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Synthesis and characterisation of some N-alkyl/aryl and N,N'-dialkyl/aryl thiourea cadmium(II) complexes: the single crystal X-ray structures of $[CdCl_2(CS(NH_2)NHCH_3)_2]_n$ and $[CdCl_2(CS(NH_2)NHCH_2CH_3)_2]$

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Abstract

A series of cadmium(II) complexes with N-alkyl or aryl and N,N'-dialkyl or diaryl thioureas (RNHCSNHR′; where R = R′ = CH_3, CH_2CH_3, C_6H_5 and or R′ = H) have been synthesised and characterised. The structures of the polymer $[CdCl_2(CS(NH_2)NHCH_3)_2]_n$ (**I**) and monomer $[CdCl_2(CS(NH_2)NHCH_2CH)_2]$ (**II**) were determined by single crystal X-ray methods. The structure (**I**) is a polymer chain built from $[CdCl_3S_3]$ distorted octahedra. Complex **II** is monomeric with a distorted tetrahedral geometry at the cadmium centre. ^1H NMR spectroscopy in deuterated dimethyl sulfoxide at room temperature had broadened NH peaks in the lower field (region 6.0–10.0 ppm) which indicates the presence of both *cis* and *trans*-isomers for the N-alkylthioureas. All the spectroscopic data obtained are consistent with the coordination of ligands by sulphur atom to the metal ion. Thermogravimetric studies show that several of these complexes decompose cleanly to CdS and may be useful in materials preparation.

Keywords: N-Alkylthiourea; Cadmium(II) complexes; Synthesis; X-ray structures

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1. Introduction

The chemistry of substituted thiourea derivatives has attracted attention because of their potential use as reagents for the separation of metal ions [1] and in biological applications such as their use: as antibacterial [2,3], antiviral [4] or antifungal agents [5,6]. In addition to their applications, the ligands are of interest as they possess various potential donor sites: the sulphur atom of the C–S group and the nitrogen atom of the NH, NHR or NRR′ groups (where R = R′ = alkyl or aryl groups). Several studies have been made on the co-ordinating ability of these ligands mainly with aim of determining the coordination mode. The N-alkyl substituted thiourea, with the coplanar N_2CS skeletal atoms can take two possible conformational forms, *trans* and *cis* whereas three different conformations are possible for N,N'-dialkyl substituted thioureas the *cis–cis*, *trans–trans* and *cis–trans* isomers (Fig. 1). NMR studies have been in efforts to determine the extent of the rotation about the S=CN bond in thioureas [7–10].

A number of studies on the structural conformation of N-methylthiourea have been carried out, both in the

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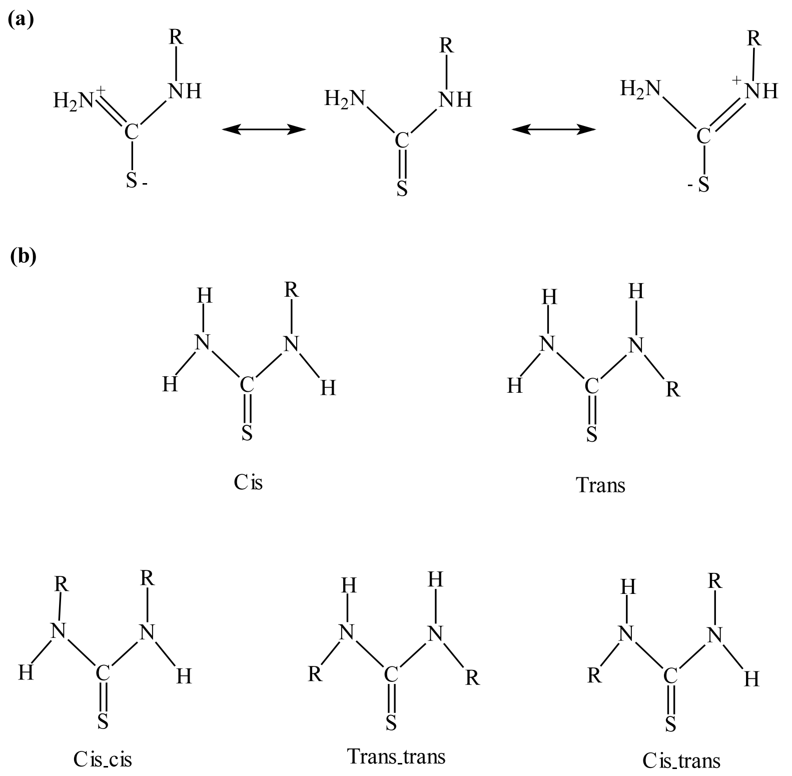

Fig. 1. Structure of substituted thiourea showing delocalisation of the π-bond (a) and conformational isomers for both mono and disubstituted alkyl/aryl thiourea (b).

solid state and solution [11–13]. It was confirmed by Mido et al. [14] through Raman and IR and X-ray structural analyses of *N*-methylthiourea that the compound assumes the *cis* configuration (Fig. 1) in the solid state. Lane et al. [11] studied the infrared spectra of several thiourea derivatives in the solid state. They found that *N*,*N*′-dimethylthiourea and *N*,*N*′-diethylthiourea were *trans–trans* isomers. Subsequent studies on the coordination of these molecules were made using infrared spectra to determine their binding sites [11,15–22]. In most complexes they bind through the sulphur atom although there are examples of complexes with *N*-bonded alkylthiourea derivatives [23]. The cadmium(II) and copper(I) complexes show marked similarity in their structures in that they form clusters [24], dinuclear [25] or polynuclear complexes [26,27] whereas other complexes are monomeric [21,22]. There is a substantial downshift in the vibrational frequencies of C=S bond when coordinated to a metal, suggesting considerable interactions between the thiourea molecules and the metals [15].

