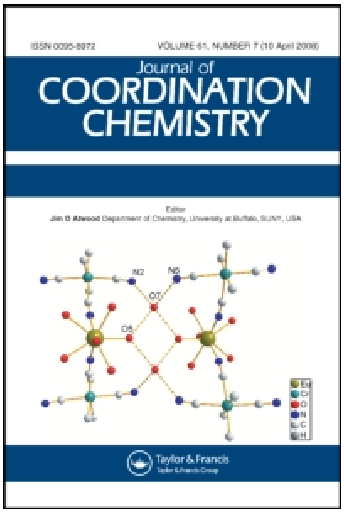

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Synthesis, characterization, and single crystal X-ray structure of the 1-furoyl-3-cyclohexylthiourea cadmium chloride complex, $Cd[C_4H_3OC(O)NHC(S)NHC_6H_{11}]_4Cl_2$

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Synthesis, characterization, and single crystal X-ray structure of the 1-furoyl-3-cyclohexylthiourea cadmium chloride complex, $Cd[C_4H_3OC(O)NHC(S)NHC_6H_{11}]_4Cl_2$

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Cadmium chloride complex of 1-furoyl-3-cyclohexylthiourea (CyTu) was prepared and characterized by elemental analysis, IR, and Raman spectroscopy. The structure of the complex was determined by single crystal X-ray methods (space group *Bbab*, $a = 20.918(1)$, $b = 23.532(1)$, $c = 23.571(1)$ Å, $\alpha = \beta = \gamma$, $Z = 8$). Each cadmium has distorted octahedral geometry, coordinated by two chlorides and the thiocarbonyl sulfurs from four CyTu molecules. All the spectroscopic data are consistent with coordination of CyTu by sulfur to cadmium.

Keywords: Aroylthiourea; Cadmium(II) complexes; Synthesis; X-ray structure

1. Introduction

The importance of aroylthioureas largely lies in heterocyclic syntheses and interesting biological activities. Aroylthioureas also have applications in metal complexes and molecular electronics [1–6]. Coordination chemistry of such derivatives is more varied than that of simple thiourea and physiochemical properties result in a number of potential technical and analytical applications [7]. Coordination compounds formed by thiourea and Zn(II), Cd(II), and Hg(II) have received renewed attention for their non-linear optical properties [8, 9] and convenient preparation of semiconducting materials based on CdS through thermal decomposition of those complexes [10, 11]. Simple thiourea $(H_2N)_2CS$ is usually a planar ligand, where both S and N are donor sites able to participate in coordination. Substituted-thioureas, however, show a more diverse coordination chemistry because of their conformational isomerism, steric

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effects, and presence of donor sites on the substituent groups and intramolecular interactions. These chelating agents are remarkable agents for analytical chemistry, especially for the trace analysis of metals in complex matrices. A variety of metal chelates have been described [5]. Many transition metal complexes with such thiourea derivatives have been reported, and the structures with O,S-binding to metal ions in alkaline media have been proposed, based on a series of physicochemical methods [5, 7]. With d^{10} metal ions (Zn(II), Cd(II), Hg(II), Ag(I), and Cu(I)), thiourea and its derivatives coordinate through the sulfur only [4]. We previously studied the Raman and IR spectra of two series of 1-furoylthiourea derivatives in order to identify vibrations involving contributions from motions within the thioureido (NCSN) core [12] and have shed light on the suitability of thiourea derivatives as Cd(II) ionophores. In this work our interest lies in studying the binding of 1-furoyl-3-cyclohexylthiourea to cadmium through sulfur of the CS as such compounds could be used as precursors in preparation of CdS nanoparticles. We report the X-ray structural analysis and the IR and Raman spectra of the complex.

2. Experimental

2.1. *Chemicals*

The thiourea derivative $C_4H_3OC(O)NHC(S)NHC_6H_{11}$ (CyTu) was synthesized according to a previous report [13], by converting furoyl chloride into furoyl isothiocyanate and then condensing with cyclohexylamine. $CdCl_2$ was obtained from Fluka Chemical Co., Germany. Ethanol (analytical grade) was used without further purification.

