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Adduct Formation of Cadmium(II) N,N-*cyclo*-Hexamethylenedithiocarbamate, $[Cd_2\{S_2CN(CH_2)_6\}_4]$, with Morpholine: Synthesis, Molecular Structure, and Thermal Behavior of a Crystalline Adduct *cis*-$[Cd\{NH(CH_2)_4O\}_2\{S_2CN(CH_2)_6\}_2]$

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Abstract—The reaction of $[Cd_2\{S_2CN(CH_2)_6\}_4]$ (**I**) with morpholine gives a crystalline adduct of cadmium N,N-*cyclo*-hexamethylenedithiocarbamate $[Cd\{NH(CH_2)_4O\}_2\{S_2CN(CH_2)_6\}_2]$ (**II**), whose coordination sphere includes two molecules of the donor base. The structural organization and thermal behavior of **II** is studied by X-ray diffraction analysis and simultaneous thermal analysis in comparison with the original binuclear cadmium complex **I**. The central cadmium atom (coordination number 6) coordinates two morpholine molecules and two structurally equivalent S,S'-anisobidentate ligands HmDtc to form a chromophore $[CdN_2S_4]$ with the structure of a distorted octahedron. The thermal destruction of **II** proceeds in two stages and includes consecutive steps of dissociation of the Cd–N bonds followed by the desorption of morpholine and thermolysis of the dithiocarbamate moiety of the adduct to form CdS as the final product. The structure of binuclear $[Cd_2\{S_2CN(CH_2)_6\}_4]$ is refined for a correct refinement of the geometric characteristics of compounds **I** and **II**.

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INTRODUCTION

Adducts of the dialkyldithiocarbamate cadmium complexes with organic donor bases are interesting as promising precursors of film materials and nanosized CdS powders [1–4]. The regularities of the electronic structures of heteropolynuclear *cyclo*-hexamethylenedithiocarbamate complexes determine possibilities of their practical use in technologies of the production of solar battery cells [5]. Cadmium dithiocarbamates specifically interact with monodentate N-donor bases (B) and manifest the ability to add either one or two molecules with the formation of tetragonal pyramidal adducts of the general composition $[Cd(B)(Dtc)_2]$ [6–9] and distorted octahedral adducts $[Cd(B)_2(Dtc)_2]$ [10, 11].

We have previously found that bis[μ(N,N-*cyclo*-hexamethylenedithiocarbamato-S,S',S')(N,N-*cyclo*-hexamethylenedithiocarbamato-S,S')]dicadmium, $[Cd_2\{S_2CN(CH_2)_6\}_4]$ (**I**), is an efficient chemosorbent of gold(III) from solutions of $AuCl_3$ in 2 M HCl [12]. Heteropolynuclear complex $([Au\{S_2CN(CH_2)_6\}_2]_2[CdCl_4] \cdot 3/4H_2O)_n$ was preparatively isolated as an individual form of binding gold(III). Its complicated supramolecular structure was established by X-ray diffraction analysis and includes discrete cations $[Au\{S_2CN(CH_2)_6\}_2]^+$ and polymer chains built of alternating mononuclear and binuclear cations $[Au_2\{S_2CN(CH_2)_6\}_4]^{2+}$ [12]. The reaction of cadmium N,N-*cyclo*-hexamethylenedithiocarbamate with morpholine was studied in this work. The crystalline adduct, bis(N,N-*cyclo*-hexamethylenedithiocarbamato-S,S')dimorpholinecadmium $[Cd\{NH(CH_2)_4O\}_2\{S_2CN(CH_2)_6\}_2]$ (**II**), was preparatively isolated, and its structure and thermal behavior were established and compared with those of the original binuclar complex.

EXPERIMENTAL

Synthesis of I. A solution of $Cd(NO_3)_2 \cdot 4H_2O$ in water (30 mL) (0.153 g, 0.0005 mol) was poured with vigorous stirring to a solution of sodium *cyclo*-hexamethylenedithiocarbamate $Na\{S_2CN(CH_2)_6\} \cdot 2H_2O$ (**III**) (0.233 g, 0.001 mol) in water (10 mL). A white bulky precipitate was washed by decantation, filtered, and dried in air. The yield was 87%. Single crystals of compound **II** for X-ray diffraction analysis were obtained from chloroform.

Synthesis of II. Morpholine (3 mL) was poured with moderate heating to $[Cd_2\{S_2CN(CH_2)_6\}_4]$ (0.280 g, 0.0003 mol) dissolved in toluene (10 mL). Single crystals of **II** were grown from the mother liquor at room temperature. The yield was 54%.

