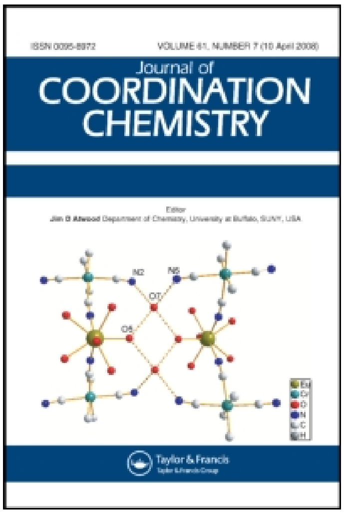

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Complexation of Zn(II), Cd(II) and Hg(II) with thiourea and selenourea: A ^{1}H, ^{13}C, ^{15}N, ^{77}Se and ^{113}Cd solution and solid-state NMR study

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Zinc(II), cadmium(II) and mercury(II) complexes of thiourea (TU) and selenourea (SeU) of general formula $M(TU)_2Cl_2$ or $M(SeU)_2Cl_2$ have been prepared. The complexes were characterized by elemental analysis and NMR (^{1}H, ^{13}C, ^{15}N, ^{77}Se and ^{113}Cd) spectroscopy. A low-frequency shift of the C=S resonance of thiones in ^{13}C NMR and high-frequency shifts of N–H resonances in ^{1}H and ^{15}N NMR are consistent with sulfur or selenium coordination to the metal ions. The Se nucleus in $Cd(SeU)_2Cl_2$ in ^{77}Se NMR is deshielded by 87 ppm on coordination, relative to the free ligand. In comparison, the analogous Zn(II) and Hg(II) complexes show deshielding by 33 and 50 ppm, respectively, indicating that the orbital overlap of Se with Cd is better. Principal components of ^{77}Se and ^{113}Cd shielding tensors were determined from solid-state NMR data.

Keywords: Thiourea; Selenourea; Zn(II), Cd(II), Hg(II) complexes; NMR; CP MAS NMR

1. Introduction

Coordination compounds formed by bidentate thiourea (TU) with d^{10} metal ions (Zn^{2+}, Cd^{2+}, Hg^{2+}) have recently received renewed attention. This arises for two main reasons: their nonlinear optical properties [1,2], and the convenient preparation of semiconducting materials based on CdS through thermal decomposition of the complexes [3,4].

Most of the compounds reported in the present paper have been studied by X-ray crystallography and FT-Raman spectroscopy [5]. Marcos *et al.* [6], for example, have reported X-ray structure determinations of bis(TU) cadmium halides. These complexes have tetrahedral geometry where Cd is surrounded by two halides and by two TU bonded via S. We recently reported the complexation of thiourea with silver(I) in solution, studied using ^{13}C and ^{109}Ag NMR spectroscopy [7]. The study provided

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evidence that various stoichiometries are possible for silver(I)–thiourea complexes in solution. In this paper, we present an NMR study of $Zn(TU)_2Cl_2$, $Cd(TU)_2Cl_2$ and $Hg(TU)_2Cl_2$, and their analogs containing selenourea. For the first time, we have observed ^{13}C and ^{15}N isotopic effects on chemical shifts using labeled ligands. The information obtained from solution and solid-state NMR studies aids in a better understanding of the structural features of cadmium binding sites of metalloproteins and enzymes.

2. Experimental

2.1. *Chemicals*

$ZnCl_2$, $CdCl_2$, $HgCl_2$, thiourea, selenourea and DMSO-d_6 were obtained from Fluka Chemical Co., Germany. ^{13}C- and ^{15}N-labeled thiourea was obtained from Isotec Co., USA. Unlabeled thiourea was mixed with ^{13}C, ^{15}N 98% labeled material. Both labeled (10%) and unlabeled (90%) compounds were mixed thoroughly before use in syntheses.

2.2. *Preparation of complexes*

$M(TU)_2Cl_2$ and $M(SeU)_2Cl_2$ (M = Zn, Cd or Hg) were prepared at room temperature by mixing solutions of thiourea or selenourea with $ZnCl_2$, $CdCl_2$ and $HgCl_2$ in a minimum amount of distilled water (2 to 10 cm^3) in the mol ratio of 1 : 2 (metal : ligand) and stirring for 1 to 2 h [6]. Isolated products were dried thoroughly. Analyses, melting points and NMR data are reported in tables 1 to 8. IR data were reported earlier [5].

