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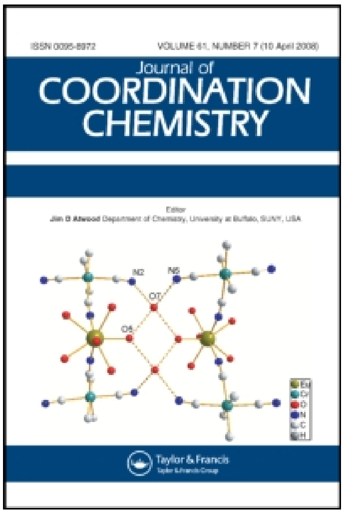

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
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Synthesis and spectroscopic characterization of cadmium(II) complexes of thiones and thiocyanate

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First published on: 10 December 2009

To cite this Article Ali, Saqib , Malik, Muhammad Riaz , Isab, Anvarhusein A. and Ahmad, Saeed(2009) 'Synthesis and spectroscopic characterization of cadmium(II) complexes of thiones and thiocyanate', Journal of Coordination Chemistry, 62: 3, 475 — 480, First published on: 10 December 2009 (iFirst)

To link to this Article: DOI: 10.1080/00958970802226395
URL: http://dx.doi.org/10.1080/00958970802226395

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Journal of Coordination Chemistry
Vol. 62, No. 3, 10 February 2009, 475–480

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Synthesis and spectroscopic characterization of cadmium(II) complexes of thiones and thiocyanate

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(*Received 1 February 2008; in final form 1 April 2008*)

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Cadmium(II) complexes of thiones and thiocyanate, $[(>C{=}S)_2Cd(SCN)_2]$, have been prepared and characterized by IR and NMR spectroscopy. An upfield shift in the $>C{=}S$ resonance of thiones in the ^{13}C NMR and downfield shift in N–H resonance in ^{1}H NMR are consistent with sulfur coordination to cadmium(II). The presence of ν(N–H) of thiones in IR spectra of the complexes indicates the thione forms of the ligands in the solid state; some contribution of the thiolate form was observed in one complex. The appearance of a band around $2100\,cm^{-1}$ in IR and a resonance around 132 ppm in ^{13}C NMR indicates the binding of thiocyanate to cadmium(II).

Keywords: Cadmium(II) complexes; Thiones; Thiocyanate; NMR spectroscopy

1. Introduction

Heterocyclic thiones are among the ligand systems used to mimic bio-relevant metal-sulfur interactions [1–5], for example, metallothioneins are coordinated to Cu, Zn and Cd through cysteine-sulfurs [6]. Chemical interest of thiones lies in the fact that they are potentially ambidentate or multi-functional donors with exocyclic S and heterocyclic N available for coordination; their biological interest arises from their structural analogy to thiolated nucleosides [2–5, 7]. We have been investigating the coordination chemistry of $>C{=}S$ ligands with d^{10} metal ions in an attempt to assess their mode of binding and to study their physical properties [8–14]. Consequently, we have reported complexes of Cu(I), Ag(I), Au(I), Cd(II) and Hg(II) with a number of thiones such as imidazolidine-2-thione [8–14]. Although several cadmium(II) complexes of thiones have been prepared and characterized using NMR

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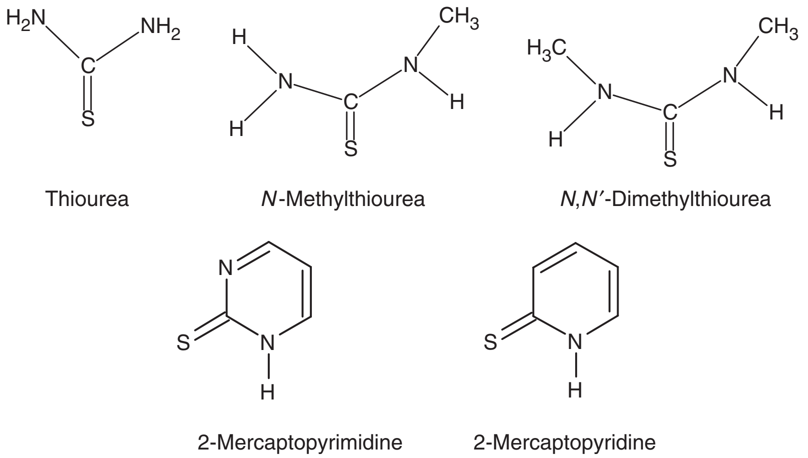
Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2009 Taylor & Francis
DOI: 10.1080/00958970802226395



Scheme 1. Structures of thiones used in the study.