Compounds **I–III** were characterized by the data of ^{13}C MAS NMR spectroscopy, δ, ppm: for **I**, 203.9 (32)*, 200.7 (30)* (1 : 1, $-S_2CN=$); 59.4, 58.1, 57.3, 54.5 (1 : 1 : 1 : 1, $=NCH_2-$); 29.9, 29.8, 29.2, 28.6, 28.0, 27.3, 26.3, 26.1 (1 : 1 : 1 : 1 : 1 : 1 : 1 : 1, $-CH_2-$); for **II**, 206.0 ($-S_2CN=$); 57.8, 56.2 (1 : 1, $=NCH_2-$); 28.6, 27.8 (2 : 2, $-CH_2-$); 69.6, 68.7 (1 : 1, $-OCH_2-$); 46.9, 45.5 (1 : 1, $=NCH_2-$); for **III**, 206.3 ($-S_2CN=$); 60.3, 55.5 (1 : 1, $=NCH_2-$); 29.8, 27.0, 26.2, 24.9 (1 : 1 : 1 : 1, $-CH_2-$). Asymmetric $^{13}C-^{14}N$ doublets [13, 14] are given in Hz and designated by asterisk (*).

X-ray diffraction analysis of structure **II** and the refinement of structure **I**[1] were performed at 200(2) K on a Bruker Smart Apex II (MoK_α radiation, λ = 0.71073 Å, graphite monochromator). An X-ray absorption correction was applied by equivalent reflections. Structures **I** and **II** were determined by a direct method and refined by least squares in the anisotropic approximation of non-hydrogen atoms. The positions of hydrogen atoms were calculated geometrically and included in refinement in the riding model. In structure **I**, the C(4)–C(7) atoms are statistically disordered between the positions (A) and (B) with site occupancies of 0.80(1) and 0.20(2), respectively. Data were collected and edited and the unit cell parameters were refined using the APEX2 [16] and SAINT [17] programs, respectively. All calculations on structure determination and refinement were performed using the SHELXTL/PC programs [18]. The main crystallographic data and the structure refinement results are presented in Table 1. Selected bond lengths and angles are listed in Tables 2 and 3.

The coordinates of atoms, bond lengths, and angles in the determined structures were deposited with the Cambridge Crystallographic Data Centre (nos. 940762 (**II**) and 940763 (**I**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam. ac.uk).

The ^{13}C MAS NMR spectra were recorded on a CMX-360 pulse spectrometer (Agilent/Varian/Chemagnetics InfinityPlus) with a working frequency of 90.52 Hz, a superconducting magnet (B_0 = 8.46 T), and Fourier transform. Proton cross-polarization was used in spectra recording. The $^{13}C-^{1}H$ dipole–dipole interactions were suppressed by proton decoupling using the radiofrequency field corresponding to the resonance frequency of protons [19]. For the ^{13}C MAS NMR measurements, samples (~60 mg) were placed in ceramic ZrO_2 rotors 4.0 mm in diameter and rotated at the magic angle using frequencies of 4700–5600 Hz, a scan number of 2400–8200, a duration of π/2 proton pulses of 4.7–5.0 μs, a $^{1}H-^{13}C$ contact time of 1.7–2.0 ms, and an interval between excitation pulses of 3–4 s. Isotropic ^{13}C chemical shifts (δ) were measured relatively to one component of crystalline adamantane (δ = 38.48 ppm relatively to tetramethylsilane). The magnetic field homogeneity was controlled by the width of the reference line of adamantane: 2.6 Hz.

The thermal properties of compounds **I** and **II** were studied by simultaneous thermal analysis (STA) including both the simultaneous detection of thermogravimetry (TG) and differential scanning calorimetry (DSC) curves. The study was carried out on a STA 449C Jupiter instrument (NETZSCH) in aluminum crucibles under caps with a hole providing the vapor pressure during thermolysis equal to 1 atm. The heating rate was 10°C/min to 600°C in an argon atmosphere. The weight of the samples was 1.952–4.346 mg. The accuracy of temperature measurements was ±0.7°C, and that of the weight change was $\pm 1 \times 10^{-4}$ mg. After thermal analysis, the residual substance was studied with a JSM 6390LV JEOL scanning electron microscope (Japan) equipped with an Oxford INCA Energy 350-Wave microanalysis system (England) with the energy and wavelength dispersion. The qualitative determination of the chemical composition was carried out by the microprobe method using an energy dispersion spectrometer.

RESULTS AND DISCUSSION

The ^{13}C MAS NMR spectrum of crystalline adduct **II** (Fig. 1) includes signals from the =NC(S)S–, $=NCH_2-$, and $-CH_2-$ groups of the *cyclo*-hexamethylenedithiocarbamate ligands (HmDtc) and the $-OCH_2-$ and $=NCH_2-$ groups of the morpholine molecules. The single resonance ^{13}C signal from the =NC(S)S– groups showed the structural equivalence of the HmDtc ligands. The chemical shift of the dithiocarbamate groups (206.0 ppm) increased significantly compared to that of the original binuclear complex $[Cd_2\{S_2CN(CH_2)_6\}_4]$ (see section Synthesis), on the one hand, indicates the terminal structural function of the HmDtc ligands. On the other hand, it indicates a noticeable weakening of the total strength of their binding in adduct **II**. The ratio of integral intensities of the ^{13}C signals from different structural groups suggests that the internal sphere of the metal contains two coordinated morpholine molecules. It was established by the mathematical simulation of the ^{13}C signals caused by morpholine that each of them was a superposition of two closely lying lines (1 : 1), indicating the pairwise structural nonequivalence of the $-OCH_2-$ and $=NCH_2-$ groups. Thus, according to the MAS ^{13}C NMR data, adduct **II** is characterized by the high-symmetrical structure including equiva-

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[1] The structure of the original binuclear cadmium complex determined earlier [15] is characterized by a high *R* factor (13.6%). Therefore, the task of the correct correspondence with the structure of adduct II required refinement: an exacter determination of the positional and thermal parameters of atoms, bond lengths, and angles.