2.2. *Preparation of $Cd[C_4H_3OC(O)NHC(S)NHC_6H_{11}]_4Cl_2$*

The complex is formed when 0.1 M ethanolic solutions (10 mL) of CyTu (1 mmol, 0.2520 g) and cadmium chloride (1 mmol, 0.1834 g) are mixed at room temperature in 1 : 1 molar ratio. The mixture was left to evaporate until the complex precipitated. White precipitate was obtained after 2 h. The solid was collected by filtration, washed thoroughly with ethanol, and dried *in vacuo*. Yield 47% (0.0698 g); m.p. decomposes at 198°C; Anal. Calcd C, 48.3; H, 5.4; N, 9.4; S, 10.7; Cd, 9.4. Found: C, 48.7; H, 5.9; N, 9.5; S, 10.2; Cd 9.4. IR (Nujol mull) (cm^{-1}): 3339(w), 2923(m), 2853(m), 1681(s), 1552(s), 1515(s), 1465(s), 1377(s), 1175(m), 1019(m), 764(s), and 747(w). Raman (cm^{-1}): 3123(w), 3113(w), 2945(m), 2852(m), 1685(s), 1555(m), 1471(s), 1377(m), 938(m), 882(m), 798(m), 750(m), and 208(m). Single crystals suitable for X-ray analyses were obtained by recrystallization from ethanol.

2.3. *Instrumentation*

Elemental analyses were performed with a Leco automatic analyzer CHNS 932 model. ICP cadmium analyses were carried out with a plasma spectrometer Iris Intrepid from Thermo Elemental. The melting point was determined with a Reichert-Jung rheostat coupled to Reichert-Thermovar binoculars and a RS-3.722 digital thermometer.

Infrared spectra were recorded on a FT-IR spectrophotometer (from Atti Mattson, Genesis Series) in the spectral range of 4000–400cm^{-1} using Nujol mulls to avoid mechano-chemical reactions with KBr [14]. IR spectra recorded in pressed KBr disks and of the compound dispersed on a KBr window were dissimilar. Raman spectra were collected by a capillary sample technique using a Perkin–Elmer system 2000 NIR-FT-RAMAN and a Lexel model 98 krypton ion laser ($\lambda = 647.1$ nm). The laser power at the sample surface was restricted to 40 mW. The spectral band pass of the Raman spectrometer was 4 cm^{-1} and the 90° configuration was used with an incidence angle of 60° on the metal surface when taking surface-enhanced Raman scattering (SERS) spectra.

2.4. *Crystallography*

The $Cd[C_4H_3OC(O)NHC(S)NHC_6H_{11}]_4Cl_2$ complex was measured at low temperature (150 K) to diminish disorder of the atoms in the unit cell. The crystal was really small and very difficult to handle. The R value is high because the quality of the crystal used was not good enough. There were spurious peaks responsible for the large residual density but all the atoms could be assigned. Crystallographic data were collected on an Enraf-Nonius Kappa-CCD diffractometer using Mo-Kα radiation ($\lambda = 0.71073$ Å) [15]. Data collection for the complex was carried out with the *COLLECT* program [16]; integration and scaling of the reflections were performed with the HKL Denzo-Scalepack system of programs [17]. Data were corrected for Lorentz and polarization effects, with absorption corrections being carried out using the multi-scan method [18]. The structure was solved by the Patterson method using *SHELXS*-97 [19] and refined anisotropically (non-hydrogen atoms) by full-matrix least-squares on F^2 using a *SHELXL*-97 [20] program. All the H atoms were calculated geometrically (C–H = 0.96 Å) as fixed contributions in structure factor calculations but not refined. The program ORTEP-3 [21] was used for drawing the molecules. WINGX [22] was used to prepare materials for publication. Crystal data, basic information about the data collection and structure refinement, the final discrepancy indices and other parameters at the conclusion of refinement are given in table 1.

3. Results and discussion

3.1. *Single crystal X-ray study*

The thermal ellipsoid plot showing the coordination geometry and crystallographic numbering scheme employed for $Cd[C_4H_3OC(O)NHC(S)NHC_6H_{11}]_4Cl_2$ is depicted in figure 1. Selected atomic distances and bond angles are listed in table 2. The crystal structure of the complex is based on a monomer with two *trans* ligands in the unit cell.

The cadmium in each unit, $CdCl_2S_4$, is six-coordinate by sulfurs from four CyTu molecules and two chlorides (figure 2). The range (from 2.769(2) to 2.775(3) Å) of Cd–S bond distances is longer than the related dichlorotetrakis–(phenylthiourea) cadmium(II) [23] distance (Cd–S; 2.621(1)–2.729(1) Å) and the Cd–Cl bond length (2.519(8) Å) is shorter than the dichlorotetrakis-(phenylthiourea) cadmium(II) (2.759(1) Å) [23]. The complex has an inversion center located on the Cd(II).