2.3. *NMR measurements*

All NMR measurements were carried out on a Jeol JNM-LA 500 NMR spectrophotometer at 297 K using 0.10 M solutions of the complexes in DMSO-d_6. ^{13}C NMR spectra were obtained at 125.65 MHz with ^1H broadband decoupling. Conditions were: 32 k data points, 0.967 s acquisition time, 1.00 s pulse delay and 45° pulse angle. ^{15}N NMR spectra were recorded at 50.55 MHz using $^{15}NH_4NO_3$ as external reference, and which lies at −358.63 ppm relative to pure $MeNO_2$ [8]. The conditions for ^{15}N were: 32 K data points, 0.721 s acquisition time, 2.50 s delay time, 60° pulse

Table 1. Elemental analyses of the [(TU/SeU)–MCl_2] (M = Zn, Cd or Hg) complexes.

	Found (Calc.) %			
Complex	C	H	N	Mp (°C)
$Zn(TU)_2Cl_2$	7.73 (8.32)	2.41 (2.77)	18.77 (19.41)	138–140
$Cd(TU)_2Cl_2$	8.04 (7.16)	2.19 (2.38)	17.88 (16.70)	205–208
$Hg(TU)_2Cl_2$	5.75 (5.67)	1.25 (1.89)	14.86 (13.22)	248–252[a]
$Zn(SeU)_2Cl_2$	5.83 (6.28)	1.97 (2.09)	13.02 (14.64)	158–160d
$Cd(SeU)_2Cl_2$	5.57 (5.58)	1.81 (1.86)	12.71 (13.04)	220–222d
$Hg(SeU)_2Cl_2$	4.43 (4.63)	1.70 (1.54)	10.70 (10.81)	302–303d

[a] Decomposition.

Table 2. ^{1}H and ^{13}C NMR chemical shift differences between free and bound ligands in DMSO-d_6 (ppm).

Species	δ (^{1}H)	Δ ^{1}H	δ (^{13}C)	Δ[a] ^{13}C
TU	7.1		183.7	
$Zn(TU)_2Cl_2$	7.3	0.28	181.4	2.3
$Cd(TU)_2Cl_2$	7.5 7.8	0.48 0.72	180.0	3.7
$Hg(TU)_2Cl_2$	8.12 8.42	1.07 1.37	176.7	6.9

a = Δ = The chemical shift difference between free and bound TU.

Table 3. ^{1}H, ^{13}C and ^{77}Se NMR chemical shift differences between free and bound ligands in DMSO-d_6 (ppm).

Species	δ (^{1}H)	Δ ^{1}H	δ (^{13}C)	Δ ^{13}C	δ (^{77}Se)	Δ[a] ^{77}Se
SeU	7.7 7.4		180.0		215.3	
$Zn(SeU)_2Cl_2$	7.7 7.9	0.06 0.26	177.1	2.9	182.2	33.1
$Cd(SeU)_2Cl_2$	8.1 8.3	0.52 0.71	172.8	7.15	128.3	87.0
$Hg(SeU)_2Cl_2$	8.6 8.8	0.96 1.21	170.3	9.7	165.3	50.0

a = Δ = The chemical shift difference between free and bound SeU.

Table 4. ^{13}C and ^{15}N NMR chemical shifts (ppm), isotopic chemical shifts (ppm) and coupling constants (Hz) in DMSO-d_6.

	^{13}C			^{15}N	
Species	δ ^{13}C	$^{1}J(^{13}C–^{15}N)$	δ ^{14}N ICS[a]	δ ^{15}N	δ ^{12}C ICS[b]
TU	183.63[c]	14.5	183.70	−271.05	−271.20
$Zn(TU)_2Cl_2$	181.39[b]	15.0	181.43	−269.21	−269.15
$Cd(TU)_2Cl_2$	179.99[c]	15.0	180.00	−267.64	−267.52
$Hg(TU)_2Cl_2$	176.69[c]	17.5	176.70	−264.66	−264.54
SeU[d]	178.65[e]	15.0	178.68	−262.00[c]	−261.94

[a] Isotopic chemical shifts due to ^{14}N. [b] Isotopic chemical shifts due to ^{12}C. [c] Triplet. [d] Appropriately labeled SeU complexes of Zn(II), Cd(II) and Hg (II) were not prepared because of their insolubility and the expense of the chemicals involved. [e] SeU has only one ^{15}N label, giving a doublet coupled to ^{13}C.