Thiourea has also been used in the deposition of CdS thin films from aqueous solutions [28]. In this work our interest lies in studying the binding of the substituted thiourea molecules to cadmium through sulphur atom of the CS group as such compounds could be used as precursors in the preparation of CdS nanoparticles. We report the X-ray structural analysis of the two complexes and the infrared and NMR spectra of the cadmium(II) complexes of the *N*-methyl-, *N*-ethyl-, *N*-phenylthiourea and their *N*,*N*′-disubstituted analogues.

2. Experimental

2.1. Materials and instrumentation

Cadmium chloride, *N*-methylthiourea, *N*-ethylthiourea, *N*-phenylthiourea, *N*,*N*′-dimethylthiourea, *N*,*N*′-diethylthiourea, *N*,*N*′-diphenylthiourea obtained from Aldrich, were used as purchased. Ethanol (analytical grade) was used without further purification. X-ray data was collected on an Enraf Nonius CAD-4 diffractometer. Microanalysis was performed on a CARLO ERBA elemental analyser for C, H, N, S while for Cd a Horizon ICP Fisons elemental analyser was used. Infrared spectra were recorded on FT-IR Perkin–Elmer Paragon 1000 spectrophotometer as nujol mulls. NMR spectra were recorded on a Varian Associates Inova spectrometer (400 and 300 MHz). Thermogravimetric and differential thermal analysis (TGA and DTA) were performed up to 800 °C on Shimadzu analysers TGA-50 and DTA-50 with nitrogen flow and heating rate of 10 °C min^{-1}.

2.2. *Preparation of the complexes*

All compounds were prepared using a similar methods as outlined below.

2.3. *$[CdCl_2(CS(NH_2)NHCH_3)_2]_n$ (**I**)*

In a typical experiment a hot solution of *N*-methylthiourea (0.150 g, 1.66 mmol) in ethanol (10 ml) was added into a heated solution of cadmium chloride (0.153 g, 0.83 mmol) in ethanol (15 ml). The mixture was stirred and refluxed for 2 h. The colourless solution was filtered to remove any traces of unreacted materials while hot and was left in an open beaker at room temperature to crystallise by slow evaporation. Transparent cubic crystals were obtained after 24 h. The product was filtered, washed twice with ethanol and dried under vacuum. Yield 55.6% m.p. 233 °C *Anal*. Calc. C, 13.2; H, 3.3; N, 15.4; S, 17.6; Cd, 30.9 Found: C, 13.3; H 3.3; N 15.0; S 16.9; Cd 31.3. IR (nujol mull) cm^{-1}: 3342(m), 3293(m), 3195(m), 3140(m), 2925(vs), 2854(s), 1676(sh), 1625(vs), 1573(vs), 1488(w), 1462(s), 1417(m), 1303(m), 1172(m), 1144(m), 991(vw), 779(m), 720(m), 618(w), 579(w), 532(m), 489(m), 361(s). ^1H NMR (δ, DMSO-d_6) ppm: 7.78, 7.48 and 6.95 (br, NH, NH_2); 2.80 and 2.64 (br, CH_3). $^{13}C\{^1H\}$ NMR (δ, DMSO-d_6) ppm: 183.73 and 179.90 (s, CS); 30.85 and 29.73 (s, CH_3).

2.4. *$CdCl_2(CS(NH_2)NHCH_2CH_3)_2$ (**II**)*

Yield 67% m.p. 201 °C *Anal*. Calc. C, 18.4; H, 4.1; N, 14.3; S, 16.4; Cd, 28.7. Found: C, 18.4; H 4.1; N 14.3; S 16.4; Cd 28.9. IR (nujol mull) cm^{-1}: 3348(m), 3302(w), 3241(m), 3164(s), 1643(s), 1573(vs), 1569(s), 1497(sh), 1317(s), 1109(s), 1011(m), 815(w), 779(w), 718(m), 689(m), 625(m), 567(w), 485(s). ^1H NMR (δ, DMSO-d_6) ppm: 8.09, 7.61 and 6.96 (br, NH, NH_2); 3.06 (br, 4H, CH_2); 1.03 (t, 6H, CH_3). $^{13}C\{^1H\}$ NMR (δ, DMSO-d_6) ppm: 182.32 and 176.64 (s, CS); 38.86 (s, CH_2) 14.89 and 13.97 (s, CH_3).

2.5. *$CdCl_2(CS(NH_2)NHC_6H_5)_2$ (**III**)*

Yield 94% m.p. 210 °C *Anal*. Calc. C, 34.5; H, 3.3; N, 11.5; S, 13.2; Cd, 23.1. Found: C, 35.1; H 3.4; N 11.7; S 13.4; Cd 23.5. IR (nujol mull) cm^{-1}: 3418(m), 3388(m), 3295(s), 3201(s), 1621(vs), 1596(m), 1544(s), 1490(s), 1456(s), 1320(m), 1272(m), 1191(m), 1062(w), 912(w), 857(vw), 792(m), 756(s), 721(s), 692(s), 633(m), 597(s), 562(s), 492(s), 447(w). ^1H NMR (δ, DMSO-d_6) ppm: 9.78 (s, 6H, NH, NH_2); 7.47 (d, 4H, C_6H_5); 7.31 (t, 4H, C_6H_5); 7.11 (t, 2H, C_6H_5). $^{13}C\{^1H\}$ NMR (δ, DMSO-d_6) ppm: 179.38 (s, CS); 139.29, 128.30, 124.29 and 123.38 (s, C_6H_5).

