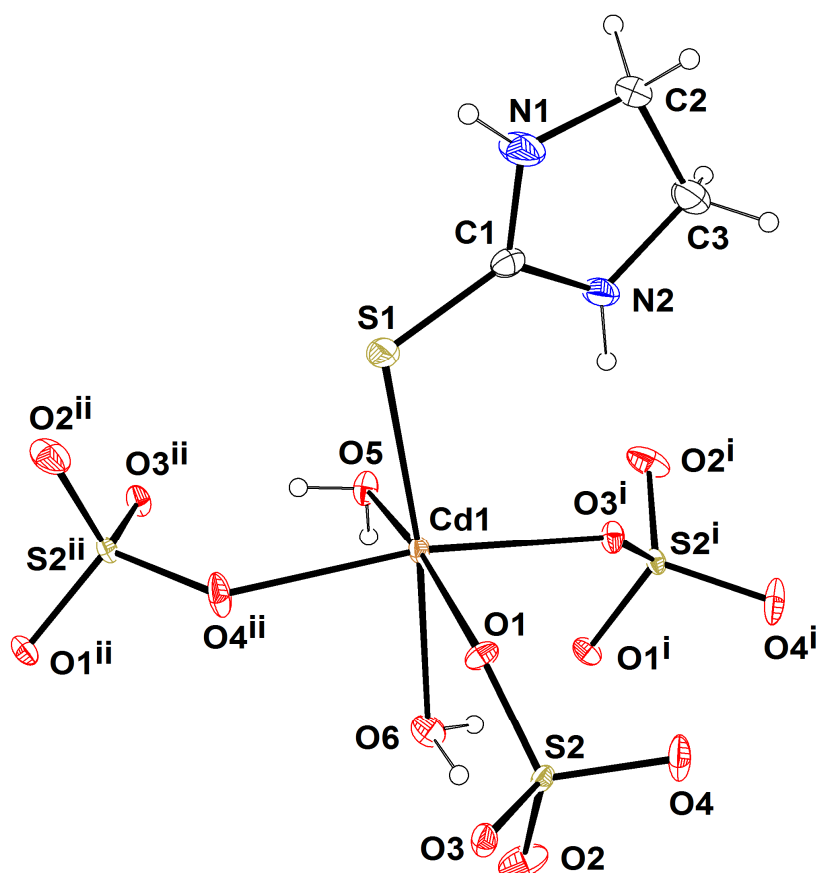


Figure 1. ORTEP diagram of the molecular structure of compound **1** showing the atomic labeling scheme. Thermal ellipsoids have been drawn at 50% probability level. Symmetry codes: $i = x+1/2, y, -z+1/2$; $ii = 1-x, y+1/2, -z+1/2$

The sulfate anion, acting as a tridentate ligand, is bridging two cadmium ions in one 12-membered ring motif and a third cadmium ion in an adjacent motif. The fourth sulfate oxygen atom is non-coordinated. The stacked 2D networks are interconnected through N-H...O hydrogen bonding interactions involving a layer of imidazolidinethione ligands and the coordinated water molecules (Figure 3). The H-bond parameters are given in Table 3.

