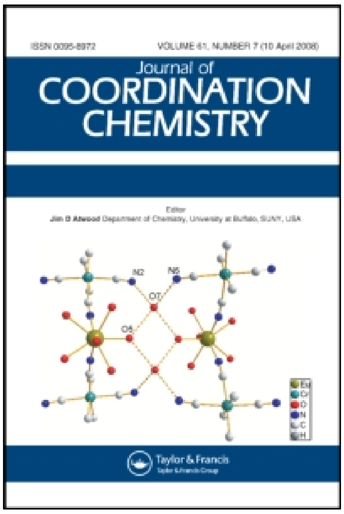

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Synthesis and characterisation of a novel polymeric Cd complex, *catena*-(μ-thio)[bis(*N*-phenylthiourea] bis(dimethylsulphoxide)dichlorocadmium(II)

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Synthesis and characterisation of a novel polymeric Cd complex, *catena*-(μ-thio)[bis(*N*-phenylthiourea] bis(dimethylsulphoxide)dichlorocadmium(II)

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A new Cd(II) complex, $[CdL(DMSO)_2Cl_2]_n$, L = bis(*N*-phenylthiourea), has been synthesized and its crystal structure determined from single-crystal diffraction data. The compound is orthorhombic, space group $Pna2_1$, with $a = 18.728(1)$, $b = 12.2601(8)$, $c = 22.879(1)$ Å, $V = 5253.3(6)$ Å^3. L acts as an exobidentate neutral ligand and Cd is octahedral, being bonded to two S atoms, two terminal Cl ions and two DMSO solvent molecules. The structure is that of a one-dimensional polymer, with chains running parallel to the *b* axis. Polymeric chains are stabilized by N–H···Cl hydrogen bonding, while intermolecular S···O contacts connect the chains. Thermal decomposition of the complex starts at 120°C by desolvation and is continuous over the recorded temperature range.

Keywords: Cadmium(II) complex; Bis(*N*-phenylthiourea); X-ray crystal structure

1. Introduction

Owing to their complexing ability, thiourea and its derivatives are often used as analytical reagents for qualitative and quantitative determination of metal ions [1]. They are otherwise versatile compounds, showing application potential in different areas. They improve the stability, reactivity and selectivity of chemically modified electrodes used for voltammetric determination of metal ions [2] and bis(*N*-phenylthiourea) has been patented as a collector for precious metal ions from sulfide ores [3]. In addition, the biological activity and the antiviral potential of substituted thioureas has been described [4–6]. However, for their effective application as antiviral plant protection

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agents, activity must be increased, and this can be achieved by complex formation with metal ions [7].

We are engaged in systematic studies of transition metal complexes of pyrazole derivatives, with the aim of determining effects that different substituents have on complexing properties of the ligands and the reaction pathways of complex formation [8–12]. To our knowledge, 3,5-dimethyl-1-*N*-phenylthiocarboxamide pyrazole has not been reported. In attempts to synthetize this ligand using the method of Buttkus and Bose [13], we obtained bis(*N*-phenylthiourea), L, instead. Since scission of the 1-*N*-pyrazole substituent in an acidic medium sometimes yields the corresponding thiourea and 3,5-dimethylpyrazole, the formation of L is not completely unexpected [14]. Bis(*N*-phenylthiourea) was reported by Furlani and Tarantelli [15] and subsequently by Akinchan *et al.* [16], who carried out a spectroscopic characterization and determined the crystal structure of the compound. Recently, two new complexes of bis(*N*-phenylthiourea) with Hg(II) and Ni(II) have been synthesized [17]. The coordination modes in these two cases were discussed on the basis of molecular structures proposed from spectroscopic evidence, as the crystal structures of the complexes were not determined. In this article, we report the synthesis of a novel Cd(II) complex of bis(*N*-phenylthiourea), its crystal structure, IR spectrum and thermal decomposition behaviour.