2.6. *$CdCl_2(CS(NHCH_3)_2)_2$ (**IV**)*

Yield 98% m.p. 203 °C *Anal*. Calc. C, 18.4; H, 4.1; N, 14.3; S, 16.4; Cd, 28.7. Found: C, 18.4; H 4.1; N 14.3; S 16.4; Cd 28.9. IR (nujol mull) cm^{-1}: 3286(vs), 3045(w), 1592(vs), 1536(vs), 1308(s), 1190(m), 1150(m), 1040(s), 1023(m), 721(s), 673(m), 569(s), 546(s), 445(w). ^1H NMR (δ, DMSO-d_6) ppm: 7.53 (br, 4H, NH), 2.78 (br, s, 12H, CH_3). $^{13}C\{^1H\}$ NMR (δ, DMSO-d_6) ppm: 181.75 (s, CS); 31.07 (s, CH_3).

2.7. *$CdCl_2(CS(NHC_6H_5)_2)_2$ (**V**)*

Yield 91% m.p. 198 °C *Anal*. Calc. C, 48.8; H, 3.8; N, 8.8; S, 10.0; Cd, 17.6. Found: C, 48.8; H 3.8; N 8.8; S 10.0; Cd 17.6. IR (nujol mull) cm^{-1}: 3333(m), 3162(m), 1614(sh), 1593(s), 1543(vs), 1508(s), 1313(w), 1295(m), 1249(m), 1129(vs), 1073(w), 1024(w), 1003(w), 941(s), 899(w), 761(s), 725(m), 690(vs), 633(m), 601(s), 508(m), 473(w). ^1H NMR (δ, DMSO-d_6) ppm: 9.79 (s, 4H, NH); 7.48 (d, 4H, C_6H_5); 7.32 (t, 4H, C_6H_5); 7.11 (t, 2H, C_6H_5). $^{13}C\{^1H\}$ NMR (δ, DMSO-d_6) ppm: 179.38 (s, CS); 139.29, 128.30, 124.29 and 123.38 (s, C_6H_5).

2.8. *$CdCl_2(CS(NHCH_2CH_3)_2)_2$ (**VI**)*

Yield N.A. m.p. 204 °C *Anal*. Calc. C, 26.8; H, 5.4; N, 12.5; S, 14.4; Cd, 25.1. Found: C, 27.0; H 5.6; N 12.5; S 15.4; Cd 26.7. IR (nujol mull) cm^{-1}: 3342(m), 3312(w), 3198(m), 3159(s), 1650(vs), 1583(s), 1529(s), 1477(m), 1308(m), 1092(s), 808(s), 785(m), 758(m), 692(w), 627(m), 562(w), 485(m). ^1H NMR (δ, DMSO-d_6) ppm: 7.36 (br, NH); 3.32 (br, 8H, CH_2); 1.04 (t, 12H, CH_3). $^{13}C\{^1H\}$ NMR (δ, DMSO-d_6) ppm: 182.76 (s, CS); 43.83 (s, CH_2) and 19.59 (s, CH_3).

2.9. *Crystallography*

The intensity data were collected on a CAD-4 diffractometer and Mo Kα radiation ($\lambda = 0.71069$ Å) using $\omega - 2\theta$ scan. The unit cell parameters were determined by least-squares refinement on diffractometer angles [**I**, $10.93° \leqslant \theta \leqslant 12.88°$, **II**, $9.06° \leqslant \theta \leqslant 12.98°$] for 25 automatically centred reflections [29]. All data were corrected for Lorentz-polarization effects by XCAD4 [30] and for absorption by semi-empirical methods (ψ scan) [31]. The structure was solved by Patterson method using DIRDIF-99,[32] and refined anisotropically (non-hydrogen atoms) by full-matrix least-squares on F^2 using SHELXL-97 [33] program. The H atoms were calculated geometrically and refined with a riding model. The program ORTEP-3 [34] PLATON [35] was used for drawing the molecules. WINGX [36] used to prepare material for publication. Experimental data is given in Table 2.

2.10. X-ray diffraction

X-ray diffraction patterns on powdered samples were measured on Phillips X'Pert materials research diffractometer using secondary graphite monochromated Cu Kα radiation ($\lambda = 1.54060$ Å) at 40 kV/50 mA. Samples were supported on glass slides. Measurements were taken using a glancing angle of incidence detector at an angle of 2°, for 2θ values over 20°–60° in steps of 0.05° with a scan speed of $0.01°2\theta$ s^{-1}.

3. Results and discussion

A series of substituted thiourea cadmium(II) complexes were prepared by first reacting alkylthioureas and cadmium chloride (2:1 mole ratio), in hot ethanol, followed by reflux. The products were obtained as air stable colourless to white crystals, formed upon concentrating the solution at room temperature. The analytical and spectroscopic data are consistent with the proposed formulation of the complexes. Their melting points suggest that they are monomers in general which ranges from 198 to 210 °C, in contrast polymeric $[CdCl_2(CS(NH_2)NHCH_3)_2]_n$, melts at 233 °C.

4. Spectroscopic studies

Mido et al. [14] and Matsuura and co-workers [17] were able to confirm from their spectral observations and the single crystal X-ray structure analysis that the *N*-methylthiourea molecule is in a *cis* form as opposed to the *trans* form. There are a number of features that relate to the binding of ligand molecules to the metal. In $[CdCl_2(CS(NH_2)NHCH_3)_2]_n$, the C=S out-of-plane bending mode (πC=S) and its stretching vibrational mode (νC=S) shows a remarkable shifts from 636 and 495 cm^{-1} to 618 and 489 cm^{-1}, respectively. The vibrational mode (both stretching and bending) due to the C–N bond appear at 1557, 1298 and 1149 cm^{-1} and are shifted to 1573, 1303 and 1172 cm^{-1}, respectively in the complex. The changes, which range from 5 to 20 cm^{-1} are attributed to the weakening of the C–N or C=S bonds on coordination. The CS bond tends to loose its double bond character whereas the CN bond gains electron density raising its bond character. A similar observation was made for all other complexes in their IR spectra associated with CS and CN modes of vibration (Table 1) consistent with the previously reported data [11,18,20,22].