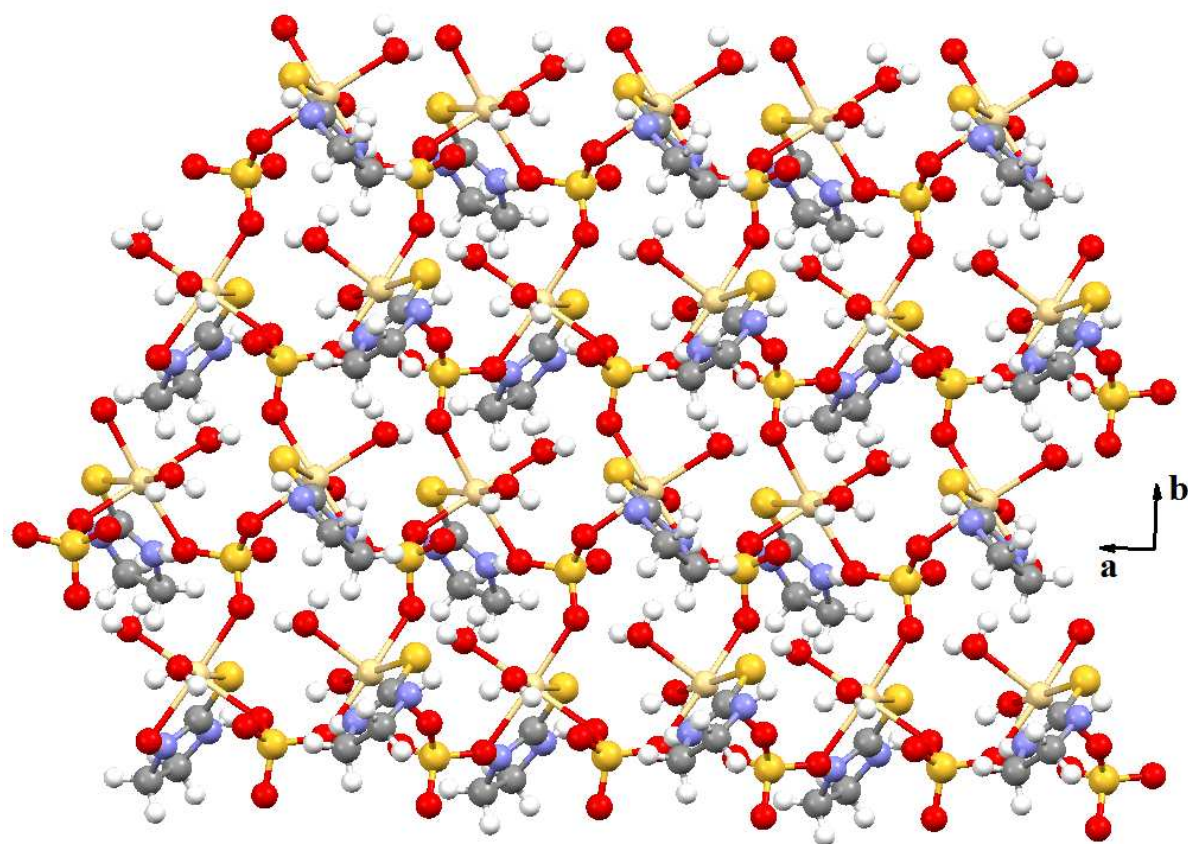


Figure 2. View of the 2D network in compound 1

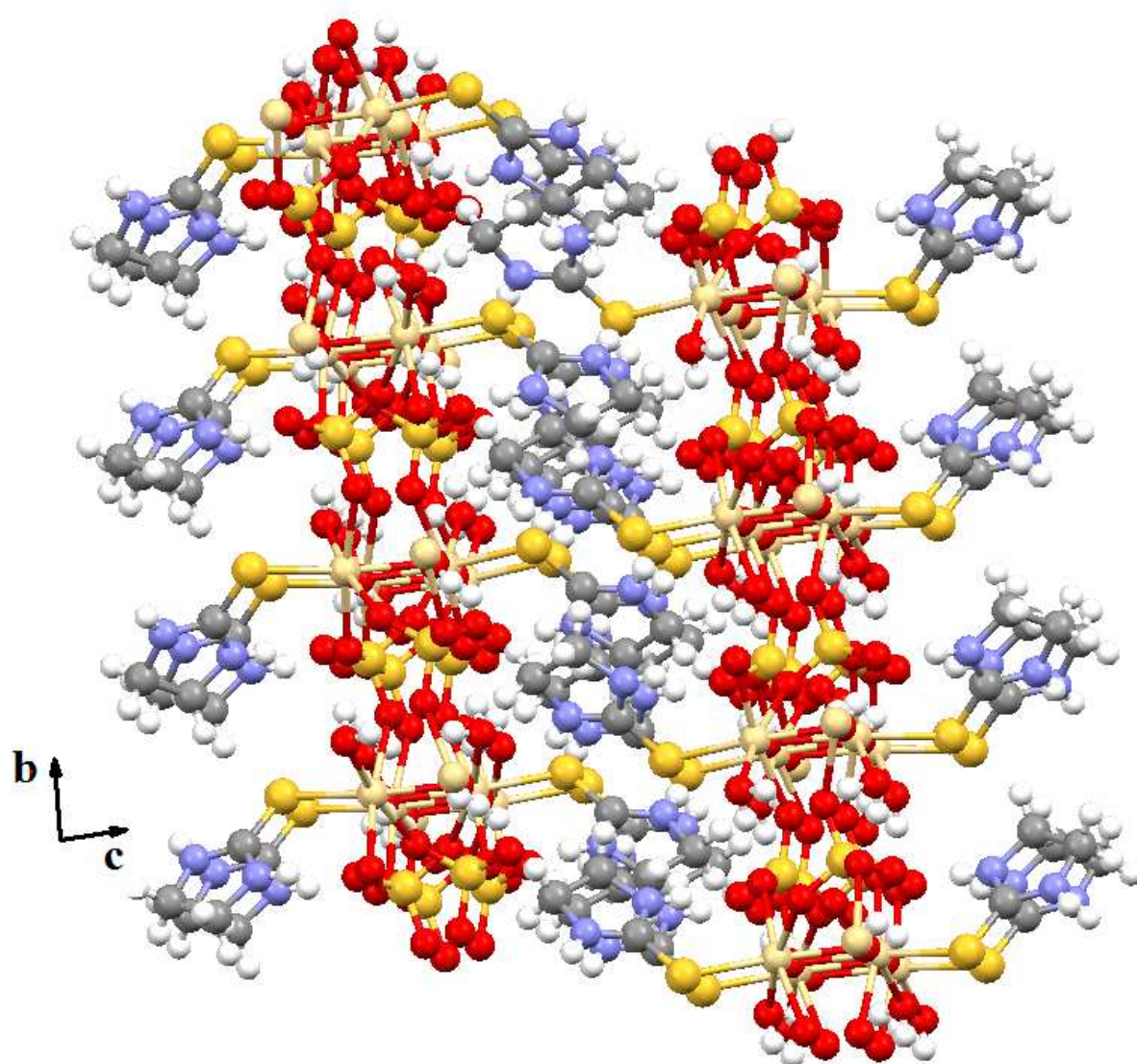


Figure 3. Stacking of the 2D networks in compound **1** to form a 3D structure

The molecular structures of **2** along with the atom labeling scheme is displayed in Figure 4 and, selected bond distances and angles are listed in Table 2. The compound crystallizes in *C2/c* space group. The solid state structure consists of a 2D polymer based on $[\text{Cd}(\text{Imt})_2(\text{N}_3)_2]$ units. The azide anion forms an end-to-end bridge between two cadmium ions resulting into a 2D network based on a 16-membered ring motif $[\text{CdN}_3]_4$ (Figure 5). Within the 2D network, the cadmium ion is bonded to 4 nitrogen atoms, each belonging to an azide anion, in addition to two sulfur atoms of the terminal imidazolidine-2-thione ligands in a *trans* position. The geometry around the metal ion is distorted octahedral. The *cis* bond angles are in the range $81.99(4) - 100.72(4)^\circ$, while the *trans* angles are between $171.28(5)$ and $177.07(4)^\circ$. The Cd-N bond distances fall in the range $2.3589(15) \text{ \AA} - 2.4884(15) \text{ \AA}$. These are in agreement with those reported for other azido cadmium compounds [34,43,44]. The two Cd-S bond lengths are $2.6114(5)$ and $2.6205(5) \text{ \AA}$ respectively, which are slightly greater than in **1** ($2.5354(6) \text{ \AA}$). The Cd-N=N moieties are bent with the bond angles of $125.33(10)$ - $134.97(11)^\circ$ respectively. The N_3^- ions are symmetrical and nearly linear. The structure of **2** is somewhat similar to that of a related complex, $[\text{Cd}(\text{Diaz})_2(\text{N}_3)_2]_n$ [34]. The 2D network sheets pack to give layers separated by a second layer formed by the axially coordinated Imt ligands (Figure 6). The solid state structure exhibits a complex network of hydrogen bonding interactions of the type N-H...N and N-H...S. The H-bond parameters are mentioned in Table 3.