2. Experimental

All reagents were of analytical grade and used without further purification. IR spectra were recorded at room temperature using KBr pellets, in the range 4000–400 $\mathrm{cm^{-1}}$ on a ThermoNicolet NEXUS 670 FTIR spectrophotometer. Elemental analyses were carried out by standard procedures. Thermal analyses were performed using Perkin Elmer Pyris 1 TGA and DSC instruments, with a sample mass of circa 3 mg and a heating rate of $10^\circ\mathrm{C\,min^{-1}}$, in a nitrogen atmosphere. Pt and Al sample holders were used for TG and DSC, respectively.

2.1. *Synthesis*

2.1.1. Ligand, L. Furlani and Tarantelli synthesized bis(*N*-phenylthiourea) by a reaction of *N*4-phenylthiosemicarbazide (PhTSC) and phenylisothiocyanate [15], while Akinchan and Drozdzewski prepared the same ligand by reacting phenyl isothiocyanate with hydrazine [16–18]. In our procedure, the starting compounds were *N*-phenylthiosemicarbazide and acetylacetone (Hacac) and the synthesis of the ligand was performed following the method reported by Buttkus and Bose [13]. A suspension of 6 mmol (1.0 g) of PhTSC in 5 $\mathrm{cm^3}$ of water was added to 3 mmol (0.3 $\mathrm{cm^3}$) of Hacac, suspended in 3 $\mathrm{cm^3}$ of acetate buffer, pH 5. The mixture was stirred at room temperature for 2 h until a resin ball formed. After 24 h the ball was separated and dissolved in 10 $\mathrm{cm^3}$ of MeOH. The solution was treated with 5 $\mathrm{cm^3}$ of 2 $\mathrm{mol\,dm^{-3}}$ HCl in MeOH on a steam bath for 1 h. After standing the mixture overnight at room temperature, the white plate-like crystals that had formed were filtered off, washed with MeOH and air-dried. Yield: 57% (0.52 g). *Anal.* Calcd (%): C, 55.35; H, 5.43; N, 18.35. Found: C, 55.60; H, 4.67; N, 18.53. IR: ν(N–H) 3212 and 3116 $\mathrm{cm^{-1}}$, δ(N–H) 1547, 1189, 932–900 and 550 $\mathrm{cm^{-1}}$, ν(C–N) 1449 $\mathrm{cm^{-1}}$ and ν(C=S) 748 $\mathrm{cm^{-1}}$ [17–19].

2.1.2. $[CdL(DMSO)_2Cl_2]_n$. The complex was prepared by mixing a solution containing 0.1 mmol (0.020 g) of $CdCl_2 \cdot H_2O$ in 9 cm^3 of MeOH with 0.08 mmol (0.024 g) of bis(*N*-phenylthiourea) in 1 cm^3 of DMSO. After the reaction mixture was stirred at room temperature for 30 mins, crystallization began. White crystalline product was filtered off after 24 h, washed with MeOH and air-dried. Single crystals in the shape of very thin needles could be isolated from this product. Yield: 70% (0.035 g). *Anal.* Calcd (%): C, 33.68; N, 8.73; H, 4.08. Found: C, 33.54; N, 8.71; H, 4.02. Relative to characteristic IR bands of L, only ν(C=S) undergoes any significant shift (11 cm^{-1}) to lower frequency (737 cm^{-1}), indicating coordination of bis(*N*-phenylthiourea) through sulphur of the C=S group. Characteristic ν(S=O) bands of coordinated DMSO appear at 1001 and 950 cm^{-1}. Both occur at lower frequency than the corresponding band in free DMSO, suggesting its coordination through the oxygen atom [19]. Intermolecular S···O interactions between adjacent DMSO molecules (*vide infra*) contribute to the splitting of this absorption band.

2.2. *Crystallography*

Single crystals of the ligand (with approximate dimensions 0.02 × 0.04 × 0.10 mm) and the complex (with approximate dimensions 0.04 × 0.04 × 0.40 mm) were selected for data collection. All data were collected on a Bruker AXS SMART diffractometer equipped with an APEX CCD detector, a Bede Microsource® generator (Mo Kα radiation) and an Oxford Cryosystems N_2 Cryostream. In both cases, a full sphere of data was collected with a frame width of 0.3° and a counting time of 30 s per frame. Diffraction data were integrated using the program SAINT [20]. A multiscan absorption correction was applied to the raw data [21]. The crystal structures were solved by direct methods implemented in the program SIR92 [22] and refined by full-matrix least-squares against F^2 in the Crystal's suite [23].