Table 1. Crystallographic data, experimental details, and refinement parameters for the structures of $[Cd_2\{S_2CN(CH_2)_6\}_4]$ (**I**) and $[Cd\{NH(CH_2)_4O\}_2\{S_2CN(CH_2)_6\}_2]$ (**II**)

Parameter	Value	
	I	**II**
Empirical formula	$C_{28}H_{48}N_4S_8Cd_2$	$C_{22}H_{42}N_4O_2S_4Cd$
M	921.98	635.24
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$Pccn$
a, Å	11.1010(4)	17.7348(5)
b, Å	10.5547(4)	12.4210(4)
c, Å	15.8279(6)	12.7424(4)
β, deg	101.8490(10)	90
V, Å^3	1815.00(12)	2806.95(15)
Z	2	4
ρ_{calcd}, g/cm^3	1.687	1.503
μ, mm^{-1}	1.658	1.102
F(000)	936	1320
Crystal size, mm	0.40 × 0.30 × 0.13	0.50 × 0.40 × 0.32
Data collection θ range, deg	2.06–34.39	2.00–33.74
Reflection index ranges	$-17 \le h \le 17$, $-16 \le k \le 16$, $-24 \le l \le 25$	$-27 \le h \le 27$, $-13 \le k \le 19$, $-19 \le l \le 19$
Measured reflections	26652	27283
Number of independent reflections	7290 ($R_{int} = 0.0196$)	5570 ($R_{int} = 0.0221$)
Number of reflections with $I > 2\sigma(I)$	6566	4450
Refinement method	Full-matrix least squares for F^2	
Number of refinement variables	226	150
Goodness-of-fit	1.026	1.047
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0212$, $wR_2 = 0.0541$	$R_1 = 0.0278$, $wR_2 = 0.0686$
R factors for all reflections	$R_1 = 0.0249$, $wR_2 = 0.0559$	$R_1 = 0.0383$, $wR_2 = 0.0745$
Extinction coefficient	Was not refined	
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.774/–0.550	1.067/–0.482

lent HmDtc ligands and morpholine molecules. In order to check these conclusions, structure **II** was determined by X-ray diffraction analysis.

The unit cell of compound **II** includes four formula units $[Cd\{NH(CH_2)_4O\}_2\{S_2CN(CH_2)_6\}_2]$ (Table 1). The projection on the *xz* plane shows that structure **II** includes four alternating adduct molecules with different spatial orientations (Fig. 2). The metal atom (coordination number 6) coordinates two S,S'-bidentate HmDtc ligand and two morpholine molecules (chair conformation) to form the distorted octahedral chromophore $[CdN_2S_4]$ with the *cis*-oriented morpholine heterocycles (Fig. 3). Note that, for a similar adduct of cadmium benzoylacetonate including coordinated 2-methylpyridine molecules, the metastable *trans* isomer was preparatively isolated along with the stable *cis*-isomeric form [20]. As expected from the ^{13}C MAS NMR data, the dithiocarbamate ligands and morpholine molecules are structurally equivalent. The cadmium atom lies on the rotational twofold axis, which is also characteristic of the corresponding adduct of cadmium methylpiperazinedithiocarbamate with pyridine [10]. Interestingly, each adduct of zinc and copper(II) dithiocarbamates also can formally include two molecules of donor bases: morpholine [21] or pyridine [22]. However, the internal sphere of these adducts includes only one molecule, while the second (solvating) molecule is localized in the external sphere.

The Cd–N bond lengths (2.4458 Å) in adduct **II** are well consistent with the corresponding data for octahedral dipyridinates of cadmium methylpipera-

Table 2. Interatomic distances (*d*) and bond angles (ω) and torsion angles (φ) in structure **II**