Table 1
Selected IR data for *N*-alkyl- and *N*,*N*′-dialkylthiourea complexes

Complex	Vibrational modes (wave numbers, cm^{-1})			
	νC=S+νC–N	πC=S	νC=S	νC–N
I	779	618	489	1557, 1298, 1149
II	718	625	485	1573, 1569, 1317, 1011
III	756	633	492	1621, 1596, 1544, 1320, 1062
IV	721	569	546	1592, 1536, 1308, 1190
VI	758	627	485	1583, 1529, 1477, 1308, 1092
V	761	633	473	1614, 1593, 1543, 1249, 1073

The NMR spectra of complexes (**I**–**VI**) were recorded at room temperature in deuterated dimethylsulfoxide (CD_3SOCD_3) at 300 and 400 MHz. There is a collapse in the multiplicity of the signals of protons associated with the nitrogen atoms, either neighbouring or directly bonded to them. This observation is consistent with studies of these compounds by variable temperature NMR [10]. At higher temperatures the peaks for the substituted thioureas become well resolved, whereas at lower temperatures there is broadening and coalescence of the peaks associated with NH. This effect is attributed to the slow rotation around the S=CN bond at low temperature and it appears that only two of the three possible rotational isomers of *N*,*N*′-diethylthiourea are present, namely the *cis*–*cis* and the *cis*–*trans* [7]. The *trans*–*trans* isomer is not detectable, probably due to the steric interaction between the two trans-ethyl groups. The low-energy barrier to free rotation around the S=CN bond in thioureas is evidenced by the low temperature at which different isomers have different resonance frequencies due to the competition between the two amide bonds for electron delocalisation (Fig. 1(a)). There was further evidence in NMR studies that the rotation about this amide bond is either rapid or one isomer predominates over the other [8]. However, resonances due to the *cis* and *trans* rotational isomers have been reported for *N*-methylthiourea molecule [9] with the methyl group *cis* to the sulfur atom resonating at higher field compared to the *trans* methyl.

The ^{1}H NMR spectra of both complexes **I** and **II**, gave three broad peaks at low field (6.96–8.10 ppm) due to the NH protons. Two broad signals at 2.80 and 2.64 ppm for the methyl groups in complex **I** were observed, which coincide with the $^{13}C\{^{1}H\}$ NMR signals at 30.85 and 29.73 ppm. The two CH_2 signals on the ^{1}H NMR spectrum of complex **II** appears at 3.31 and 3.06 ppm, whereas one of the signals due to the carbon on CH_2 group appears to have merged with the solvent peaks on the $^{13}C\{^{1}H\}$ NMR spectrum while the second peak appears at 38.36 ppm. The carbon atoms of the CS group of complex **I** gave two signals at 183.73 and

Table 2
Crystal data and detailed structure refinement for complex **I** and **II**

	I	**II**
Empirical formula	$C_4H_{12}CdCl_2N_4S_2$	$C_6H_{16}CdCl_2N_4S_2$
Formula weight	363.60	391.65
Temperature (K)	160(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	triclinic	triclinic
Space group	$P1$	$P1$
Unit cell dimensions		
a (Å)	6.975(8)	8.547(7)
b (Å)	9.162(8)	9.841(10)
c (Å)	9.944(6)	9.902(10)
α (°)	71.97(6)	95.50(8)
β (°)	76.27(6)	114.44(6)
γ (°)	69.75(8)	101.36(9)
Volume (Å^3)	560.8(9)	728.6(12)
Z	2	2
Density (calculated) (Mg m^{-3})	2.153	1.785
Absorption coefficient (mm^{-1})	2.757	2.130
F(000)	356	388
Crystal size (mm)	0.50 × 0.13 × 0.05	0.40 × 0.40 × 0.30
θ Range for data collection (°)	2.18–24.98	2.31–24.99
Index ranges	$0 \leqslant h \leqslant 8$, $-10 \leqslant k \leqslant 10$, $-11 \leqslant l \leqslant 11$	$-10 \leqslant h \leqslant 9$, $0 \leqslant k \leqslant 11$, $-11 \leqslant l \leqslant 11$
Reflections collected	2184	2780
Independent reflections	1964 ($R_{int} = 0.0063$)	2558 ($R_{int} = 0.0080$)
Completeness to θ (24.98°) (%)	99.5	99.7
Max/min transmission	0.8744 and 0.3394	0.5675 and 0.4830
Goodness-of-fit on F^2	1.055	1.092
Final R indices	$R_1 = 0.0201$, $wR_2 = 0.0537$	$R_1 = 0.0378$, $wR_2 = 0.0968$
R indices (all data)	$R_1 = 0.0236$, $wR_2 = 0.0553$	$R_1 = 0.0542$, $wR_2 = 0.1043$
Extinction coefficient	0.0285(13)	
Largest difference peak and hole (e Å^{-3})	0.647 and −0.769	1.837 and −0.593

179.90 ppm on the $^{13}C\{^1H\}$ NMR spectrum, which were close to those of complex **I** (182.32 and 176.64 ppm), which is consistent with the presence of the two rotational isomers, i.e. the *cis* and *trans* isomers in these *N*-alkylthiourea complexes **I** and **II**. Both the ^1H and ^{13}C NMR spectra of complex **III** gave resonances, which indicates the dominance of the *cis* isomer. Similarly to the *N*,*N′*-dialkylthiourea complexes (**IV** and **VI**), only a single broad signal was observed in the lower field of the ^1H NMR spectra.