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spectroscopy and X-ray crystallography [7, 14–21], no spectroscopic reports are available about the coordination behavior of thiones towards cadmium thiocyanate. As a part of our continuing interest in the structural chemistry of metal-sulfur interactions, we report here the synthesis of a number of cadmium(II) thiocyanate complexes of thiones and their characterization by IR, ^{1}H and ^{13}C NMR spectroscopy. We hope the study would provide useful information about the nature of cadmium(II) complexes with sulfur containing biological ligands. The structures of thiones used in this study are shown in scheme 1.

2. Experimental

2.1. *Chemicals*

$CdCl_2 \cdot H_2O$ and thiourea were obtained from Merck Chemical Co., Germany. Methylthiourea (Metu), dimethylthiourea (Dmtu), mercaptopyrimidine (Mpm) and mercaptopyridine (Mpy) were obtained from Acros Organics, USA.

2.2. *Preparation of complexes*

The complexes were prepared by adding an aqueous solution of 0.2 g KSCN (2 mmol) to 0.2 g $CdCl_2 \cdot H_2O$ (1 mmol) in water followed by addition of 2 mmolar methanolic solution of the respective thiones (Mpm was dissolved in water-methanol on heating) and stirring the mixture for 25–30 min. For the complexes of Tu, Metu and Mpm, mixing resulted in white or yellowish precipitates, which were filtered, washed with methanol and air-dried. In the preparation of $[(Dmtu)_2Cd(SCN)_2]$ and $[(Mpy)_2Cd(SCN)_2]$, mixing resulted in colorless or yellow solution. The products were obtained on evaporation of the solvent. The product yield is about 50–60%. The melting points of the complexes are given in table 1.

Table 1. Melting points and selected IR absorptions (cm^{-1}) of $[(>C{=}S)_2Cd(SCN)_2]$ complexes.

Species	M.p. (°C)	υ(C=S)	$\upsilon(NH_2)$	υ(C–N)	υ(SCN)
$Cd(SCN)_2$	–	–	–	–	2097
Tu	–	732	3156, 3365	1473	–
$[(Tu)_2Cd(SCN)_2]$	165–166	703	3194, 3370	1512	2062
Metu	–	634	3163, 3245	1488	–
$[(Metu)_2Cd(SCN)_2]$	141–142	633	3184, 3345	1521	2050, 2091
Dmtu	–	641	3203	1521	–
$[(Dmtu)_2Cd(SCN)_2]$	138–140	672	3281	1534	2034, 2075
Mpm	–	626	3055	1494	–
$[(Mpm)_2Cd(SCN)_2]$	274–276	670	3081	1470	2058
Mpy	–	613	3176	1487	–
$[(Mpy)_2Cd(SCN)_2]$	145–146	615	3188	1509	2025, 2035

2.3. *IR measurements*

The solid-state IR spectra of the ligands and their thiocyanato cadmium(II) complexes were recorded on a Perkin–Elmer FTIR 180 spectrophotometer using KBr pellets over the range $4000-400\,cm^{-1}$.

2.4. *^{1}H and ^{13}C NMR measurements*

The ^{1}H NMR spectra of the complexes in DMSO-d_6 were obtained on a Jeol JNM-LA 500 NMR spectrometer operating at 500.00 MHz at 297 K. The ^{13}C NMR spectra were obtained at 125.65 MHz with ^{1}H broadband decoupling at 297 K. The spectral conditions were: 32 K data points, 0.967 s acquisition time, 1.00 s pulse delay and 45° pulse angle. The ^{13}C chemical shifts were measured relative to TMS.