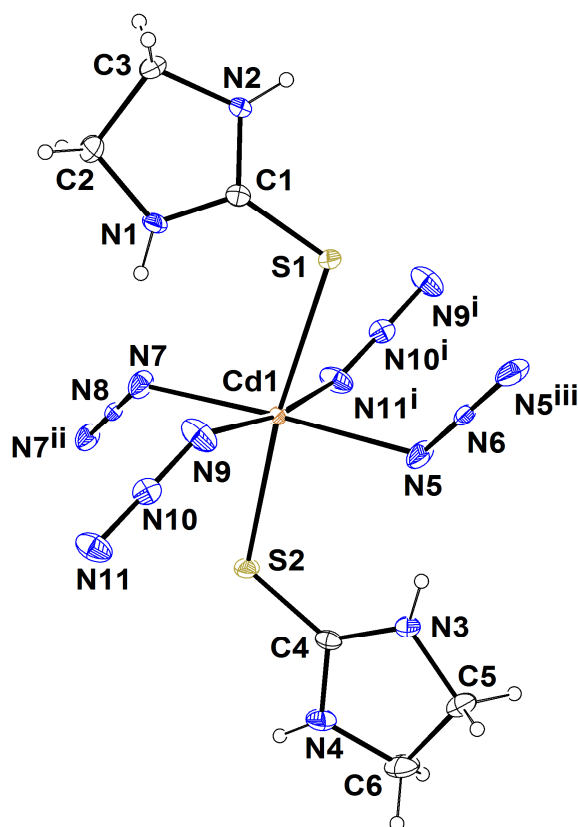


Figure 4. ORTEP diagram of the molecular structure of compound **2** showing the atomic labeling scheme. Thermal ellipsoids have been drawn at 50% probability level. Symmetry codes: i = x, 1+y, z ; ii = -x+1/2, -y+3/2, 1-z ; iii = 1-x, y, -z+3/2