Bond	*d*, Å	Bond	*d*, Å
Cd(1)–N(2)	2.4458(12)	C(4)–C(5)	1.498(3)
Cd(1)–S(1)	2.6212(4)	C(5)–C(6)	1.517(3)
Cd(1)–S(2)	2.7605(4)	C(6)–C(7)	1.509(3)
S(1)–C(1)	1.723(2)	N(2)–C(8)	1.461(2)
S(2)–C(1)	1.724(2)	N(2)–C(11)	1.473(2)
N(1)–C(1)	1.339(2)	C(8)–C(9)	1.516(3)
N(1)–C(2)	1.475(2)	C(10)–C(11)	1.513(2)
N(1)–C(7)	1.483(2)	O(1)–C(9)	1.414(2)
C(2)–C(3)	1.513(3)	O(1)–C(10)	1.411(2)
C(3)–C(4)	1.514(3)		
Angle	**ω, deg**	**Angle**	**ω, deg**
Cd(1)N(2)C(8)	110.46(10)	N(1)C(2)C(3)	113.37(14)
Cd(1)N(2)C(11)	113.10(9)	N(1)C(7)C(6)	114.1(2)
N(2)Cd(1)S(1)	97.46(3)	C(2)C(3)C(4)	114.3(2)
N(2)Cd(1)S(2)	91.95(3)	C(3)C(4)C(5)	114.9(2)
Cd(1)S(1)C(1)	89.09(5)	C(4)C(5)C(6)	114.7(2)
Cd(1)S(2)C(1)	84.58(5)	C(5)C(6)C(7)	115.4(2)
S(1)Cd(1)S(2)	67.031(12)	N(2)C(8)C(9)	113.4(2)
S(1)C(1)S(2)	119.26(9)	N(2)C(11)C(10)	111.96(13)
N(1)C(1)S(1)	119.65(12)	C(8)N(2)C(11)	109.75(13)
N(1)C(1)S(2)	121.08(12)	O(1)C(9)C(8)	111.3(2)
C(1)N(1)C(2)	121.13(14)	O(1)C(10)C(11)	111.59(14)
C(1)N(1)C(7)	120.3(2)	C(10)O(1)C(9)	109.24(14)
C(2)N(1)C(7)	118.6(2)		
Angle	**φ, deg**	**Angle**	**φ, deg**
Cd(1)S(1)S(2)C(1)	177.91(10)	S(1)C(1)N(1)C(7)	173.67(14)
S(1)Cd(1)C(1)S(2)	178.24(9)	S(2)C(1)N(1)C(2)	174.22(12)
S(1)C(1)N(1)C(2)	−5.8(2)	S(2)C(1)N(1)C(7)	−6.4(2)

zinedithiocarbamate (2.417 Å [10]) and cadmium methylphenyldithiocarbamate (2.479 and 2.390 Å [11]). However, the strength of the discussed bond lengths is noticeably inferior to that for Cd–N in tetragonal pyramidal (methyl-)pyridinates of the di-*iso*-butyldithiocarbamate (2.300 Å [8]) and methylphenyldithiocarbamate complexes (2.294 Å [11]) and the adduct of cadmium ethylphenyldithiocarbamate with ethyloxazoline (2.256 Å [6]). The weakening of bonds of the N-donor bases with the central cadmium atom in adduct **II** and similar compounds [10, 11] is caused by steric factors. The strength of the binding ligands HmDtc in adduct **II** (Cd–S 2.6212 and 2.7605 Å) is also lower than that in binuclear complex **I**: Cd–S 2.5498 and 2.6086 Å (for terminal ligands).

The anisobidentate coordination of the =NC(S)S– groups results in the formation of two four-membered metallocycles [CdS_2C], which are bound by the common cadmium atom into the bicyclic group [CS_2CdS_2C]. The metallocycles are characterized by very short Cd···C/S···S distances: 3.114/2.974 Å (which is substantially smaller than the sum of van der Waals radii of the corresponding pairs of atoms: 3.38/3.60 Å [23–25]). The geometry of these cycles somewhat deviates from the planar one due to the inflection along the S–S axis: the interpla-

Table 3. Interatomic distances (*d*) and bond angles (ω) and torsion angles (φ) in structure **I***

