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Research paper

# Synthesis and crystal structures of cadmium(II) complexes of 1,3-diazinane-2-thione (diaz); $[Cd(diaz)_4Cl_2]$, $[Cd(diaz)_2(NCS)_2]$ and $[Cd(diaz)_2(N_3)_2]_n$

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## ABSTRACT

Three cadmium(II) complexes of 1,3-diazinane-2-thione (diaz); dichloridotetrakis(1,3-diazinane-2-thione)cadmium(II), $[Cd(diaz)_4Cl_2]$ (**1**), bis(thiocyanato-*κN*)bis(1,3-diazinane-2-thione)cadmium(II), $[Cd(diaz)_2(NCS)_2]$ (**2**) and poly[diazidobis(1,3-diazinane-2-thione)cadmium(II)], $[Cd(diaz)_2(N_3)_2]_n$ (**3**) were prepared and their crystal structures were determined by X-ray crystallography. The compounds **1** and **2** exist in the monomeric forms as discrete nonionic molecules. In **1**, the cadmium atom is octahedrally coordinated by two *trans* chloride ions and four diaz ligands, while in **2**, it is bound to two thione molecules and two thiocyanato ions through nitrogen atoms in a tetrahedral environment. The structure of **1** is stabilized by intramolecular N—H···Cl hydrogen bonds and layers are formed by additional intermolecular N—H···S hydrogen bonds. The crystal structure of **2** is characterized by intermolecular N—H···S hydrogen bonding and S···S interactions. The complex **3** exists in the form of a polymeric chain consisting of $[Cd(diaz)_2(N_3)_2]$ units. In **3** each cadmium atom is octahedrally coordinated by two *trans* diaz ligands and four doubly-bridging, μ(1,3) azide groups. The coordination chain is stabilized by additional N—H···N intrachain hydrogen bonds and, overall a 3D network is formed by interchain N—H···N and N—H···S hydrogen bonds. The complexes **1–3** were also characterized by IR and NMR spectroscopy, and the spectroscopic data indicated the coordination of ligands to cadmium(II).

## 1. Introduction

The interest in coordination chemistry of heterocyclic thiones arises from the presence of heterocyclic skeleton in many biomolecules [1–4] and because of their potential use as selective reagents for extraction of heavy metals [5]. Imidazolidine-2-thione (imt) and diazinane-2-thione (diaz) are the simple heterocyclic ligands that can be used as models to study bio-relevant metal-sulfur interactions. The known complexes of imt and diaz include; $[Cd(imt)_2(SCN)_2]_n$ [6], $[Cd(imt)_2Cl_2]$ [7], $[Cd(imt)_2Br_2]$ [8], $[Cd(imt)_2I_2]$ [8], $[Cd(diaz)_2Cl_2]$ [9], $[Cd(diaz)_2I_2]$ [10], $[Cd(diaz)_4]SO_4$ [11] and $[Cd(diaz)_2(acetate)_2]$ [12]. Most of the cadmium(II) complexes of thiones show tetrahedral geometry with thiones acting as terminal *S*-bonded ligands [7–17], *e.g.*, in $[Cd(imt)_2Cl_2]$ [6] and $[Cd(diaz)_2Cl_2]$ [9] and $[Cd(mpy)_4](NO_3)_2$ [14]. In some cases, polymeric species are formed through bridging sulfur or nitrogen atoms [4,6,16–21], *e.g.*, $[Cd(imt)_2(SCN)_2]_n$ [6]. In polymeric complexes cadmium atom usually adopts distorted octahedral coordination environment. A few monomeric complexes showing octahedral coordination are also known [21,22]. Among the polymeric complexes, the thiocyanato and azido complexes are of special interest because these bridging ligands can be used as building blocks for the preparation of supramolecular structures [17–21,23–25]. It is interesting to note that the crystal structures of known Cd-diaz complexes are different from each other. $[Cd(diaz)_2Cl_2]$ and $[Cd(diaz)_2I_2]$ are nonionic tetrahedral molecules [9,10]; $[Cd(diaz)_4]SO_4$ [11] is an ionic complex, while $[Cd(diaz)_2(CH_3COO)_2]$ [12] (diaz = 1,3-diazinane-2-thione or tetrahydropyrimidine-2-thione) exists as a distorted octahedral complex. As a sequel work of our ongoing research program on the structural analysis of cadmium-thione complexes [9–12,17,26–33], we report