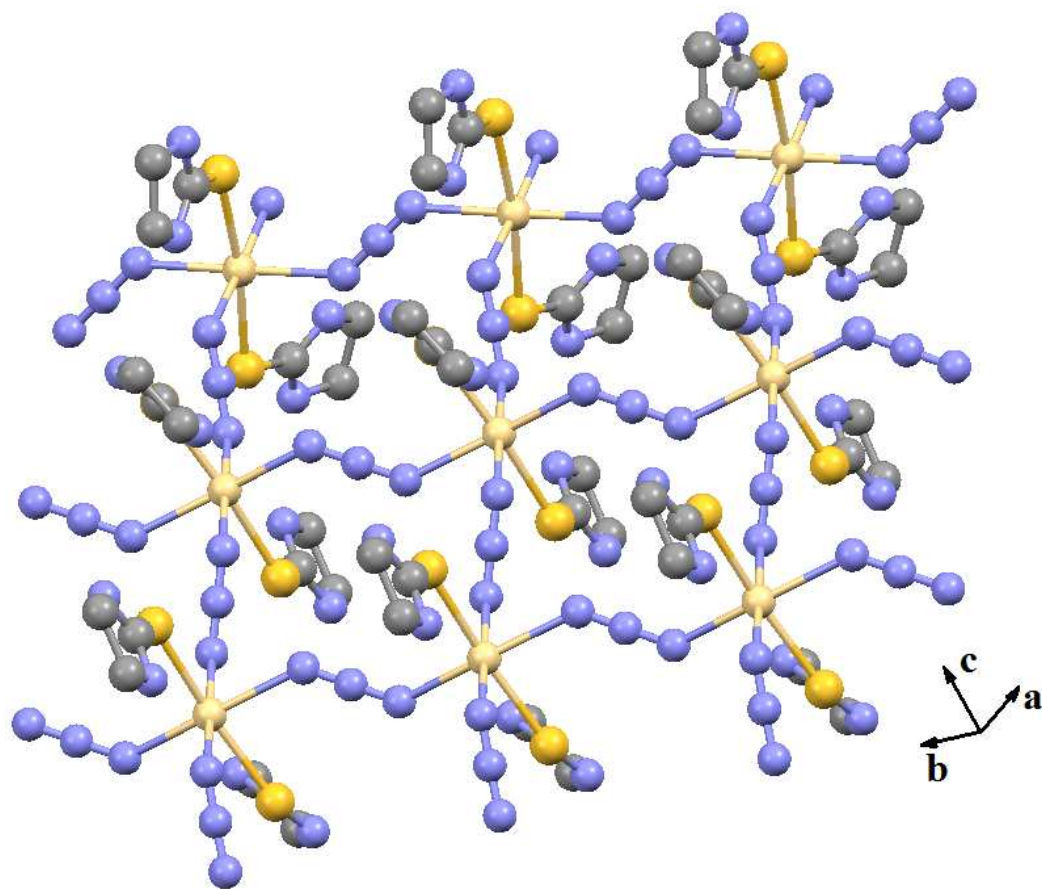


Figure 5. View of the 2D network in compound 2

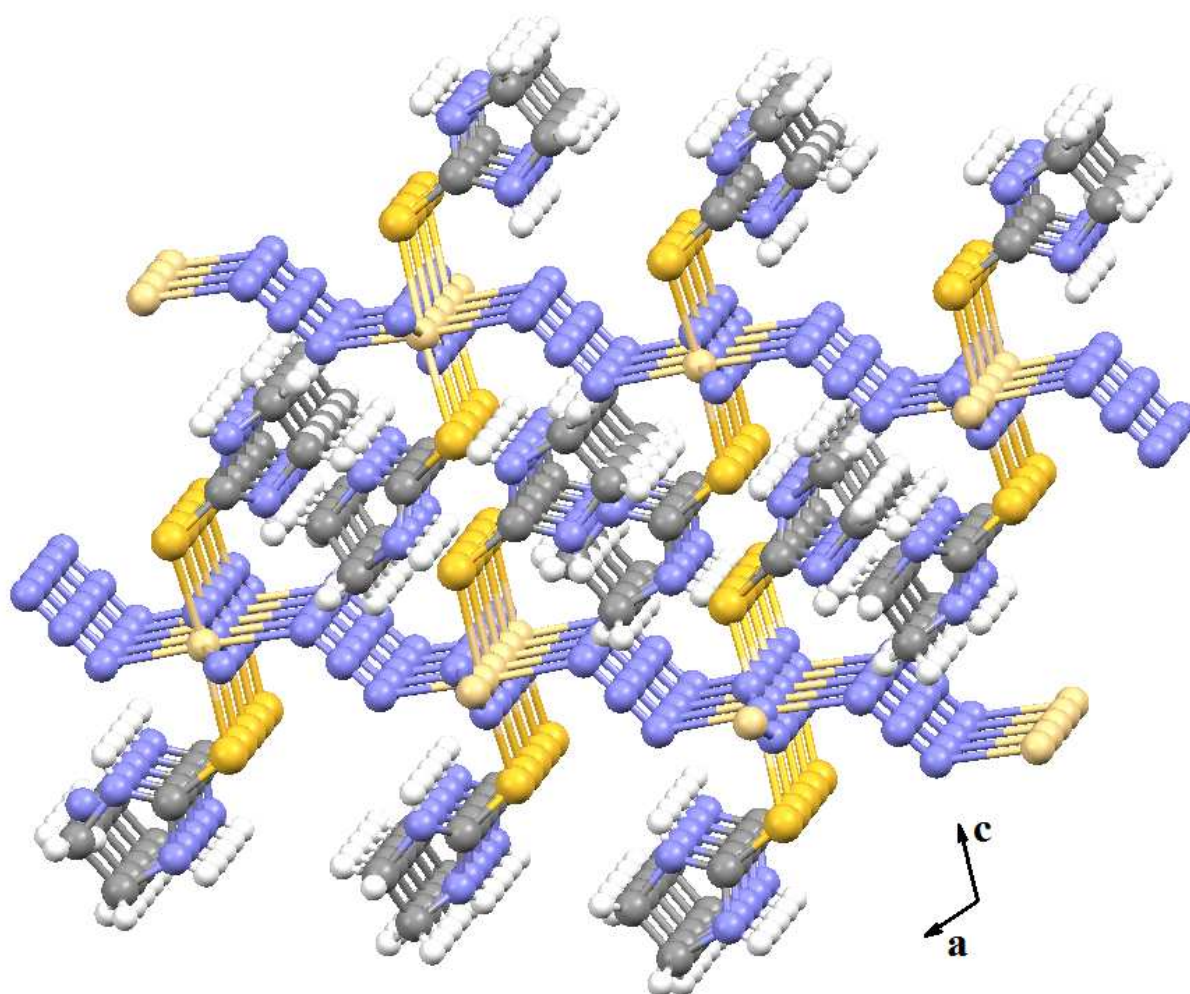


Figure 6. View of the packing of the 2D networks in compound **2** in the form of a 3D network

3.2. IR and NMR Studies

The reaction of $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$ with Imt in a 1:1 molar ratio resulted in a product of composition $[\text{Cd}(\text{Imt})(\text{H}_2\text{O})_2(\text{SO}_4)]$ (**1**), while the sequential addition of Imt and NaN_3 to $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$ yielded $[\text{Cd}(\text{Imt})_2(\text{N}_3)_2]_n$ (**2**). In the spectra of complexes **1** and **2**, the bands characteristic of free Imt ($\nu(\text{C}=\text{S})$, $\nu(\text{N}-\text{H})$, $\nu(\text{C}-\text{N})$) were observed around 1200, 3200, 1500 cm^{-1} , respectively. These values are close to those reported for other similar complexes [17,34,46-49]. The $\nu(\text{C}=\text{S})$ band expected around 500 cm^{-1} could not be observed because of the instrumental detection limit. The C=S stretching is shifted to lower frequencies upon Cd-S bonding, while the C-N and

N-H bands are shifted towards higher frequency due to increasing in double bond character of the C-N bond [17,47]. The N-H bending vibration was detected near 1500 cm^{-1} . The S-O vibrations in SO_4 complexes are observed at 1164 and 975 cm^{-1} [35,50]. A peak at 3416 cm^{-1} in $[\text{Cd}(\text{Imt})(\text{H}_2\text{O})_2(\text{SO}_4)]$ marks the presence of water in the complex. For **2**, the $\nu(\text{N}_3)$ stretching vibration was detected at 2031 cm^{-1} . Weak signals around 2890 cm^{-1} were also observed due to the C-H stretching of methylene groups. The IR spectra of complex **1** and **2** are shown in Figures S1 and S2 respectively (Supporting Information, SI).