Bond	*d*, Å	Bond	*d*, Å
Terminal ligands		Bridging ligands	
Cd(1)–S(1)	2.5498(4)	Cd(1)–S(3)	2.5594(3)
Cd(1)–S(2)	2.6086(4)	Cd(1)–S(4)	2.8843(3)
S(1)–C(1)	1.7348(13)	Cd(1)–S(4)^a	2.5852(3)
S(2)–C(1)	1.7260(13)	S(3)–C(8)	1.7172(11)
N(1)–C(1)	1.326(2)	S(4)–C(8)	1.7561(11)
N(1)–C(2)	1.467(2)	N(2)–C(8)	1.3274(14)
N(1)–C(7*A*)	1.478(2)	N(2)–C(9)	1.478(2)
N(1)–C(7*B*)	1.476(5)	N(2)–C(14)	1.477(2)
C(2)–C(3)	1.525(2)	C(9)–C(10)	1.528(2)
C(3)–C(4*A*)	1.542(3)	C(10)–C(11)	1.524(2)
C(3)–C(4*B*)	1.479(4)	C(11)–C(12)	1.531(2)
C(4*A*)–C(5*A*)	1.513(2)	C(12)–C(13)	1.531(2)
C(4*B*)–C(5*B*)	1.500(4)	C(13)–C(14)	1.521(2)
C(5*A*)–C(6*A*)	1.512(3)		
C(5*B*)–C(6*B*)	1.576(13)		
C(6*A*)–C(7*A*)	1.507(3)		
C(6*B*)–C(7*B*)	1.506(4)		
Angle	**ω, deg**	**Angle**	**ω, deg**
S(1)Cd(1)S(3)	132.368(12)	S(1)Cd(1)S(4)^a	123.434(11)
S(1)Cd(1)S(4)	91.386(9)	S(2)Cd(1)S(4)^a	112.215(12)
S(2)Cd(1)S(3)	109.896(11)	S(3)Cd(1)S(4)^a	101.137(10)
S(2)Cd(1)S(4)	151.789(12)	S(4)Cd(1)S(4)^a	95.729(9)
Terminal ligands		Bridging ligands	
S(1)Cd(1)S(2)	70.435(11)	S(3)Cd(1)S(4)	66.265(9)
C(1)S(1)Cd(1)	86.00(4)	C(8)S(3)Cd(1)	93.13(4)
C(1)S(2)Cd(1)	84.32(4)	C(8)S(4)Cd(1)	81.92(4)
S(1)C(1)S(2)	118.56(7)	C(8)S(4)Cd(1)^a	99.27(4)
N(1)C(1)S(1)	119.88(10)	Cd(1)S(4)Cd(1)^a	84.271(9)
N(1)C(1)S(2)	121.56(10)	S(3)C(8)S(4)	118.68(6)
C(1)N(1)C(2)	122.18(12)	N(2)C(8)S(3)	120.68(9)
C(1)N(1)C(7*A*)	120.3(2)	N(2)C(8)S(4)	120.60(9)
C(1)N(1)C(7*B*)	127.1(9)	C(8)N(2)C(9)	120.59(10)
C(2)N(1)C(7*A*)	117.5(2)	C(8)N(2)C(14)	122.68(10)
C(2)N(1)C(7*B*)	110.0(10)	C(9)N(2)C(14)	116.70(10)
C(7*A*)N(1)C(7*B*)	10.7(9)	N(2)C(9)C(10)	110.23(10)
N(1)C(2)C(3)	112.46(13)	N(2)C(14)C(13)	113.61(11)
N(1)C(7*A*)C(6*A*)	116.4(2)	C(9)C(10)C(11)	114.89(11)
N(1)C(7*B*)C(6*B*)	103.0(6)	C(10)C(11)C(12)	116.09(11)
C(2)C(3)C(4*A*)	114.01(15)	C(11)C(12)C(13)	113.63(12)
C(2)C(3)C(4*B*)	118.0(3)	C(12)C(13)C(14)	114.52(12)
C(4*A*)C(3)C(4*B*)	25.3(3)		
C(3)C(4*A*)C(5*A*)	118.5(2)		
C(3)C(4*B*)C(5*B*)	108.3(5)		
C(4*A*)C(5*A*)C(6*A*)	114.6(2)		
C(4*B*)C(5*B*)C(6*B*)	108.9(6)		
C(5*A*)C(6*A*)C(7*A*)	115.8(2)		
C(5*B*)C(6*B*)C(7*B*)	115.2(11)		
Angle	**φ, deg**	**Angle**	**φ, deg**
Cd(1)S(1)S(2)C(1)	170.30(8)	Cd(1)S(3)S(4)C(8)	178.88(7)
S(1)Cd(1)C(1)S(2)	171.90(7)	S(3)Cd(1)C(8)S(4)	179.04(6)
S(1)C(1)N(1)C(2)	−3.8(2)	S(3)C(8)N(2)C(9)	4.5(2)
S(1)C(1)N(1)C(7*A*)	176.9(2)	S(3)C(8)N(2)C(14)	−177.9(1)
S(1)C(1)N(1)C(7*B*)	−173.2(6)	S(4)C(8)N(2)C(9)	−177.74(8)
S(2)C(1)N(1)C(2)	175.7(1)	S(4)C(8)N(2)C(14)	−0.1(2)
S(2)C(1)N(1)C(7*A*)	−3.6(3)		
S(2)C(1)N(1)C(7*B*)	6.4(6)		

* Symmetry transformation: ^{a} $-x + 2, -y + 2, -z$.

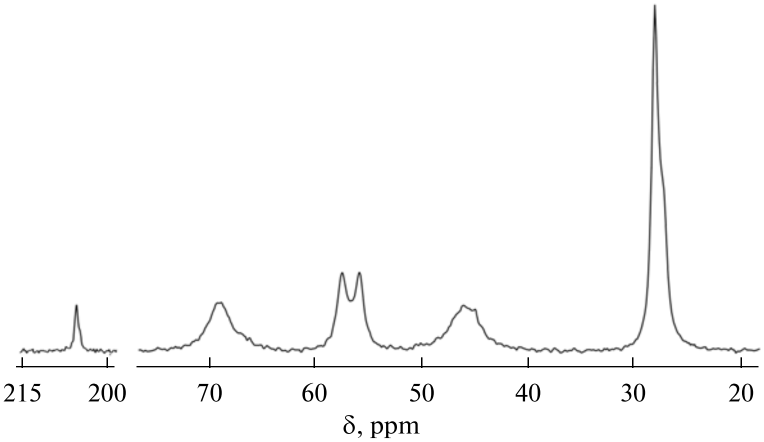

Fig. 1. The ^{13}C CP/MAS NMR spectrum of crystalline adduct **II** *cis*-$[Cd\{NH(CH_2)_4O\}_2\{S_2CN(CH_2)_6\}_2]$ (8220/5600); scan number/rotation frequency of the sample (in Hz) is given in parentheses.