Crystallographic details are summarized in Table 1. The crystal structure of the ligand at 120 K does not differ from the published room temperature structure [16], apart from effects of thermal contraction. It is therefore not discussed further here.

Table 1. Crystallographic details for L and $[CdL(DMSO)_2Cl_2]_n$ complex.

Chemical formula	$C_{14}N_4S_2H_{14}$	$CdC_{18}N_4S_4Cl_2O_2H_2$
Molecular weight (amu)	151.2	642.0
Crystal system	Monoclinic	Orthorhombic
Space group	*C*2/*c*	*Pna*2$_1$
a (Å)	26.759(3)	18.728(1)
b (Å)	6.3056(6)	12.2601(8)
c (Å)	9.4622(9)	22.879(1)
β (°)	105.459(2)	
V (Å^3)	1538.8(3)	5253.3(6)
Z	4	8
T (K)	120	120
Calculated density (g cm^{-3})	1.31	1.62
μ (mm^{-1})	0.34	13.75
Total number of reflections	10287	44733
Number of observed reflections	2226	6150
Number of parameters refined	119	553
R_{int} (%)	1.6	7.00
R (%)	4.05	8.09
wR (%)	6.64	12.28

However, all geometric parameters used for comparison with the structure of the complex refer to our determination of the ligand crystal structure at 120 K.

3. Results and discussion

$[CdL(DMSO)_2Cl_2]_n$ crystallizes in the polar noncentrosymmetric space group $Pna2_1$. At the early stages of the refinement, the absolute structure was refined and the Flack parameter value obtained was 0.54(5), suggesting that the sample was a racemic twin. Friedel pairs were subsequently merged for the final cycles of the refinement. There are two formula units in the crystallographic asymmetric unit, but molecular units do not exist as separate entities. Instead, a one-dimensional polymeric structure is formed, such that $[CdL(DMSO)_2Cl_2]_n$ chains run parallel to the *b* axis (Figure 1).

The Cd atoms have distorted octahedral coordination, with bond angles between 80 and 98°. Each Cd atom bonds to two S atoms of bis(*N*-phenylthiourea) ligand, two terminal Cl ions and the coordination sphere is completed by two molecules of the DMSO solvent. S atoms act as bridges in the polymeric chains. Orientational disorder occurs in one of the DMSO units, and this was modelled as two half-occupied $–S–(CH_3)_2$ fragments. The selected bond lengths and angles for $[CdL(DMSO)_2Cl_2]$ are listed in table 2.

The phenyl rings in the coordinated ligand are essentially planar, with the largest deviation from the mean planes of 0.02 Å, while the maximum deviation from planarity of the $–N_2CS$ groups is slightly larger, 0.03 Å. The two unique C–N–C–N torsion angles in the complex are 122.28° for C30–N15–N16–C36 and −124.82° for C34–N22–N17–C31. These are very similar to the corresponding torsion angle (−122.04°) in the structure of the ligand. While the geometry of the central backbone of the ligand thus remains largely unchanged [17], significant changes in the orientation of the phenyl rings occur during complexation. In the structure of the ligand, the $–N_2CS$ group forms a dihedral angle of 84.5° with the neighbouring phenyl ring. In $[CdL(DMSO)_2Cl_2]$, four such unique dihedral angles exist and they are 53.6 and