Table 1. Summary of crystallographic data and structural parameters of $Cd[C_4H_3OC(O)NHC(S)NHC_6H_{11}]_4Cl_2$.

Empirical formula	$C_{48}H_{64}CdCl_2N_8O_8S_4$
Formula weight	1191.4
Temperature (K)	250
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	*Bbab*
Unit cell dimensions (Å, °)	
a	20.918(1)
b	23.532(1)
c	23.571(1)
$\alpha=\beta=\gamma$	90°
Volume ($Å^3$)	11602.6(9)
Z	8
Density (Calcd) ($Mg\,m^{-3}$)	1.361
Absorption coefficient (mm^{-1})	0.667
$F(000)$	4912
Crystal size (mm^3)	0.12 × 0.01 × 0.05
θ range for data collection (°)	2.9–26.81
Index ranges	$-25\leq h\leq 26$; $-29\leq k\leq 28$; $-29\leq l\leq 29$
Reflections collected	6039
Independent reflections	3499 ($R_{int}=0.1440$)
Absorption correction t min.	0.904
Absorption correction t max.	0.944
Goodness-of-fit on F^2	1.03
Final R indices	$R=0.089$; $wR=0.274$
Extinction coefficient largest difference peak and hole ($e\,Å^{-3}$)	1.54 and −0.71

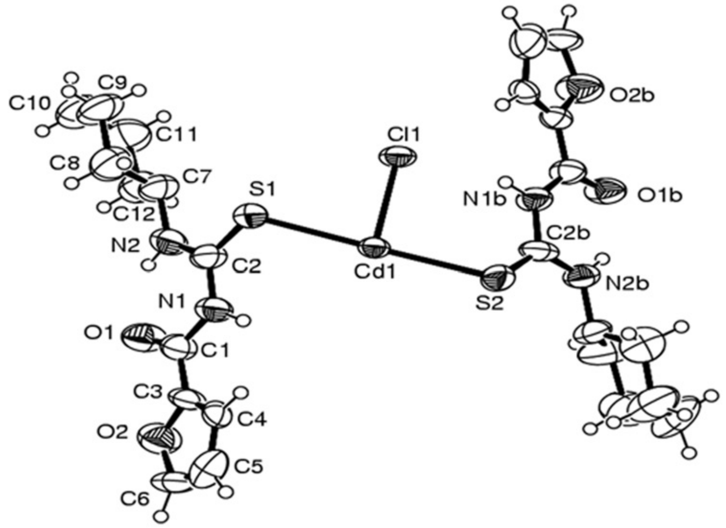

Figure 1. ORTEP drawing of $Cd[C_4H_3OC(O)NHC(S)NHC_6H_{11}]_4Cl_2$ with ellipsoids at 50% probability: the *trans* configuration of two CyTu molecules is observed.

Table 2. Selected bond lengths (Å) and angles (°) of $Cd[C_4H_3OC(O)NHC(S)NHC_6H_{11}]_4Cl_2$.

Cd(1)–Cl(1)	2.519(8)	N(1)–C(1)	1.414(1)	C(7)–C(12)	1.521(3)
Cd(1)–S(1)	2.775(2)	N(2)–C(2)	1.343(1)	C(7)–C(8)	1.524(3)
Cd(1)–S(2)	2.769(2)	N(2)–C(7)	1.491(1)		
S(1)–C(2)	1.691(9)				
Cl(1)–Cd(1)–Cl(2_a)	178.40(8)	Cl(1)–Cd(1)–S(2)	95.51(6)	N(1)–C(2)–S(1)	119.6(7)
S(1)–Cd(1)–S(2)	174.17(7)	Cl(1)–Cd(1)–S(1)	85.06(6)	S(2)–Cd(1)–S(1)	174.17(8)
S(1)–Cd(1)–Cl(2_a)	87.89(8)	N(2)–C(2)–N(1)	116.1(8)	N(2)–C(2)–S(1)	124.3(6)