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**Table 1**
Crystal and structural refinement data of **1**, **2** and **3.**

| | 1 | 2 | 3 |
|---|---|---|---|
| Formula | $C_{16}H_{32}CdCl_2N_8S_4$ | $C_{10}H_{16}CdN_6S_4$ | $C_8H_{16}CdN_{10}S_2$ |
| Formula Weight | 648.03 | 460.93 | 428.83 |
| Crystal system | Triclinic | monoclinic | triclinic |
| Space Group | *P*-1 | *I* 2/*a* | *P*-1 |
| *a*, *b*, *c* (Å) | 8.697(2), 9.2169(19), 9.382(2) | 14.5752(4), 8.8285(2), 14.3041(4) | 9.4681(9), 9.9741(8), 10.2132(9) |
| $\alpha$, $\beta$, $\gamma$ (deg) | 119.04(2), 103.798(19), 91.467(18) | 90, 112.765(3), 90 | 62.065(9), 65.323(9), 64.533(9) |
| *V* ($Å^3$) | 629.6(3) | 1697.23(8) | 740.55(14) |
| *Z* | 1 | 4 | 2 |
| $\rho$ calc (g $cm^{-3}$) | 1.709 | 1.804 | 1.923 |
| μ ($mm^{-1}$) | 12.182 | 1.780 | 1.767 |
| *F*(000) | 330 | 920 | 428 |
| Crystal size (mm) | 0.3 × 0.2 × 0.1 | 0.4 × 0.3 × 0.3 | 0.24 × 0.24 × 0.22 |
| Temperature (K) | 120 | 110 | 115 |
| $\lambda$ (Å) | 1.54184 (Cu K$\alpha$) | 0.71073 (Mo K$\alpha$) | 0.71073 (Mo K$\alpha$) |
| $\theta$ range (deg) | 5.311–65.978 | 3.031–24.992 | 2.911–24.994 |
| *h*, *k*, *l* limits | −10:10, −10:10, −11:11 | −15:17, −10:10, −17:17 | −11:11, −9:11, −12:11 |
| Reflections; collected/ uniq. | 6267/2147<br>[*R*(int) = 0.0378] | 6586/1485<br>[*R*(int) = 0.0252] | 4340/2596<br>[*R*(int) = 0.0178] |
| Data/restrain./paramet. | 2147/4/158 | 1485/2/104 | 2596/60/203 |
| Goodness-of-fit on $F^2$ | 1.066 | 1.077 | 1.049 |
| *R* indices [$I > 2\sigma(I)$] | $R_1 = 0.0262$;<br>$wR_2 = 0.0672$ | $R_1 = 0.0156$;<br>$wR_2 = 0.0371$ | $R_1 = 0.0185$;<br>$wR_2 = 0.0404$ |
| *R* indices (all data) | $R_1 = 0.0268$;<br>$wR_2 = 0.0678$ | $R_1 = 0.0169$;<br>$wR_2 = 0.0375$ | $R_1 = 0.0205$;<br>$wR_2 = 0.0414$ |
| Largest diff. peak, hole (e $Å^{-3}$) | 0.860, −0.471 | 0.266, −0.228 | 0.355, −0.315 |

here the synthesis and crystal structures of three new Cd-diaz complexes, namely; $[Cd(diaz)_4Cl_2]$ (**1**), $[Cd(diaz)_2(NCS)_2]$ (**2**) and $[Cd(diaz)_2(N_3)_2]_n$ (**3**).

## 2. Experimental

### 2.1. Chemicals

Cadmium chloride ($CdCl_2{\cdot}H_2O$), cadmium sulfate ($CdSO_4{\cdot}8/3H_2O$), KSCN and $NaN_3$ were obtained from Merck Chemical Company, Germany. 1,3-Diazinane-2-thione (diaz) was prepared according to the procedure published in the literature [34].