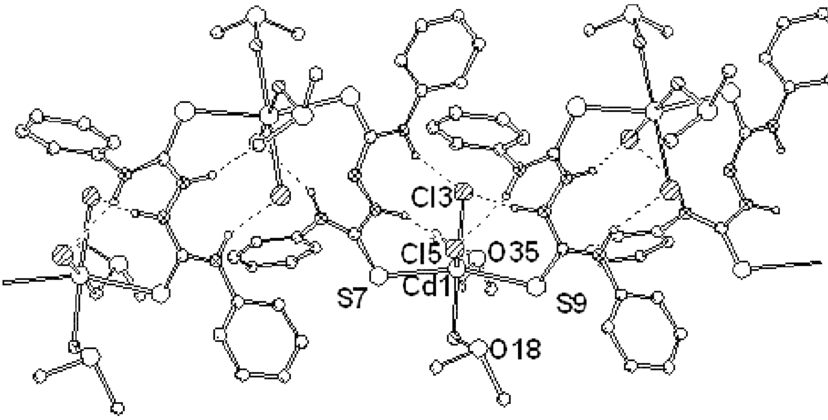

Figure 1. 1D polymeric arrangement of $[CdL(DMSO)_2Cl_2]_n$ chains parallel to the *b* axis; dotted lines depict N–H···Cl hydrogen bonds in the chains.

Table 2. Selected bond distances and angles in $[CdL(DMSO)_2Cl_2]_n$.

Cd1–Cl3	2.639(3)
Cd1–Cl5	2.620(3)
Cd1–S7	2.668(3)
Cd1–S9	2.651(4)
Cd1–O18	2.345(9)
Cd1–O35	2.280(10)
Cd2–Cl4	2.640(4)
Cd2–S14	2.626(3)
Cd2–Cl6	2.600(3)
Cd2–S8	2.661(4)
Cd2–O21	2.303(9)
Cd2–O57	2.313(12)
Cl3–Cd1–Cl5	90.32(11)
Cl3–Cd1–S7	97.07(11)
Cl5–Cd1–S7	95.76(11)
Cl3–Cd1–S9	93.92(11)
Cl5–Cd1–S9	97.03(12)
Cl5–Cd1–O18	91.0(2)
S7–Cd1–O18	83.3(3)
S9–Cd1–O18	85.5(3)
Cl3–Cd1–O35	95.5(3)
S7–Cd1–O35	81.3(3)
S9–Cd1–O35	84.9(3)
O18–Cd1–O35	83.2(4)
Cl4–Cd2–S14	97.91(12)
Cl4–Cd2–Cl6	91.96(12)
S14–Cd2–Cl6	96.31(12)
Cl4–Cd2–S8	97.60(11)
Cl6–Cd2–S8	96.14(11)
Cl4–Cd2–O21	89.6(3)
S14–Cd2–O21	84.5(3)
S8–Cd2–O21	82.7(3)
S14–Cd2–O57	83.2(4)
Cl6–Cd2–O57	93.5(4)
S8–Cd2–O57	80.1(4)
O21–Cd2–O57	84.9(5)

69.0° for one independent ligand molecule, and 51.2 and 74.6° for the other. This twisting of the phenyl substituents is presumably favourable from a steric point of view, as it results in an essentially perpendicular arrangement of adjacent phenyl rings along the polymeric chain. This allows maximum spatial separation, with dihedral angles between neighbouring rings of 96, 90, 98 and 90°. This is illustrated in the packing diagram of $[CdL(DMSO)_2Cl_2]$, shown in Figure 2. The structure within the chains is stabilized by N–H···Cl hydrogen bonding (Figure 1, Table 3). Intermolecular S···O non-bonded contacts provide connectivity between the chains. The S···O distance of 3.04 Å is significantly shorter than the sum of the van der Waals radii [24]. Similar interactions in complexes with coordinated DMSO molecules have been reported in the literature [25–27].

Molecular structures proposed on the basis of spectroscopic studies suggest different coordination modes of L in its Hg(II) and Ni(II) complexes [17]. Bis(*N*-phenylthiourea) appears to act as a monoanionic bidentate in the case of $Ni(L{-}H)_2$, while in $Hg_2(L{-}2H)Cl_2$ it coordinates as a dianionic bis(bidentate) chelate. This results in the formation of a square planar Ni(II) complex and a dinuclear three-coordinate Hg(II) complex. In both cases L coordinates through its thiolato sulphur and hydrazine