Table 5. ^{13}C NMR chemical shifts (ppm) of unlabeled TU in CD_3OD and $(CD_3)_2CO$ at different temperatures.

	CD_3OD		$(CD_3)_2CO$	
Species	25°C	−50°C	25°C	−50°C
TU	185.46	184.26	186.27	185.53
$Zn(TU)_2Cl_2$	180.79	179.31	181.46	179.72
$Cd(TU)_2Cl_2$	182.16	180.53	181.91	180.25

Table 6. Solid-state ^{77}Se isotropic chemical shifts (ppm) and shielding tensors.[a]

	SeU	$ZnSeU_2Cl_2$	$CdSeU_2Cl_2$	$HgSeU_2Cl_2$
δ_{iso}	180.0[b]	(i) 124.1 (ii) 152.0	140.3	(i) 207.0 (ii) 262.2
σ_{11}	−480	(i) 383 (ii) 420	283	(i) 159 (ii) 127
σ_{22}	−410	(i) 215 (ii) 226	96	(i)−6 (ii)−52
σ_{33}	349	(i) −970 (ii) −1101	−801	(i) −787 (ii) −862
$\Delta\sigma$	709	(i) −1269 (ii) −1424	−990	(i) −864 (ii) −900
η	0.1	(i) 0.20 (ii) 0.20	0.28	(i) 0.29 (ii) 0.30

[a] $\delta_{iso} = -(\sigma_{11} + \sigma_{22} + \sigma_{33})/3$; $\Delta\sigma = \sigma_{33} - 0.5(\sigma_{11} + \sigma_{22})$; $\eta = (\sigma_{22} - \sigma_{11})/(2/3)\Delta\sigma$. [b] Weighted average of five different isotropic shifts, 165–201 ppm [26].

Table 7. Solid-state ^{113}Cd isotropic chemical shifts (ppm) and shielding tensors.[a]

	$Cd(TU)_2Cl_2$	$Cd(SeU)_2Cl_2$
δ_{iso}	429.6	458.0
σ_{11}	−563	−589
σ_{22}	−480	−501
σ_{33}	−245	−284
$\Delta\sigma$	277	261
η	0.45	0.51

[a] $\delta_{iso} = -(\sigma_{11} + \sigma_{22} + \sigma_{33})/3$; $\Delta\sigma = \sigma_{33} - 0.5(\sigma_{11} + \sigma_{22})$; $\eta = (\sigma_{22} - \sigma_{11})/(2/3)\Delta\sigma$.

Table 8. Solid-state ^{13}C isotropic chemical shifts (ppm) of thiocarbonyl and selenocarbonyl carbon atoms.

TU	181.6	SeU	175.0
$Zn(TU)_2Cl_2$	166.7, 160.9	$Zn(SeU)_2Cl_2$	170.0
$Cd(TU)_2Cl_2$	175.7	$Cd(SeU)_2Cl_2$	173.2
$Hg\ (TU)_2Cl_2$	177.0	$Hg(SeU)_2Cl_2$	171.4, 167.8

angle and approximately 5000 scans. ^{77}Se NMR spectra were recorded at 95.35 MHz using SeO_2 in D_2O as external reference, and which lies at 1301 ppm relative to pure $(CH_3)_2Se$ [9]. The conditions for ^{77}Se were: 32 K data points, 0.311 s acquisition time, 2.0 s delay time, 55° pulse angle and approximately 2000 scans.