The *N*-phenyl and *N*,*N′*-diphenylthiourea complexes **III** and **V** gave similar peaks in both ^1H and $^{13}C\{^1H\}$ NMR spectra; 9.78 (NH group) and a set of three peaks at 7.47 (doublet), 7.31 (triplet) and 7.11 (triplet) (phenyl group) and; 179.38 and 179.94 (CS group) and a set of four signals at 139.3, 128.3, 124.3, 123.4 and 139.8, 128.9, 124.9, 124.1 (C_6H_5), respectively. Two signals were observed in both the ^1H (7.53 ppm-NH and 2.78 ppm-CH_3) and $^{13}C\{^1H\}$ (181.75 ppm-CS and 31.07 ppm-CH_3) NMR spectra of complex **IV**. The NMR results showed that there is a detectable amount of *trans*-isomer in the *N*-alkylthiourea (complexes **I** and **II** whereas no *trans*-isomer was detected for the arylthiourea complex **III**.

5. X-ray studies

Details of the crystal data and structure refinements are provided in Table 2. Selected bond distances and bond angles of $[CdCl_2(CS(NH_2)NHCH_3)_2]_n$ (**I**) and $CdCl_2(CS(NH_2)NHCH_2CH_3)_2$ (**II**) are shown in Table 3. Figs. 2 and 3 shows the ORTEP diagrams of the two complexes showing labelling of the non-hydrogen atoms.

5.1. $[CdCl_2(CS(NH_2)NHCH_3)_2]_n$ (*I*)

The structure of complex **I** (Fig. 2) comprises of a polymeric chain with alternating bridging groups through the two chlorides and sulphur atoms. The cadmium ion in each unit, $CdCl_3S_3$, consists of three Cd–Cl bonds and three Cd–S bonds. There are two bridging bonds and one non-bridging bond for each type of ligand. The Cd–S bond distances are slightly longer than for the corresponding dichloro bis(S-thiourea)Cd (Cd–S; 2.517 Å), which ranges from 2.632(2) Å for the terminal *N*-methylthiourea ligand to 2.744(2) and 2.789(4) Å for the bridging ligands.

A similar observation was made for the Cd–Cl bond distances, which ranges from 2.576(2) Å for the terminal chlorides and, 2.642(3) and 2.704(2) Å for the bridging chloride ligands. In each monomer unit, the metal core is constituted by three chloride and three *N*-methylthiourea ligands. Hence the formulation of the chemical structure, $[CdCl_2(CS(NH_2)NHCH_3)_2]_n$. Sun et al. [37] made similar observation in the bond distances of Cd–S in a mixed ligands cadmium(II) complex of xanthic acid and *N*,*N′*-bis(4-methoxyphenyl)thiourea. The xanthate chelating ligand has longer bond distances (2.831 Å) for the bridging sulfur atoms and shorter distances (2.606 Å) for the non-bridging ones. The C–S and C–N bond distances for the terminal methylthiourea ligand, 1.721(3) and 1.322(4) Å (average of C2–N3 and C2–N4), respectively, agrees with those of thiourea molecules reported in the Cambridge Structural Database i.e. 1.726 (C–S) and 1.322 Å (C–N). The additional C–N bond due to the methyl substituent is 1.451(4) Å. The C–S and C–N bond distances for the bridging methylthiourea ligands, 1.738(3) and 1.315(4) Å (average of C1–N1 and C1–N2), respectively, are within the expected range of bond distances of thiourea molecules. The C–N and C–S

Table 3
Selected bond distances (Å) and bond angles (°) for complex **I** and **II**

I		**II**	
Bond distances (Å)			
Cd(1)–Cl(1)	2.576(2)	Cd(1)–Cl(3)	2.500(3)
Cd(1)–Cl(2)	2.704(3)	Cd(1)–Cl(2)	2.455(3)
Cd(1)–S(1)	2.7443(17)	Cd(1)–S(3)	2.497(4)
Cd(1)–S(2)	2.6324(17)	Cd(1)–S(4)	2.519(3)
Cd(1)–Cl(2) [a]	2.642(3)	S(3)–C(12)	1.721(5)
Cd(1)–S(1) [b]	2.789(4)	S(4)–C(9)	1.738(7)
S(1)–C(1)	1.738(3)	N(5)–C(9)	1.329(9)
S(2)–C(2)	1.721(3)	N(5)–C(10)	1.402(9)
N(1)–C(1)	1.315(4)	N(6)–C(9)	1.361(9)
N(3)–C(2)	1.323(4)	N(7)–C(12)	1.312(7))
N(2)–C(1)	1.316(4)	N(7)–C(13)	1.453(7)
N(2)–C(4)	1.452(2)	N(8)–C(12)	1.312(7)
N(4)–C(2)	1.322(4)		
N(4)–C(3)	1.450(4)		
Bond angles (°)			
Cl(1)–Cd(1)–Cl(2) [a]	171.88(2)	Cl(2)–Cd(1)–Cl(3)	106.45(9)
S(1)–Cd(1)–S(2)	169.00(3)	S(3)–Cd(1)–S(4)	111.28(9)
Cl(2)–Cd(1)–S(1) [b]	172.78(2)	Cl(2)–Cd(1)–S(3)	113.84(10)
S(1)–Cd(1)–Cl(2)	93.31(8)	Cl(2)–Cd(1)–S(4)	112.82(9)
S(2)–Cd(1)–Cl(2)	97.65(7)	Cl(3)–Cd(1)–S(3)	107.74(11)
Cl(1)–Cd(1)–Cl(2)	88.31(9)	Cl(3)–Cd(1)–S(4)	103.96(10)
Cl(2)–Cd(1)–Cl(2) [a]	83.86(9)	Cd(1)–S(3)–C(12)	106.5(2)
Cl(1)–Cd(1)–S(2)	83.73(7)	Cd(1)–S(4)–C(9)	97.7(3)
Cl(1)–Cd(1)–S(1)	95.78(6)	S(3)–C(12)–N(8)	122.2(4)
S(2)–Cd(1)–Cl(2) [a]	99.44(6)	S(4)–C(9)–N(5)	120.4(5)
S(2)–C(2)–N(3)	122.7(2)	N(5)–C(9)–N(6)	117.7(6)
S(2)–C(2)–N(4)	118.5(2)	S(4)–C(9)–N(6)	121.9(5)
S(1)–C(1)–N(1)	121.9(2)	S(3)–C(12)–N(7)	117.5(4)
S(1)–C(1)–N(2)	118.5(2)	N(7)–C(12)–N(8)	120.3(5)