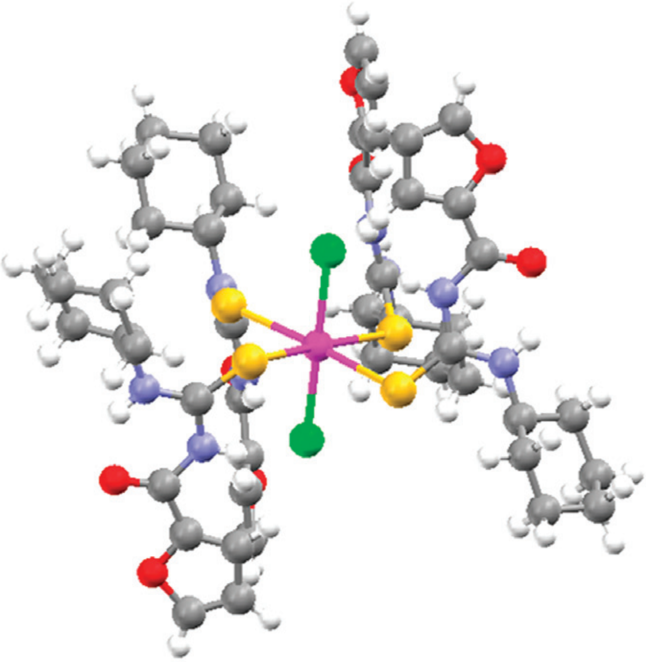

Figure 2. View of the complex $Cd[C_4H_3OC(O)NHC(S)NHC_6H_{11}]_4Cl_2$ (structure optimized without label atoms).

The coordination polyhedra around Cd(II) is a distorted octahedron. Four CyTu ligands are S-bonded. Figure 2 shows the nearly coplanar arrangement of CyTu units within the complex.

Though *trans* Cl–Cd–Cl and S–Cd–S bond angles are relatively close to 180° (from 178.4(8)° to 174.2(7)°). The *cis* S–Cd–S and S–Cd–Cl bond angles around the cadmium ions vary from 97.9(7)° to 85.16(6)°, deviating considerably from 90°, explained by the steric interaction between the substituents on thiourea. The Cd–S–C angles are 111.1(3)°, slightly greater than the tetrahedral value. The S–C–N and N–C–N bond angles are within the expected range of tetrahedral (from 113.4(7)° to 124.5(5)°). The C–N and C–S bonds are intermediate between a single and double bond, but closer to a normal C=N double bond distance (1.27 Å) and normal C–S single distance (1.81 Å), attributed to delocalization of electron in the thioamide bonds [5]. Due to formation of the Cd–S bond, the C–S bond distance of CyTu increases from 1.667(2) to 1.691(9) Å, while the C–N distances become shorter. There are two pairs of intramolecular NH···O hydrogen bonds of 2.642(8)–2.648(9) Å between the *trans* thioamide proton to the C=S group and the carbonyl oxygen of CyTu (table 3).

This intramolecular bond interaction is observed in free CyTu [13]. In the free CyTu (see Supplementary material) an intramolecular hydrogen bond is also expected between the furan O atom and the *cis* thioamide proton to the C=S group [24]. In the complex, this intramolecular bond interaction is not present, probably due to electronic repulsion between donors, the oxygen furan atoms (in opposite direction) and the chlorides. Two bifurcated NH···Cl hydrogen bonds of 3.243(7) and 3.314(7) Å (table 3) between the *cis* thioamide protons and the chlorides are observed (see Supplementary material). Although the NH···Cl distances are near the acceptable limit ($D > 3.6$ Å) to be considered as hydrogen bonds, the angles tend towards linearity ($\theta > 150°$) (table 3). In this case, both angular and distance considerations justify these two hydrogen bond interactions NH···Cl. Similar hydrogen bonds are also observed for dichlorotetrakis–(phenylthiourea) cadmium(II) [23].

There are also CH···π interactions with the chlorides. All these non-covalent interactions stabilize the structure of the complex molecules in the unit cell (see Supplementary material).

3.2. *IR spectra*

The N–C and C=S bonds participate in the vibrational spectra of thiourea derivatives through six different motions [25, 26]. Despite the complexity of the spectra, most of the bands could be tentatively assigned. Our assignment was done by comparison with previous assignment for free CyTu [12]. Some general conclusions were derived from the comparative analysis of the spectra and especially in relation to the changes detected after coordination of the CyTu to the Cd(II) center through their thiocarbonyl sulfur. The main changes observed are summarized in table 4 and the spectra recorded are shown in "Supplementary material".