In ^1H NMR spectra of the complexes, the N-H signal of Imt shifted downfield ppm from its position in the free ligand. Deshielding of the N-H proton is related to an increase of the π electron density in the C-N bond upon complexation [17,34]. In ^{13}C NMR, the C=S resonance of Imt displayed a small upfield shift compared to the uncomplexed ligand as observed for other cadmium(II) complexes of thiones [17,34,45,46]. The upfield shift is attributed to a lowering of the C=S bond order upon coordination and a shift of $\text{N}\rightarrow\text{C}$ electron density producing a partial double bond character in the C-N bond [34,36]. The C-N resonances exhibited a slight downfield shift, which is due to an increase in p character of this bond. The NMR spectra of the complexes are provided as Supporting Information (Figures S3 – S6).

4. Conclusion

This paper describes the synthesis and structural characterization of 1,3-imidazolidine-2-thione (Imt), $[\text{Cd}(\text{Imt})(\text{H}_2\text{O})_2(\text{SO}_4)]_n$ (**1**) and $[\text{Cd}(\text{Imt})_2(\text{N}_3)_2]_n$ (**2**). The X-ray structures of the complexes show that both of them exist in the form of two dimensional polymers with each cadmium atom being octahedrally coordinated. The polymers are assembled through triply-bridging sulfate and doubly-bridging, $\mu(1,3)$ azide ions in case of **1** and **2** respectively. The 2D polymers are extended by hydrogen bonding interactions resulting in 3D network structures. The Cd-S bond lengths reflect that Imt is more strongly bound to cadmium in complex **1**. The spectroscopic as well as the X-ray structure data are consistent with a significant C-N double bond character in the SCN_2 moiety of the coordinated Imt.