2.4. *Solid-state NMR*

Natural abundance ^{77}Se, ^{113}Cd and ^{13}C solid-state NMR spectra were obtained on a Jeol LAMBDA 500 spectrometer operating at 95.35, 110.85 and 125.65 MHz, respectively, corresponding to a magnetic field of 11.74 T, at a temperature of 25°C. Samples were packed into 6-mm zirconia rotors. Cross-polarization and high-power decoupling were used. A pulse delay of 10 s and contact time of 6.0 ms were used for selenium observation while a pulse delay of 7.0 s and a contact time of 5.0 ms were used for cadmium and carbon observations in CP MAS experiments. The magic angle spinning rates were from 3000 to 5000 Hz. Selenium chemical shifts were referenced using the secondary reference $(NH_4)_2SeO_4$, by setting the ^{77}Se peak to +1040.2 relative to $(CH_3)_2Se$. The cadmium chemical shifts were referenced using the secondary reference $Cd(NO_3)_2 \cdot 4H_2O$, by setting the peak to −132.2 ppm relative to aqueous 0.1 M $Cd(ClO_4)_2$ solution. ^{13}C chemical shifts were referenced to TMS by setting the high-frequency isotropic peak of solid adamantine to 38.56 ppm. Both the ^{77}Se spectra and ^{113}Cd spectra containing spinning side-band manifolds were analyzed using a program based on the procedure of Maricq and Waugh [10] and developed at Durham University, UK, run on a Unix platform.

3. Results and discussion

3.1. *Solution NMR studies*

In ^{1}H NMR of all TU complexes, the NH proton of TU shifts downfield with respect to that of uncoordinated TU [11,12]. The smallest shift between free and bound TU was observed for Zn(II) and the highest for Hg(II). Deshielding of the N–H proton is related to an increase in π electron density in the C–N bond upon complexation [11,12]. These metals do not bind through the N atom, as confirmed by X-ray studies [6], and their solution and solid-state chemistry is very similar. As shown in table 4, the signal appears as a doublet showing coupling with nitrogen (^{15}N labeled). The doublet in free TU was not clear so the coupling constant $^1J_{N-H}$ was resolved by ^{15}N NMR. There is a significant change in the $^1J_{N-H}$ coupling constant as the number of TU ligands is changed (table 2).

^{13}C NMR of free TU shows a triplet due to coupling to two equivalent ^{15}N atoms. Upon complexation with MCl_2, the C=S carbon of TU shifts to low frequency compared to the free ligand. The shift is attributed to a lowering of the C=S bond order upon coordination and a shift of N → C electron density producing partial double bond character in the C–N bond [11–13]. ^{13}C NMR chemical shifts between free and bound TU also show a similar trend (table 2), with Hg(II) > Cd(II) > Zn(II). Lopez-Torres *et al.* [14] have studied the complexation of benzylbisthiosemicarbazone with Zn(II), Cd(II) and Hg(II) nitrates. They found a similar bonding pattern for these metal ions to the thione ligand, when the metal is bonded, *inter alia*, to the thione group and forms octahedral complexes. The thione carbon is shifted highest in the Hg(II) complex.

We have run solution NMR in less coordinating solvents (methanol-d_4 and acetone-d_6) at both 25 and −50°C for the complexes. Data are reported in table 5. The $Hg(TU)_2Cl_2$ complex was not soluble in either solvent. The data reveal that there is no exchange on the NMR timescale at these temperatures.

Table 3 shows similar observations for ^{1}H and ^{13}C NMR chemical shifts for SeU complexes. However, for SeU the difference is greater in ^{13}C shifts; thus for $Hg(TU)_2Cl_2$ and $Hg(SeU)_2Cl_2$ the shifts are 6.9 and 9.7 ppm, respectively, indicating the softer nature of Se, which binds more strongly to Hg compared to S.

The ^{15}N NMR spectrum of TU appears as a doublet by coupling with ^{13}C. In the ^{15}N NMR spectrum of the complexes an opposite trend to that for ^{13}C was observed.

As shown in table 4, the ^{15}N resonance of TU is shifted downfield on coordination, consistent with an increase in C–N double bond character [12,13]. A similar observation was found in the reactions of TU with gold(I) complexes [15]. There is a decrease in downfield shift as the number of TU groups attached to MCl_2 increases. A smaller, high-frequency shift instead of a large low-frequency shift in the ^{15}N NMR rules out TU bonding to MCl_2 through nitrogen. Metal binding through nitrogen should involve a low-frequency shift of at least 50 ppm, as observed in some platinum(II) complexes [16,17]. However, small shifts observed for ^{15}N NMR (table 4) again confirm that N is not involved in coordination. As noted in table 3, the $Cd(SeU)_2Cl_2$ complex has the highest ^{77}Se chemical shift difference compared to its analogous $Zn(SeU)_2Cl_2$ and $Hg(SeU)_2Cl_2$ complexes.