### 2.2. Synthesis of complexes

Complex **1** was prepared by mixing 0.50 g (4.2 mmol) of diaz in 20 mL methanol and 0.21 g (1.0 mmol) cadmium chloride in 5 mL water and stirring the mixture for 30 min. The off-white crystals were obtained by slow evaporation of the filtered solution.

The complexes **2** and **3** were prepared by adding 0.24 g (2.0 mmol) of diaz in 20 mL methanol to an aqueous solution (10 mL) of cadmium sulfate (0.26 g, 1.0 mmol). After stirring the solution for 30 min, 2 mmoles of KSCN or $NaN_3$ in 10 mL water were added. The mixtures were stirred further for 30 min. The light brown solutions were filtered and the filtrates were kept at room temperature for crystallization. As a result, yellow crystalline products were obtained, which were washed with methanol and dried.

### 2.3. Spectroscopic data

$^1H$ NMR (500 MHz, DMSO, 297 K, ppm): $[Cd(diaz)_4Cl_2]$ (**1**), $\delta = 8.13$; $[Cd(diaz)_2(NCS)_2]$ (**2**), $\delta = 8.00$; $[Cd(diaz)_2(N_3)_2]_n$ (**3**), $\delta = 8.21$; diaz, $\delta = 7.81$.

$^{13}C$ NMR (125.65 MHz, DMSO, ppm): $[Cd(diaz)_4Cl_2]$ (**1**), $\delta = 173.54$, 40.30, 19.30; $[Cd(diaz)_2(NCS)_2]$ (**2**), $\delta = 173.79$, 132.57, 40.00, 18.95; $[Cd(diaz)_2(N_3)_2]_n$ (**3**), $\delta = 172.64$, 40.20, 18.77; diaz, $\delta = 175.62$, 39.76, 19.19.

### 2.4. IR and NMR measurements

The IR spectra were recorded on a Nicolet 6700 or iS5 FTIR spectrophotometer using KBr pellets over the range 4000–500 $cm^{-1}$. The $^1H$ and $^{13}C\{^1H\}$ NMR spectra in 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.

### 2.5. X-ray structure determination

Data of single crystals were collected on an Oxford Gemini S diffractometer with CuK$\alpha$ radiation for **1** and using MoK$\alpha$ radiation for **2** and **3** respectively. For data collection, cell refinement, and data reduction of **1**, the software CrysAlisPro 411 [35] and of **2** as well as **3**, the software CrysAlisPro 28 [36] was used. The structures were solved by direct methods with SHELXS-2013 [37] and refined by full-matrix least-squares procedures on $F^2$ with SHELXS-2013 [37]. All non-hydrogen atoms were refined anisotropically. The carbon-bonded hydrogen atoms were inserted on ideal positions and refined using a riding model with appropriate SHELXL constraints. The positions of nitrogen-bound hydrogen atoms were taken from difference Fourier maps. Crystal and structural refinement data of **1**–**3** are provided in Table 1.

## 3. Results and discussion

### 3.1. IR and NMR studies

The compound **1**, $[Cd(diaz)_4Cl_2]$ was prepared by adding 4 equivalents of diaz to $CdCl_2{\cdot}H_2O$ On the other hand, when 2 equivalents of diaz were added to cadmium chloride, the usual product, $[Cd(diaz)_2Cl_2]$ was isolated [9]. The reaction of $CdSO_4{\cdot}8/3H_2O$ with diaz and KSCN or $NaN_3$ in a 1:2:2 M ratio resulted in a product of empirical composition, $[Cd(diaz)_2X_2]$ ($X = SCN, N_3$). The IR spectrum of complex **1** is shown in Fig. S1 (SI). In the IR spectra of the complexes, the characteristic bands observed were; $\nu(C{=}S)$ around 1200 and $\nu(N{-}H)$ at 3200 $cm^{-1}$. The presence of these bands is consistent with the coordination of diaz to cadmium(II)