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Supplementary Information

Crystallographic data for compounds **1** and **2** have been deposited with the Cambridge Crystallographic Data Center via the CCDC Numbers 1571100 and 1571101, respectively. 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.

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Table 1. Crystal data and details of the structure refinement for compounds **1** and **2**.

Compound	1	2
Formula	C ₃ H ₁₀ CdO ₆ N ₂ S ₂	C ₆ H ₁₂ CdN ₁₀ S ₂
Formula Weight	346.65	400.78
Crystal system	Orthorhombic	Monoclinic
Space Group	<i>Pbca</i>	<i>C2/c</i>
<i>a</i> , <i>b</i> , <i>c</i> , Å	9.5479(13), 10.9719(14), 19.069(2)	25.671(3), 6.7473(9), 15.814(2)
α , β , γ , deg	90, 90, 90	90, 108.622(2), 90
<i>V</i> , Å ³	1997.6(4)	2595.7(6)
<i>Z</i>	8	8
ρ_{calc} , g/cm ³	2.305	2.008
μ (MoK α), mm ⁻¹	2.611	2.119
F(000)	1360	1584
Crystal size (mm)	0.420 x 0.280 x 0.240	0.680 x 0.420 x 0.220
Temperature, K	150(2)	150(2)
λ (MoK α), Å	0.71073	0.71073
θ range, deg	3.019 - 27.484	3.133 - 27.482
<i>h</i> , <i>k</i> , <i>l</i> limits	-12:12, -14:14, -22:24	-33:33, -8:7, -20:20
Reflns: Total, uniq. data, <i>R</i> _{int}	15721, 2284, 0.0255	11119, 2974, 0.0250
Observed data [<i>I</i> > 2 σ (<i>I</i>)]	2175	2810
<i>T</i> _{min} , <i>T</i> _{max}	0.398, 0.534	0.415, 0.643
Data, restraints, parameters	2284, 5, 146	2974, 4, 187
<i>R</i> ₁ , <i>wR</i> ₂ , <i>S</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.0175, 0.0422, 1.083	0.0202, 0.0489, 0.949
Largest diff. peak, hole (eÅ ⁻³)	0.482, -0.410	0.762, -0.461
$w = [\sigma^2(F_o^2) + (0.0147P)^2 + 3.5479P]^{-1}$ for 1 and $w = [\sigma^2(F_o^2) + (0.0240P)^2 + 4.9623P]^{-1}$ for 2 , where $P = (F_o^2 + 2F_c^2)/3$		

Table 2. Selected bond distances (Å) and bond angles (°) for compounds **1** and **2**