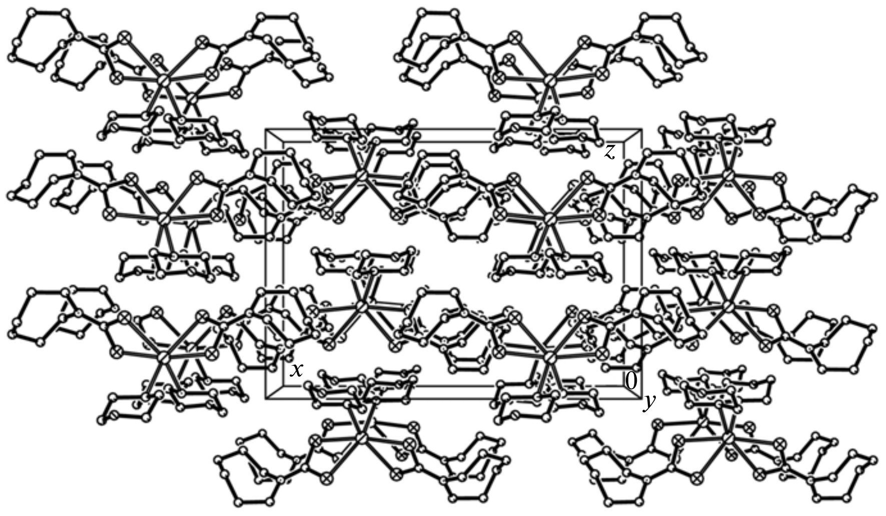

Fig. 2. Projection of the structure of adduct **II** on the *xz* plane.

nar angle between the hemicycles [CdSS] and [CSS] is 177.92° (Table 2).

The values of the CNCS torsion angles (Table 2) show that the $C_2NC(S)S$ groups are close to the planar ones with some deviation of the C(2) and C(7) atoms from the plane. The N–C(S)S bond length (1.339 Å) is intermediate between the typical values for the double C=N (1.27 Å) and ordinary C–N (1.46 Å) bonds, which shows a substantial contribution of double bonding. Both these facts indicate that sp^2 is admixed to the sp^3 state of the nitrogen and carbon atoms in the =NC(S)S-groups.

The conformation of the seven-membered heterocycles $-N(CH_2)_6$ corresponds to a skewed chair [26, 27]. The angles in the cycles take values of 113.4°–115.4°, and the CNC angle increases to 118.6° due to the admixing of the sp^2-hybrid state of nitrogen. The C–C bond lengths vary from 1.498 to 1.517 Å, and the C–N bonds are 1.475 and 1.483 Å.

Structure **I** was refined by X-ray diffraction analysis. The unit cell of the complex includes two centrosymmetric binuclear molecules $[Cd_2\{S_2CN(CH_2)_6\}_4]$ (Cd···Cd distance 3.676 Å) formed due to the joining of the mononuclear fragments $[Cd\{S_2CN(CH_2)_6\}_2]$ by two additional Cd–S bonds (Fig. 4, Table 3). Thus, the discussed complex includes two terminal HmDtc ligands and two ligands with the mixed function (chelate-bridging). The latter in the structures of the mononuclear $[Cd\{S_2CN(CH_2)_6\}_2]$ fragments exhibit the S,S'-aniso-

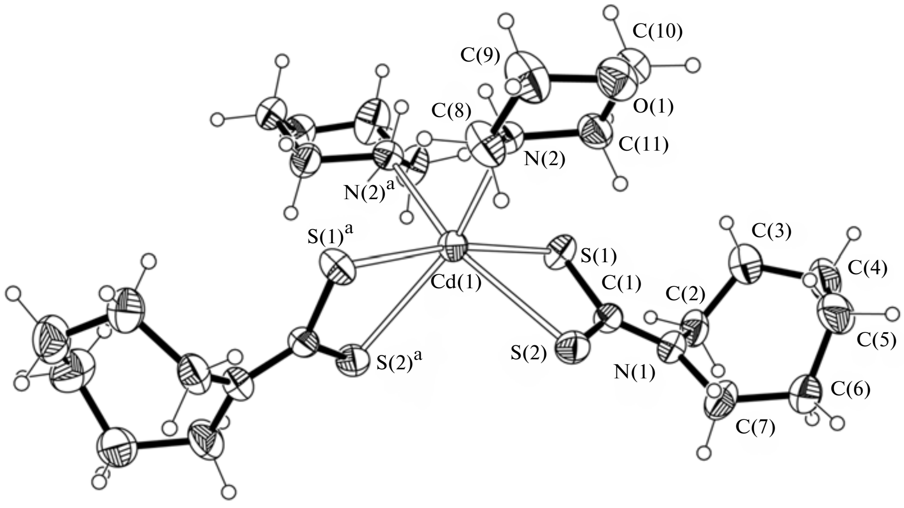

Fig. 3. Molecular structure of adduct **II**, *cis*-$[Cd\{NH(CH_2)_4O\}_2\{S_2CN(CH_2)_6\}_2]$ (ellipsoids of 50% probability; symmetry transformation: ^{a} $x + 1/2, -y + 1/2, z$).