Symmetry transformations used to generate equivalent atoms.
[a] $-x+1, -y+1, -z$.
[b] $-x, -y+1, -z$.

bonds are intermediate between a single and double bond but closer to a normal C=N double bond distance (1.27 Å) and a normal C–S single bond distance (1.81 Å).

The coordination polyhedra around the Cd(II) ion is a distorted octahedron. Three *N*-methylthiourea ligands are S-bonded. The Cl–Cd–Cl (°) and S–Cd–S (°) angles are lowered and increased from octahedral values. Though *trans* Cl–Cd–Cl, S–Cd–S and Cl–Cd–S bond angles are relatively close to 180° (varying from 169.00(3)° to 172.78(2)°). The *cis* bond angles around the cadmium ions vary from 79.71(7)° to 99.44(6)°. The smallest angles (79.71(7)° and 83.53(6)°) were observed for the bridging S-bonded *N*-methylthiourea and chloride ligands, respectively, the other bond angles especially for the terminal ligands are hence slightly below or above 90° and 180°. This forces the compound to assume a zigzag pattern with the rectangular shaped Cd_2Cl_2 bridge lying vertical and almost perpendicular to the Cd_2S_2 bridge. The Cd–S–C bond angles are slightly greater than the tetrahedral value, varying from 116.48(11)° to 118.04(11)°. The S–C–N and N–C–N bond angles are within the expected range of tetrahedral geometry (varying from 118.5(2)° to 122.7(3)°).

5.2. $CdCl_2(CS(NH_2)NHCH_2CH_3)_2$ (**II**)

The structure of complex **II** and the packing diagram are shown in Fig. 3(a) and (b), respectively. The structure is based on a discrete monomeric molecule. The coordination polyhedra around the Cd(II) ion is a distorted tetrahedral. The two *N*-ethylthiourea ligands are S-bonded to the metal atom. In this four coordinate structure, molecular units are arranged so that one of the chloride ion (Cl(3)) and the metal atom lie on a crystallographic threefold axes which relates to the two thiourea ligands and the second chlorine atom (Cl(2)). The S(3)–Cd(1)–S(4), S(4)–Cd(1)–Cl(2) and S(3)–Cd(1)–Cl(2) bond angles are 111.28(9)°, 112.82(9)° and 113.84(10)°, respectively. These angles deviate considerably from the regular tetrahedral value of 109.47°, which may be explained by the steric interaction between the two ethyl groups. Intermolecular hydrogen bonding interactions between the NH protons and both sulphide and chloride ions of adjacent molecules stabilise the molecular structure (Fig. 3(b)).

The Cd–S bonds (2.497(4) and 2.519(3) Å) are shorter than in the *N*-methylthiourea complex, which suggest that the σ-bond character of this bond is stronger. The

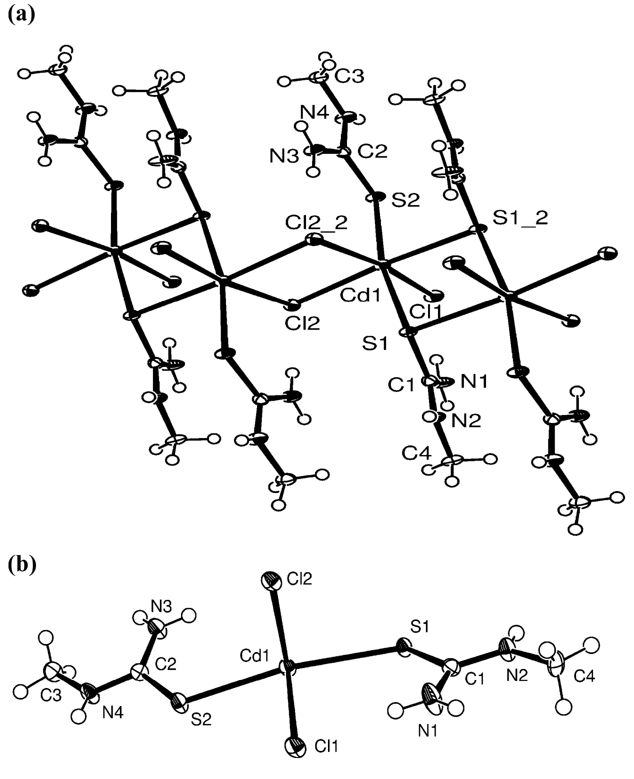

Fig. 2. (a) Polymeric structure and (b) and a parent molecular unit for $[CdCl_2(CS(NH_2)NHCH_3)_2]_n$ (**I**).