All the wavenumber shifts can be explained on the assumption that the main effect of the complexation on the thiourea is weakening of the C=S double bond resulting from the transfer to Cd(II) of lone pair from sulfur (S → M). This transfer is accompanied by an increase of ν(CN). However, most of the IR bands of CyTu and its Cd(II) complex originate in strongly coupled vibrational modes, so the interpretation of band shifts observed after coordination must be made carefully.

Table 3. Geometrical parameters for C–H···π (Å) and intramolecular hydrogen bond interactions in $Cd[C_4H_3OC(O)NHC(S)NHC_6H_{11}]_4Cl_2$.

Donor-H	Acceptor	D–H	H···A	D···A	D–H···A
N1–H1	Cl1	0.88	2.47	3.314(7)	162[a]
N1B–H1B	Cl1	0.88	2.44	3.243(7)	151
N2–H2	O1	0.88	1.94	2.642(9)	136
N2B–H2B	O1B	0.88	1.94	2.648(9)	137
C4–H4	Cl1	0.95	2.61	3.379(8)	138[a]
C4B–H4B	Cl1	0.95	2.65	3.293(7)	126
C5–H5	Cl1	0.95	2.81	3.489(1)	129[b]

Symmetry codes: [a]$-x$; y; $0.5-z$, [b]$0.5+x$; $-y$; z.

The most important features of the spectra were investigated in the following two regions.

3.2.1. The 3400–3000 cm^{-1} region. In this region, the asymmetric and symmetric NH stretching vibrational bands of free and associated NH groups are expected. Intermolecular hydrogen bonds usually produce broadening and spectral complexity of these stretches, seen as weak, not completely resolved bands (Supplementary material). This effect is pronounced in the Cd(II) complex due to modifications of the hydrogen bond network after complex formation and because the IR spectra were registered in Nujol mulls to avoid mechanochemical reactions with KBr. Despite these considerations, table 4 shows that irregular band displacement (3318–3121 cm^{-1}) associated with free NH stretches, which can be observed after coordination. The NH stretch associated to free NH shifts to higher wavenumbers since formation of S M bonds is expected to increase the electronegativity of N1. The frequency range (3139–3121 cm^{-1}) assigned to associated NH (as $–N_3H\cdots O{=}C–$) did not vary significantly in the complex, indicating that the intramolecular hydrogen bond present in the CyTu is not weakened or broken after complexation.

3.2.2. The 1750–800 cm^{-1} region. One of the most significant spectral changes caused by complex formation is increase of ν(CO). The position of the band with respect to the free ligand shifts 15 cm^{-1} to higher frequency (table 4). This means that ν(CO) strengthens after coordination, attributed to the strong inductive effect of Cd(II) that is transmitted through the –CO–NH–CS– fragment after complexation with the sulfur atom. For the complex the band was split.

The 1600–1150 cm^{-1} region shows relatively intense thioamide bands I, II, and III [25], with a large contribution from ν(CN). Although ν(CN) is strongly mixed with other vibrations (mainly NH bends and CS stretch), the higher-energy shift related to formation of a stronger double bond upon complex formation was not evident. In the complex, thioureido band I was almost constant. Thioureido band II could be assigned tentatively, as its absorption coincided with one of the intense bands of Nujol at ~1380 cm^{-1}. However, it seems the position of this band is not changed significantly (to lower wavenumbers) in the complex, though it produced a loss of intensity. Thioureido band III increased in frequency accompanied with loss of intensity, consistent with previous findings on S-coordinated substituted thiourea complexes [4, 5, 27, 28].

Table 4. Selected IR and Raman bands (cm^{-1}) of CyTu and CyTu cadmium(II) complex.

				Thioureido bands		
Sample		ν_{NH}	$\nu_{C=O}$	I	II	III
3400–600 cm^{-1} IR region						
CyTu	3318(w)	3139(w), 3121(w)	1666(s)	1515(s)	1345(s)	1193(s)
Complex	3339(w)	3140(w), 3114(w)	1681(s)	1517(s)	1349(w)	1199(m)
800–200 cm^{-1} Raman region						
	Thioureido band IV	π(CS)	δ(CS)	δ(NCN)	$\nu_{Cd–S}$	
CyTu	759(m)	547(w)	367(w)	289(w)	–	
Complex	750(m)	549(w)	366(w)	305(w)	208(m)	

Intensity: s: strong; m: medium; w: weak.