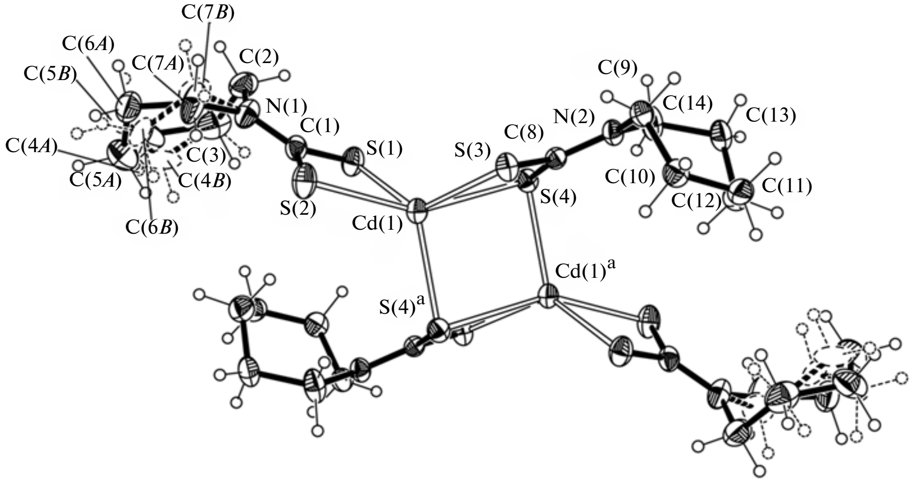

Fig. 4. Molecular structure of compound **I**, $[Cd_2\{S_2CN(CH_2)_6\}_4]$ (ellipsoids of 50% probability).

bidentate coordination: the Cd–S(3, 4) bonds (2.5594 and 2.8843 Å) are nonequivalent in length. The bridging S(4) atom forms a considerably stronger bond with the cadmium atom of the adjacent mononuclear fragment: 2.5852 Å. The discussed ligands involved in binding of two cadmium atoms form an extended eight-membered metallocycle $[Cd_2S_4C_2]$, which can be described by a chair conformation. The anisobidentate character of coordination of the terminal ligands forming the four-membered metallocycles $[CdS_2C]$ is considerably less pronounced. The seven-membered heterocycles $-N(CH_2)_6$ of these ligands are characterized by statistical disordering of the C(4)–C(7) atoms between two positions. As a whole, the cadmium atom in structure **I** is surrounded by five sulfur atoms (Cd–S 2.5498–2.8843 Å). The geometry of the $[CdS_5]$ polyhedron is intermediate between tetragonal pyramidal (TP) and trigonal bipyramidal (TBP). This geometry can quantitatively characterized by the parameter τ for complexes with the coordination number 5 [28]: $\tau = (\alpha - \beta)/60$, $\alpha > \beta$ (in our case, α and β are values of two largest SCdS angles). For the ideal TP (C_{4v}) $\tau = 0$, since $\alpha = \beta$; in the regular TBP (C_{3v}) the axial angle is L–M–L $\alpha = 180°$, and the equatorial angles are $\beta = 120°$, which determines $\tau = 1$. Therefore, polyhedra with any ratios of the TP/TBP contribution can be characterized by the parameter τ in the range from 0 to 1. In structure **I**, two largest SCdS angles are 151.789° and 132.368° (Table 3). Thus, $\tau = 0.32$ predominantly determines the TP geometry of the cadmium polyhedron with the ~32% contribution of the TBP component. In the distorted TP, the cadmium atom shifts from the plane of four sulfur atoms to the S(4)^a atom by 0.8155(2) Å.

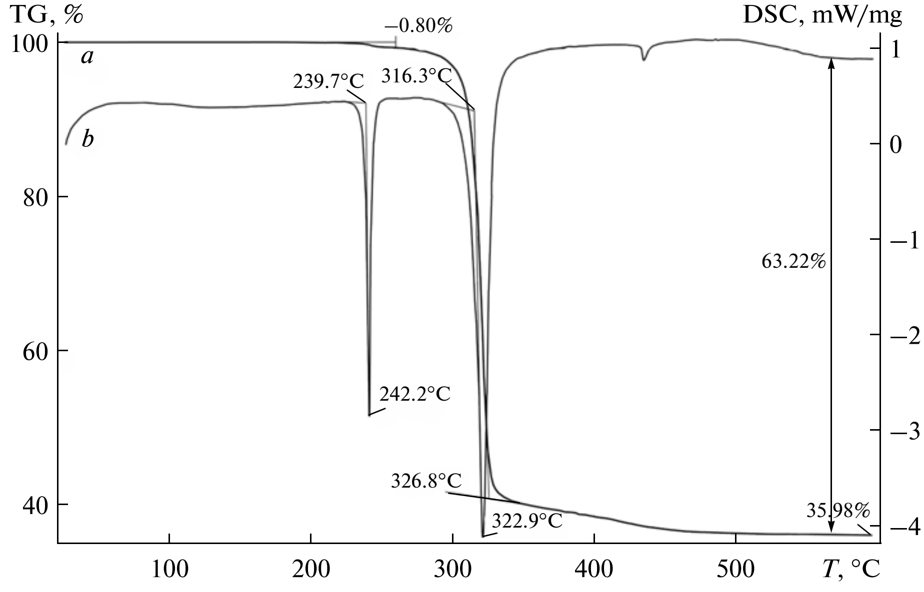

Fig. 5. (*a*) TG and (*b*) DSC curves for complex **I**.