3.2. *CP MAS NMR studies*

^{77}Se chemical shift data for the compounds studied are given in tables 3 (for solutions) and 6 (for solids). Data for selenourea are also presented for comparison. Zinc and mercury complexes show two chemically distinct selenium signals, presumably due to the presence of crystallographically inequivalent Se atoms in the unit cell (figure 1). X-ray crystallographic data are not yet available for these two compounds. Selenium bonded to Cd is more shielded than selenium bonded to either Zn or Hg [18]. This has been interpreted using electron density arguments in that the lowest unoccupied orbitals on Se involve the 5s and 4d electron shells, and these are the orbitals that are being filled in the second-row transition metal Cd. Orbital overlap of Se with a second-row transition metal would be expected to be better than that with either first- (4s, 3d) or third-row (6s, 5d) metals. Cadmium is able to provide the best overlap, according to this simple picture, and would be shielded relative to both Zn and Hg. This is borne out by our observations.

For the three selenourea complexes we observe negative ^{77}Se anisotropy, whereas for the ligand the anisotropy is positive. This arises because of apparent swapping of the

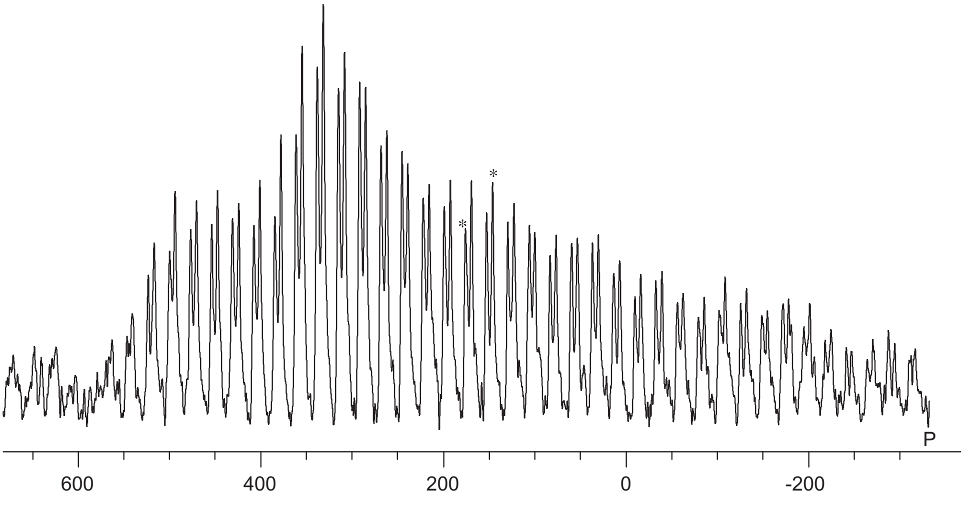

Figure 1. ^{77}Se CP MAS spectrum of $Zn(SeU)_2Cl_2$. The asterisks denote isotropic peaks.