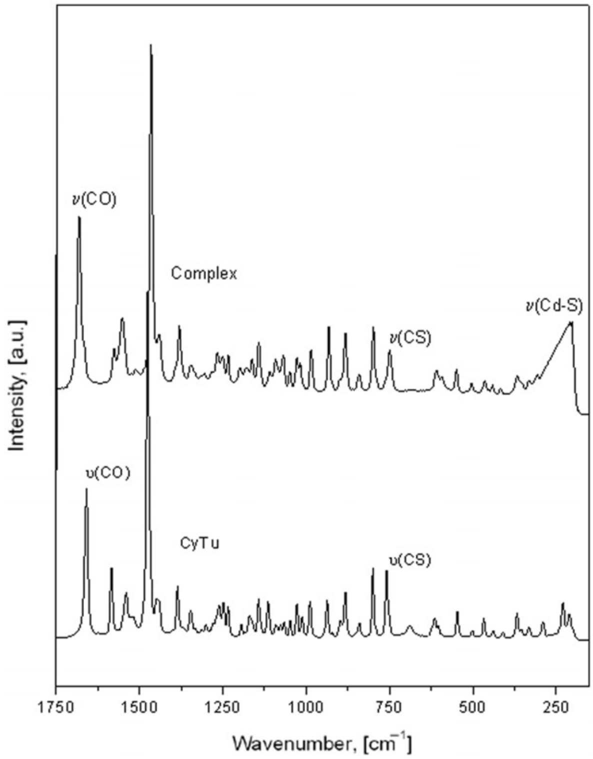

Figure 3. FT-Raman spectra of CyTu and its complex with $CdCl_2$ in the 1750–150 cm^{-1} region.

3.3. *Raman spectra*

The Raman spectra of the CyTu and $Cd[C_4H_3OC(O)NHC(S)NHC_6H_{11}]_4Cl_2$ have been interpreted (figure 3). The vibrational modes and their corresponding wavenumbers of the free ligand and Cd(II) complex are also given in table 4, together with suggested assignment. Bands I, II, and III do not produce intense Raman bands to detect changes after complexation. Because of the contribution from polar groups, these bands were better identified in IR spectra.

The analysis of Raman spectra was carried out principally to reveal the effect of coordination on the vibrational bands of the ligand in the metal complex in the region below 800 cm^{-1}. This is a spectral zone practically free of other bands, where a fundamental with a majority contribution from ν(C=S) motion (thioamide band IV) and vibrations from π(CS), δ(CS), and δ(NCN). It was also possible to identify the low-frequency Raman band related to Cd–S vibration. Certainly, the most significant spectral change caused by complex formation is decrease of the ν(CS) stretching frequency. Although this vibration is strongly coupled with other modes, our assignment of the band with the highest ν(CS) character is based on previous IR and Raman study of CyTu [12]. The band at 759 cm^{-1} in the spectrum of CyTu attributed to C=S vibration corresponds to the band at 750 cm^{-1} in the spectrum of $Cd[C_4H_3OC(O)NHC(S)NHC_6H_{11}]_4Cl_2$ (figure 3). The shift to lower wavenumbers indicates reduced double bond character of C=S, pointing to Cd–S bonding, in agreement with most thiourea complexes. For the complex, there were either slight increases or constancy of the vibrations below 650 cm^{-1} assigned to π(CS), δ(CS), and δ(NCN) motions.

In addition, we have assigned the Cd–S vibration of $Cd[C_4H_3OC(O)NHC(S)NHC_6H_{11}]_4Cl_2$ at 208 cm^{-1}, consistent with the very scarce information available for Cd(II) complexes with thiourea derivatives, which suggest that bands associated to Cd–S vibrations may be expected in the 200–300 cm^{-1} range [4].

4. Conclusions

The structure of the complex indicates that 1-furoyl-3-cyclohexylthiourea bonds through sulfur of the CS group. The complex contains four monodentate ligands per cadmium with general formula $Cd[C_4H_3OC(O)NHC(S)NHC_6H_{11}]_4Cl_2$. In addition to the X-ray results, the infrared and Raman spectroscopic results indicate a change in the character of the C=S and C–N bonds in the thioamide core on coordination.

Supplementary material

The crystallographic information file (abbreviated CIF) loading the data sets (excluding the structure factors) for the complex C has been deposited with the Cambridge Structural Data Base under deposit code CCDC 706373 (copies of these data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk or http:www.ccdc.ac.uk).

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