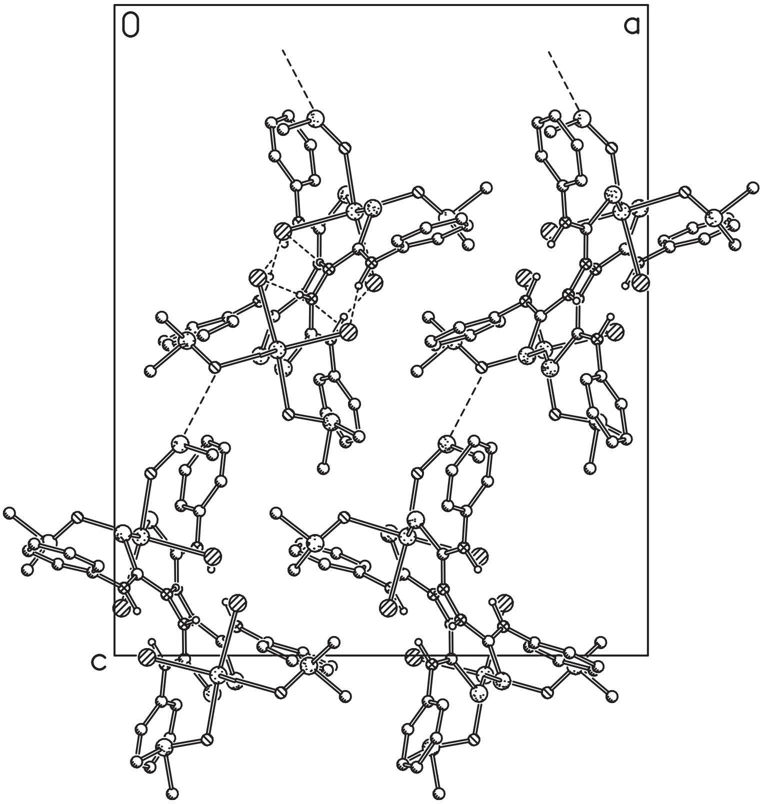

Figure 2. A view of the packing scheme in $[CdL(DMSO)_2Cl_2]_n$ shown down the crystallographic *b* axis; dotted lines depict N–H···Cl hydrogen bonds within the chains; dashed lines represent intermolecular S···O interactions between the chains.

Table 3. Hydrogen bonding in $[CdL(DMSO)_2Cl_2]_n$.

Donor	H Acceptor	H···A (Å)	D···A (Å)	D–H···A (°)
N(15)–	H(151)···Cl(3)	2.254(11)	3.186(11)	154.5(10)
N(16)–	H(161)···Cl(4)	2.180(12)	3.135(12)	159.2(11)
N(17)–	H(171)···Cl(6)	2.283(12)	3.194(12)	150.8(11)
N(22)–	H(221)···Cl(5)	2.201(12)	3.160(12)	160.1(11)
N(24)–	H(241)···Cl(6)	2.325(12)	3.255(12)	154.1(11)
N(27)–	H(271)···Cl(4)	2.259(13)	3.199(13)	155.9(12)
N(32)–	H(321)···Cl(3)	2.382(12)	3.300(12)	152.6(11)
N(33)–	H(331)···Cl(5)	2.287(13)	3.228(13)	156.5(13)

nitrogen atoms, forming five-membered metallocycles. The reported syntheses of Hg(II) and Ni(II) complexes were carried out using ethanol solutions. By contrast, in the reaction with $CdCl_2$ using a solvent mixture of methanol and DMSO, bis(*N*-phenylthiourea) acts as a monodentate neutral ligand and coordinates through the sulphur atom only, to which Cd(II) has coordination preferences due to its soft acid character [27–30].

Thermal of the complex is continuous over the recorded range (50–300°C). It starts at 120°C by evaporation of solvate molecules. The mass loss at 150°C (the inflection point of the TG curve and matching DSC derivative) corresponds to one DMSO molecule (Found: 12%, Calcd: 12.17%). This is immediately followed by the evaporation of the second solvent molecule, together with fragmentation of the ligand. Decomposition is endothermic up to 250°C and the shape of the DSC curve suggests that decomposition of the compound is accompanied by melting. The presence of the DMSO solvent seems to be a key factor for the complex formation.

Supplementary material

Full lists of crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC No. 269068); see http://www.rsc.org/suppdata for crystallographic data in cif format.

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