In spite of a complicated character of thermolysis of the dithiocarbamate complexes [29, 30], the main mass loss of complex **I** occurs in one stage. In the range from 230 to 260°C, the TG curve detects a small mass loss step of 0.80%, which reaches the steeply descending region (57.48%) with the maximum rate of mass loss at 322.3°C (Fig. 5*a*). The intense thermolysis stops at 326.8°C, and the TG curve ceases with a smooth region of the fluent desorption of the decomposition products (5.74%). The DSC curve (Fig. 5*b*) fixes two endotherms with extremes at 242.2 and 322.9°C. The former is due to the melting of the substance (extrapolated m.p. 239.7°C); and a range of 238–240°C was established by the independent determination of the mp. The latter endotherm corresponds to the thermolysis of **I** and evaporation of the decomposition products.

The TG curve demonstrates a more complicated thermal behavior of adduct **II** (Fig. 6*a*). The mass loss at the first, low-temperature stage begins already from 60°C, attaining the maximum rate at 109.1°C. The fixed mass loss (21.85%) is significantly lower than the expected value due to the desorption of two morpholine molecules (calculated 27.42%). This makes it possible to assign the next, smoother region of the TG curve to the final desorption of released morpholine, which ceases at 234°C attaining the calculated value. The final, high-temperature stage of mass loss begins from 234°C and is due to the thermal destruction of the "dithiocarbamate moiety" of the compound. The DSC curve of adduct **II** (Fig. 6*b*) includes three endotherms with extremes at 100.7, 239.3, and 292.3°C. It was found by the independent measurements of the m.p. of **II** that the first endotherm with a complicated structure caused by the release and desorption of morpholine molecules also includes the melting of the adduct that falls on 98°C. The second and third endotherms show the melting (extrapolated m.p. 237.1°C) and thermolysis of the formed cadmium *cyclo*-hexamethylenedithiocarbamate.

An analysis of the TG curves (Figs. 5*a* and 6*a*) revealed the shift of the thermolysis range of the dithiocarbamate region of adduct **II** to the low-temperature range (the extrapolated temperature of the end of the process is 304.0°C, and that for the initial complex **I** is 326.8°C). A similar effect has earlier been observed when studying the thermal behavior of the zinc dithiocarbamate complexes and their adducts with hexamethyleneimine [31]. The observed shift is explained by the fact that the detachment of morpholine molecules by adduct **II** leads to the formation of the unstable mononuclear form of complex $[Cd\{S_2CN(CH_2)_6\}_2]$, whose thermolysis (as well as melting) occurs in the region of lowered temperatures.

Upon the end of thermolysis, the crucibles contained dark powders with irregular particles 30–458 μm in size. The energy dispersion spectra make it possible to reveal the presence of cadmium, sulfur, and carbon in the samples (Fig. 6*c*). The weights of residues **I** and **II** were 35.98 and 26.91%, respectively, which agrees with the assumption of the formation of CdS (calculated 31.33% (**I**) and 22.74% (**II**)) contaminated with the thermolysis products. (Under the conditions of an atmosphere free of oxygen, the accompanying formation of carbon is usually observed.) The thermodynamic substantiation of the formation of metal sulfides upon the thermolysis of the complexes with sulfur-containing ligands is being performed [32].

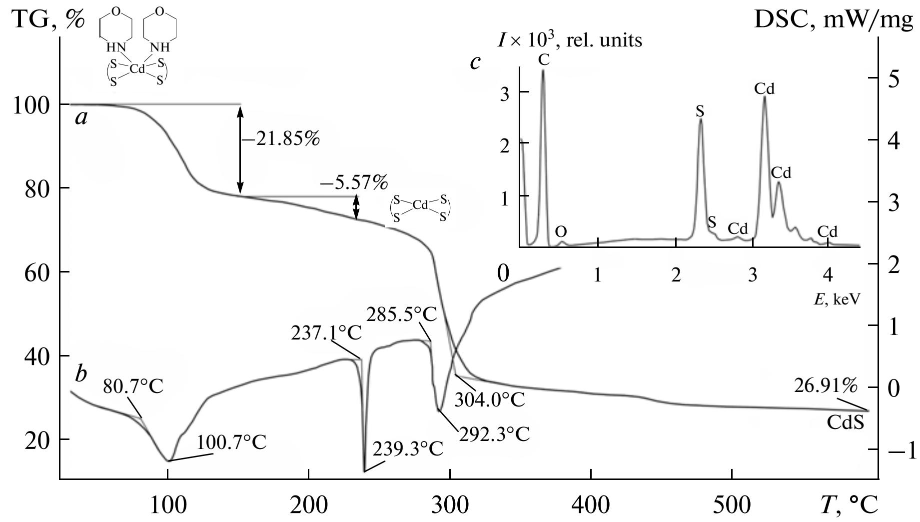

Fig. 6. (*a*) TG and (*b*) DSC curves for adduct **II**; (*c*) the energy dispersion spectrum of the residual substance after thermolysis.

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