Bond Distance		Bond angles	
(1)			
Cd1-S1	2.5354(6)	O3 ⁱ -Cd1-O1	89.87(5)
Cd1-O1	2.3627(13)	O3 ⁱ -Cd1-O4 ⁱⁱ	170.58(5)
Cd1-O3i	2.3227(14)	O3 ⁱ -Cd1-O5	88.86(5)
Cd1-O4ii	2.3318(14)	O4 ⁱⁱ -Cd1-O1	89.26(5)
Cd1-O5	2.3467(15)	O4 ⁱⁱ -Cd1-O5	90.32(5)
Cd1-O6	2.2737(15)	O5-Cd1-O1	169.67(5)
S1-C1	1.715(2)	O6-Cd1-O1	82.69(5)
N1-C1	1.326(3)	O6-Cd1-O3 ⁱ	84.53(5)
C(2)-N(1)	1.465(3)	O6-Cd1-O4 ⁱⁱ	86.05(6)
		O6-Cd1-O5	86.99(6)
		O1-Cd1-S1	92.19(4)
		O3 ⁱ -Cd1-S1	103.65(4)
		O4 ⁱⁱ -Cd1-S1	85.76(4)
		O5-Cd1-S1	98.08(4)
		O6-Cd1-S1	170.39(4)
		Cd(1)-S(1)-C(1)	107.63(7)
		N(1)-C(1)-S(1)	123.01(17)
		N(1)-C(1)-N(2)	109.79(19)
(2)			
Cd1-S1	2.6114(5)	S1-Cd1-S2	172.270(13)
Cd1-S2	2.6205(5)	N5-Cd1-S1	81.99(4)
Cd1- N5	2.3692(15)	N7-Cd1-S1	100.72(4)
Cd1- N7	2.3589(15)	N9-Cd1-S1	90.35(4)
Cd1- N9	2.4205(15)	N11 ^{iv} -Cd1-S1	85.94(3)
Cd1- N11 ⁱⁱⁱ	2.4884(15)	N5-Cd1-S2	93.15(4)
S1-C1	1.7059(17)	N7-Cd1-S2	84.03(4)
N1-C1	1.331(2)	N9-Cd1-S2	96.22(4)
N1-C2	1.469(2)	N11 ^{iv} -Cd1-S2	88.10(3)
N5-N6	1.1663(15)	N5-Cd1-N7	177.07(4)
N7-N8	1.1753(14)	N5-Cd1-N9	96.84(6)
N9-N10	1.1845(19)	N5-Cd1-N11 ^{iv}	90.46(6)
N10-N11	1.1657(19)	N7-Cd1-N9	84.29(6)
		N7-Cd1-N11 ^{iv}	88.65(5)
		N9-Cd1-N11 ^{iv}	171.28(5)
		Cd1-S1-C1	108.06(6)
		Cd1-S2-C4	114.97(5)

Symmetry code: i = x+1/2, y, -z+1/2; ii = -x+1, y+1/2, -z+1/2; iii = x, y+1, z; iv = x, y+1, z

Table 3 Hydrogen bond parameters in complexes **1** and **2** (Å, deg)^a

D-H...A	d(D-H)	d(H...A)	d(D...A)	∠(D-H-A)
(1)				
N1-H1...O5 ⁱ	0.84(2)	2.47(3)	3.105(2)	133(3)
N2-H2...O3 ⁱⁱ	0.89(3)	2.06(3)	2.913(2)	160(3)
O5-H5A...O3 ⁱⁱⁱ	0.80(2)	1.96(2)	2.751(2)	168(2)
O5-H5B...O4 ^{iv}	0.85(2)	1.93(2)	2.772(2)	170(3)
O6-H6A...O1 ⁱⁱ	0.78(3)	2.01(3)	2.746(2)	158(3)
O6-H6B...S2	0.81(3)	2.77(3)	3.4294(17)	140(2)
O6-H6B...O2	0.81(3)	1.89(3)	2.687(2)	168(3)
(2)				
N1-H1...N7	0.807(17)	2.418(19)	3.120(2)	146.0(19)
N2-H2...S2 ^v	0.811(18)	2.876(19)	3.5769(15)	146.0(18)
N2-H2...N11 ^{vi}	0.811(18)	2.507(19)	3.065(2)	127.1(18)
N3-H3...N5	0.837(18)	2.072(19)	2.884(2)	163(2)
N4-H4...N9 ^{vii}	0.814(18)	2.273(19)	3.007(2)	150.2(19)

^aSymmetry codes: i = x-1/2,-y+3/2,-z+1; ii = x+1/2,y,-z+1/2; iii = -x+1,y+1/2,-z+1/2;

iv = -x+3/2,y+1/2,z; v = x,-y+2,z+1/2; vi = x,-y+1,z+1/2; vii = x,-y+1,z-1/2

Research Highlights

- Crystal structures of $[\text{Cd}(\text{Imt})(\text{H}_2\text{O})_2(\text{SO}_4)]_n$ (**1**) and $[\text{Cd}(\text{Imt})_2(\text{N}_3)_2]_n$ (**2**); Imt = 1,3-imidazolidine-2-thione
- Compounds **1** and **2** exist as 2D polymers.
- Polymers are formed by μ_3 -SO₄ and $\mu(1,3)$ azide groups in **1** and **2** respectively.