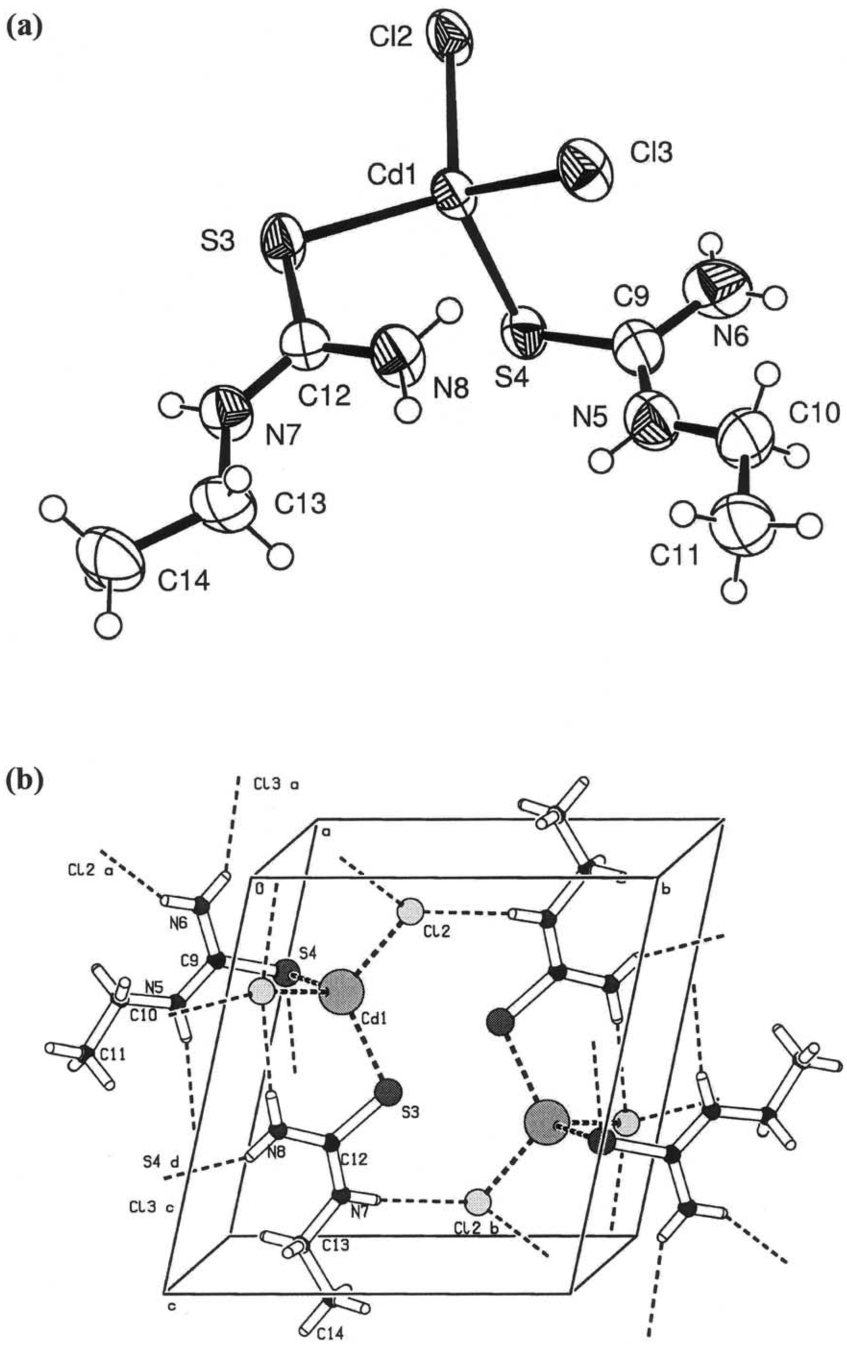

Fig. 3. Molecular structure (a) and packing diagram showing short contacts (b) for $CdCl_2(CS(NH_2)NHCH_2CH_3)_2$ (**II**) ($a = (-x, -y, -z)$, $b = (1-x, 1-y, 1-z)$, $c = (-x, -y, 1-z)$, $d = (1-x, -y, 1-z)$).

S=C (1.729(6) Å) and N–C (1.345(9) Å) bonds are close to those observed in complex **I**. In both cases the C–N and S–C bonds shows intermediate bond lengths between single and double bond, which is attributed to the delocalisation of electron in the amide bond. *N*-alkylthioureas can exist in two different configurations where the thioamide hydrogen atom and the thiocarbonyl bond are either in *cis* or *trans* form [38]. In the above described *N*-alkylthiourea complexes each thiourea ligand is in a *cis* form.

5.3. Thermal decomposition

The thermal decompositions of the complexes **I**–**VI** reported in this work were also studied by TGA and DTA methods under inert and air atmosphere. The residues obtained from these decompositions were subjected to XRD analysis. The X-ray diffraction patterns of the residues obtained from complex **II** are shown in Fig. 5 and the data listed in Table 4. Under nitrogen the complexes initially melt, the melts rapidly

Table 4
Experimental XRD data of the residues from TGA analysis of complex **II**

d(lit [a])/Å	d(exp)/Å		*hkl*
	a (Nitrogen)	*b* (Air)	
3.57	3.61	3.59	100
3.34	3.37	3.36	002
3.14	3.17	3.16	101
2.44	2.44	2.45	102
2.09	2.06	2.07	110
1.91	1.89	1.90	103
1.78	1.79	1.79	200
1.75	1.76	1.77	112
1.72	1.73	1.73	201
1.67	1.68	1.69	004

[a] Ref 1999 JCPDS.