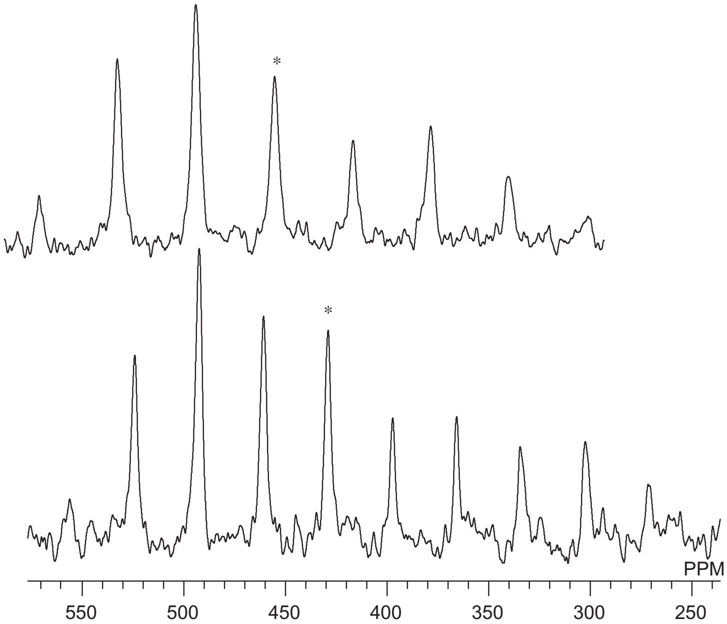

Figure 2. ^{113}Cd CP MAS spectra of (top) $Cd(TU)_2Cl_2$ and (bottom) $Cd(SeU)_2Cl_2$.

components σ_{11} and σ_{33}. The largest change from free selenourea to complexed selenourea is shown by the shielding tensor component σ_{33} of the complexes, which is more deshielded in the complex than in the free ligand. Efficient mixing of σ and π orbitals results in a large paramagnetic contribution to the total shielding of the chemical shielding tensor component perpendicular to the molecular axis [19]. Hence we can place the σ_{33} vector nearly perpendicular to the metal–Se bond. A similar orientation has been shown [20] by single-crystal NMR studies of tetrahedral $[Cd(SeR)_2(N\text{-donor})_2]$ complexes.

^{113}Cd chemical shift tensors for the two cadmium complexes (figure 2) are given in table 7. Among the chalcogens, sulfur is known [21] to be the most deshielding. However, in the selenourea complex Cd is deshielded by about 30 ppm compared to the thiourea complex. This may be rationalized by the argument, as before, that there is better overlap of Cd with Se than with S. The crystal structure of the thiourea complex shows [22] that it is four-coordinate and the tetrahedron around cadmium is distorted. This is borne out by the anisotropy parameter (277 ppm), indicating a lack of symmetry in the compound. Moreover, the asymmetry parameter (0.45) indicates that the point symmetry of site occupied by cadmium does not have axial symmetry. Similar values of the anisotropy and asymmetry parameters for the selenourea complex indicate a distorted tetrahedral structure for this complex as well.

Finally, an analysis of the orientation of the three orthogonal principal axes of the chemical shift tensor with respect to the molecular framework can be attempted. This is based [23] on the criteria that the shielding effect of a given M–L bond is maximal in the direction perpendicular to the M–L vector and that sulfur (or Se) is the most deshielding atom. On the basis of the above, the most deshielded component σ_{11} should be disposed perpendicular to the plane containing the Cd atom and the two chalcogen atoms. On the other hand, the most shielded component σ_{33} should be disposed perpendicular to the plane containing Cd and the two chlorine atoms. The σ_{22} axis is located along the intersection of the two previously mentioned planes.

^{13}C chemical shifts for the thiocarbonyl and selenocarbonyl carbons are given in table 8. Two isotropic signals were observed for $Zn(TU)_2Cl_2$ and $Hg(SeU)_2Cl_2$, presumably due to crystallographically non-equivalent molecules in the unit cell. On complexation, the thiocarbonyl and selenocarbonyl carbons move to lower frequency by as much as 15 ppm in the case of $Zn(TU)_2Cl_2$.

Devillanova and Verani [24] have studied the complexation of imidazolidine-2-selenone (ImSe) with Zn(II), Cd (II) and Hg(II) halides. The general formula proposed was $M(ImSe)_2X_2$ for all metal ions. On the basis of IR studies, they reported that all metal ions form tetrahedral complexes. In the present study, ^{13}C and ^{15}N NMR for TU and SeU clearly shows that these ligands binds to the metal ions only through S/Se, and N is not involved in binding with any metal ion.

In this study, we have demonstrated that solution and solid-state NMR are complimentary to each other; for example, ^{77}Se solution NMR shows significant chemical differences for $Cd(SeU)_2Cl_2$ compared to $Zn(SeU)_2Cl_2$ and $Hg(SeU)_2Cl_2$. The η value for $Cd(SeU)_2Cl_2$ shows similar variation. The sensitivity of the selenium nucleus to changes in its electronic environment upon complexing with metal ions in solution and in the solid state will help in interpreting more complex systems containing selenoproteins [25,26].

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