3. Results and discussion

The $[(thione)_2Cd(SCN)_2]$ complexes were obtained from reaction of cadmium chloride with thiones in a 1 : 2 molar ratio in the presence of KSCN in methanol-water. Selected IR frequencies of thiones and their cadmium thiocyanate complexes are given in table 1. In the IR spectrum of thiones, characteristic bands are observed in three frequency regions; υ(C=S) appears around $600\,cm^{-1}$, υ(C–N) bands at $1500\,cm^{-1}$ and υ(N–H) near $3200\,cm^{-1}$. The presence of N–H vibrations in the complexes confirms the thione form of the ligands in the solid state. A sharp band around $2100\,cm^{-1}$ for the C≡N stretch of SCN^- was observed for all the complexes indicating its binding with cadmium(II).

The ^{1}H and ^{13}C chemical shifts of the complexes in DMSO-d_6 are summarized in table 2. In ^{1}H NMR spectra of the complexes, the N–H signal of the thiones became less intense upon coordination and shifted downfield from their positions in free ligands. A slight downfield shift was also observed in other protons. The deshielding is related to an increase in π electron density in the C–N bond upon coordination. The appearance of a N–H signal shows that the ligands are coordinated in the thione form. Table 2 shows that N–H protons of Metu are non-equivalent (NH_2 appears

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Table 2. ^{1}H and ^{13}C chemical shifts (δ) of thiones and their Cd(SCN)$_2$ complexes in DMSO.

Species	N–H	C=S	C–N	C–5	SCN
Cd(SCN)$_2$	–	–	–		132.94
Tu	7.05	183.81	–		–
[(Tu)$_2$Cd(SCN)$_2$]	7.33	182.40	–		131.56
Metu	6.99, 7.51, 7.70	180.98, 184.00	29.79, 30.98		–
[(Metu)$_2$Cd(SCN)$_2$]	7.01, 7.56, 7.90	178.62, 183.50	29.90, 31.02		131.49
Dmtu	7.38	182.64	30.66		–
[(Dmtu)$_2$Cd(SCN)$_2$]	7.56	181.26	30.95		–
Mpm		181.90	155.00	109.96	–
[(Mpm)$_2$Cd(SCN)$_2$]		181.06	155.27	110.66	132.13
Mpy	–	177.69	137.91	137.49	–
[(Mpy)$_2$Cd(SCN)$_2$]	13.56	176.83	138.68	138.43	133.31

as a doublet). The N–H and CH$_3$ (2.85 ppm) protons of Dmtu in the complex are broad, while in our previous studies they were observed as non-equivalent (δCH$_3 = 2.80$, 3.04 ppm) [10]. The ^{1}H NMR spectrum of Mpm shows a triplet at 6.90 ppm for H-5 proton and a doublet at 8.33 ppm due to H-4 and H-6 protons. In the proton NMR spectrum of [(Mpm)$_2$Cd(SCN)$_2$], in addition to the expected peaks at 6.96 and 8.37 ppm, another set of less intense resonances but with the same intensity ratio was also observed at 7.37 and 8.71 ppm as triplet and doublet, respectively. The appearance of these resonances indicates that some Mpm has coordinated in the thiolate form.

In the ^{13}C NMR, the >C=S resonance of thiones in the complexes is shifted upfield by 0.5–3 ppm as compared to the free ligands in accord with data for complexes of copper(I) [21], silver(I) [9–11, 22], gold(I) [12, 23, 24], cadmium(II) [14, 15] and mercury(II) [25–27] with heterocyclic thiones. However, the shifts are much smaller than for the other complexes of thiones. Smaller shifts were also observed for cadmium chloride complexes of thiones [14]. The upfield shift is characteristic for sulfur coordination of thiones, ascribed to back-bonding of the metal d-orbitals to the antibonding π-orbitals of sulfur in the >C=S bond, which reduces the >C=S bond order and shields the carbon of >C=S group resulting in a shift to higher field [11–21]. Reduction in π-electron density on the exocyclic carbon-sulfur bond as a result of thione sulfur coordination to the metal is compensated by increase in bond order within the thioamide C–NH bond. As a result, a small deshielding effect is observed in other carbons. The C-3 and C-4 resonances of Mpy are at 133.22 ppm and 113.94 ppm, respectively. Assignment is based on electronegativity relationships and the splitting pattern of aromatic protons in ^{1}H NMR. The ^{13}C NMR of Metu gives two signals for >C=S and N–CH$_3$ carbons showing that the compound exists in two isomeric forms. For [(Dmtu)$_2$Cd(SCN)$_2$], two signals were expected for N–CH$_3$ carbon, as observed in our previous studies for AgCN and AuCN complexes [9, 10, 12], however, only a single less intense and broad resonance was observed, showing that methyl groups are equilibrating at different positions. The resonance at 132 ppm in the complexes indicates the coordination of SCN$^-$ to cadmium(II). Thus, the present study suggests that thiones in the presence of thiocyanate form stable complexes with cadmium(II).