transform to a pale yellow solids. In air, the compounds undergo similar changes at the start of decomposition, but as the temperature is increased the yellow solid changes further to orange and finally to dirty green, probably due to partial metathesis to the oxide. The TGA curves (Fig. 4) indicate that for each compound the loss of weight starts around 200 °C and continues to about 400 °C at which point most of the organic part of the molecule and the chloride has been lost. A period of slow loss of mass leads to the complete formation of sulphide by 500–600 °C. The percentage mass loss is in most cases close to that range expected for the stoichiometric formation of the sulfide as follows: Found (Calc.) (%), **(I)** 36.7 (39.7), **(II)** 36.4 (36.9), **(III)** 35.9 (29.6), **(IV)** 36.4 (36.9), **(V)** 25.2 (22.6) and **(VI)** 31.4 (32.3). A variety of factors confound this analysis cadmium sulfide itself has appreciable volatility as evidenced by pronounced loss of mass above 600 °C. The X-ray diffraction patterns of the residues obtained from complex **II** are shown in Fig. 5 were studied in more detail as this compound may have promise as a precursor. The residues from under both air or nitrogen atmospheres were analysed by X-ray diffraction methods (Fig. 5(a), (b)) and showed patterns consistent with the predominantly of the wurtzite phase of CdS (Table 4). The only difference between the two patterns is that the diffraction pattern in Fig. 5(a) is sharper and cleaner which might be expected under nitrogen atmosphere whereas the residue obtained under air shows is broader which may reflect some oxide formation.

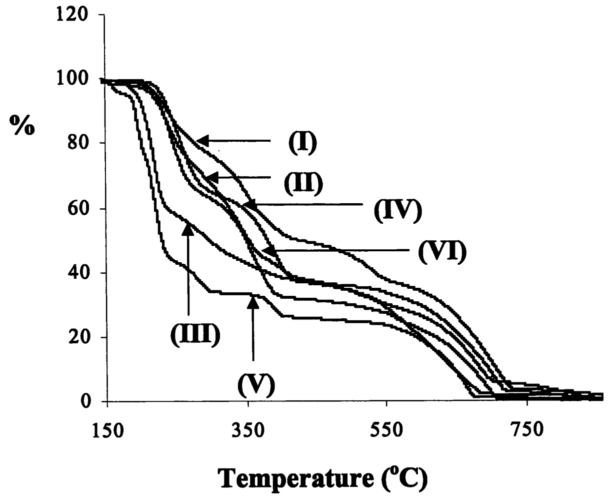

Fig. 4. TGA (under nitrogen) curves for $[CdCl_2(CS(NH_2)NHCH_3)_2]_n$ **(I)**, $CdCl_2(CS(NH_2)NHCH_2CH_3)_2$ **(II)**, $CdCl_2(CS(NH_2)NHC_6H_5)_2$ **(III)**, $CdCl_2(CS(NHCH_3)_2)_2$ **(IV)**, $CdCl_2(CS(NHC_6H_5)_2)_2$ **(V)**, $CdCl_2(CS(NHCH_2CH_3)_2)_2$ **(VI)**.

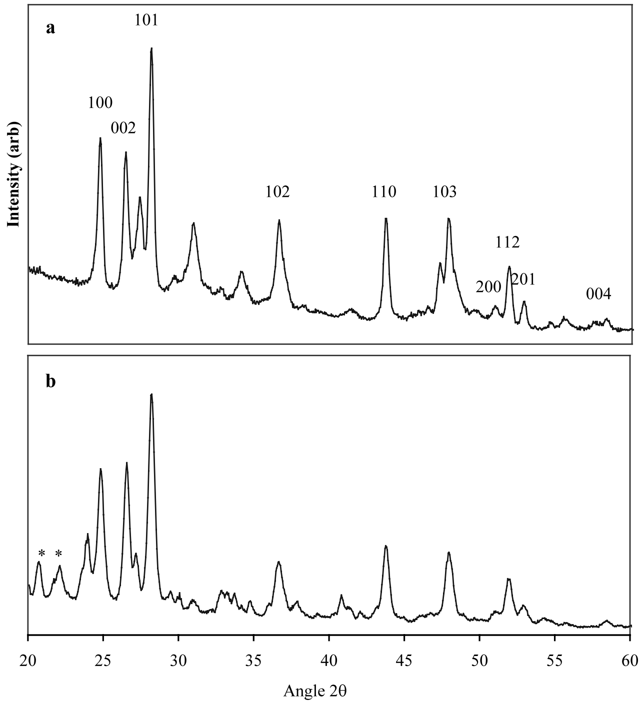

Fig. 5. XRD patterns of the residue obtained from thermal decomposition of $[CdCl_2(CS(NH_2)NHCH_2CH_3)_2]$ **(II)**, both under N_2 (a) atmosphere and in air (b) (*impurities) indexed to wurtzite CdS.

We have not observed any exothermic process in our DTA studies of these compound in contrast to the results observed for copper, zinc and tin thiourea complexes [39] in which cases the metal sulphides were converted to their metal oxides. No such gross conversion of cadmium sulfide to the oxide was observed during the work reported in this study under air.

6. Conclusion

The structure of both complexes **I** and **II** indicates that bonding of the *N*-alkylthiourea ligands is through sulphur atom of the CS group. Complex **I** is a polymer with alternating chloride and sulphur atoms bridging the adjacent metal centres. Both ligands are in the *cis* conformation, however the NMR results reveal some detectable amounts of the *trans* form in solution. In addition to the X-ray diffraction results, the infrared spectroscopic results indicate a change in the character of the C–S and C–N bond in the thioamide core on coordination. Thermogravimetric studies and the XRD data of the decomposed residue revealed the wurtzite phase CdS particles. These complexes could be used as precursors for the deposition of CdS thin films or nanoparticles.

7. Supplementary data

Crystallographic supplementary data are available from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK on request (deposit@ccdc.cam.ac.uk) quoting the deposition numbers CCDC 196111 and 196112.

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