As shown in figure 1, the ^{13}C NMR spectrum of [(Mpm)$_2$Cd(SCN)$_2$] displays two sets of resonances. The intense resonances are characteristic of the

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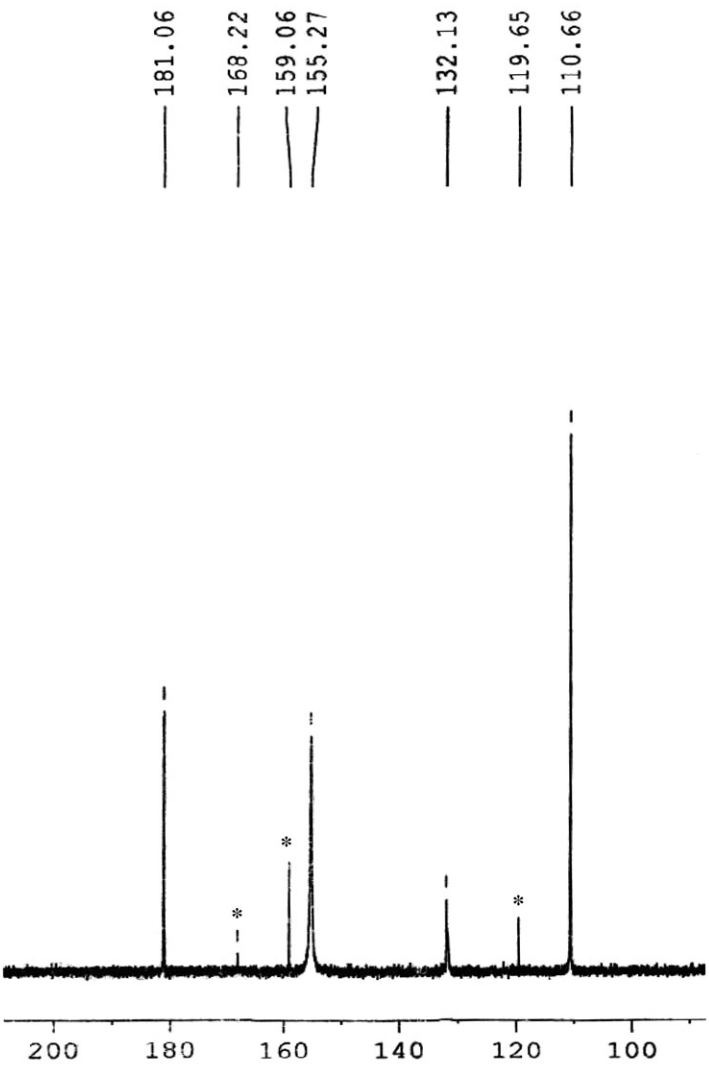

Figure 1. ^{13}C NMR spectrum of [$(Mpm)_2Cd(SCN)_2$] (showing two sets of resonances; the resonances marked with * represent the complex with Mpm binding in the thiolate form).

expected [$(Mpm)_2Cd(SCN)_2$] complex, while the set of less intense resonances (119.65, 159.06 and 168.22 ppm) indicates the presence of a complex in which Mpm has coordinated in the thiolate form. The integration of resonances in proton NMR gives a ratio of 25 : 1, suggesting that the contribution of the thiolated species is ~4%. The crystal structure of a mercury(II) complex of Mpm showing coordination of Mpm in both the thione and as a thiolate, to Hg(II) has already been reported [28]. Due to contribution of the thiolate form, the Mpm complex is expected to be more stable than the analogous Mpy complex (with thione binding site), since thiolates are comparatively stronger ligands than thiones [29]. The melting points of the complexes (table 1) are consistent with this fact.

Acknowledgements

Financial support from the Pakistan Council for Science and Technology, Islamabad, Pakistan and from King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia is gratefully acknowledged.

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