

Solution and solid-state NMR studies of thiourea, selenourea, N,N-dimethyl selenourea and their Ag(I) complexes

Mohammed I. M. Wazeer*, Anvarhusein A. Isab* and Saeed Ahmad*

Contribution from: Department of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

Received: November 13, 2005

Accepted (in revised form): December 18, 2005

Abstract

Silver(I) complexes of thiourea (TU), selenourea (SeU), N,N-dimethyl selenourea (DMSeU) have been prepared. These complexes have been characterized by elemental analysis and NMR (^1H , ^{13}C , ^{77}Se and ^{109}Ag) spectroscopy. On complexation, an upfield shift in $>\text{C}=\text{S}$ and $>\text{C}=\text{Se}$ resonances of thiones and selenones in ^{13}C NMR and low-field shifts ^{77}Se NMR are consistent with the sulfur and selenium coordination to metal ion. The principal components of the ^{77}Se shielding tensors were determined from solid-state NMR data of Ag-DMSeU complexes. The solid state ^{13}C NMR for various 1:1, 1:2, 1:3 and 1:4 ratio of Ag(I):TU indicate that TU prefers to bind to Ag(I) only in 1:1 and 1:4 ratios and other are mixture of these two ratios.

Keywords: thiourea, selenourea, N,N-dimethyl selenourea; silver(I) complexes, CP-MAS-NMR

Résumé

Nous avons préparé les complexes thiourée (TU), sélénourée (SeU), N,N-diméthyl-sélénourée (DMSeU) de l'argent (I) et nous les avons caractérisés par analyse élémentaire et spectroscopie RMN (^1H , ^{13}C , ^{77}Se et ^{109}Ag). Après complexation, un déplacement vers le champ supérieur des résonances $>\text{C}=\text{S}$ et $>\text{C}=\text{Se}$ des thiones et sélénones en RMN ^{13}C , ainsi que des déplacements vers le champ inférieur en RMN ^{77}Se , sont en accord avec la coordination du soufre et du sélénium à l'ion métallique. Les principales composantes des tenseurs

de blindage de ^{77}Se ont été obtenues à partir des données RMN état solide des complexes Ag-DMSeU. Les spectres RMN ^{13}C état solide pour divers ratios 1:1, 1:2, 1:3 et 1:4 de Ag(I):TU, indiquent que TU se lie préférentiellement à Ag(I), seulement dans les rapports 1:1 et 1:4 et que les autres complexes sont des mélanges de ces deux ratios.

Introduction

Selenium-containing ligands, e.g., selenolates and selenones, are known to form stable complexes with metal ions such as Cd(II), Hg(II) and Au(I) etc. because selenium is considered to be a soft Lewis base (1-3). Recent research has shown that silver(I) is known to interact with selenium in the body resulting in a reduction of toxicity of both the metal ion and selenium (4-5). Therefore, a systematic investigation of silver complexation with selenium-containing ligands is important from a biological point of view (6).

The present report describes the solid state NMR studies of thiourea (TU), selenourea (SeU) and N,N-dimethyl selenourea (DMSeU) complexes of Ag(I) by ^{13}C , ^{15}N and ^{77}Se NMR spectroscopy. Since these bidentate ligands are known to bind to Ag(I) via the S or Se binding site, ^{77}Se NMR will provide the most useful data about the strength of bonding to metal ions. In our previous studies of TU:Ag(I) at various molar ratios, the information was lost because solution NMR only provides the average resonances for the various species present (7). In this paper we have used solid state NMR to demonstrate that 1:1, 2:1, 3:1, 4:1 of TU:Ag(I) are actually ratios of the mixtures.

*Author to whom correspondence should be addressed: miwazeer@kfupm.edu.sa for M.I.M. Wazeer and aisab@kfupm.edu.sa for Dr. A. A. Isab

Experimental

Preparation of the Complexes

The complexes involving TU and SeU were prepared as described in the literature (8). Dimethyl selenourea (DMSeU) containing complexes were newly prepared by following a similar procedure as described earlier (8).

Anal. For (DMSeU)AgNO₃. Found (Calc): C, 11.22 (12.10); H, 2.50 (3.34); N 13.08 (12.41); M. Pt. 198-201°C for (DMSeU)₂AgNO₃ and C, 15.27 (15.77); H, 3.42 (3.11); N, 14.84 (15.72) M. Pt. 167-169°C.

NMR Measurements

All NMR measurements were carried out on a Jeol JNM-LA 500 NMR spectrophotometer at 297 K using 0.05 M solution of the complexes in DMSO-d₆. The ¹³C spectra were obtained at 125.65 MHz with ¹H broadband decoupling. The spectral conditions were: 32k data points, 0.967 sec acquisition time, 1.00 s pulse delay and 45° pulse angle. The ¹⁵N NMR spectrum was recorded at 50.55 MHz using ¹⁵NH₄NO₃ as an external reference, which lies at -358.62 ppm relative to pure MeNO₂ (7). The spectral conditions for ¹⁵N were: 32K data points, 0.721 sec acquisition time, 2.50 sec delay time, 60° pulse angle and approx. 5000 scans. All NMR (¹³C, ¹⁵N and ¹⁰⁷Ag) chemical shifts and coupling constants for selenourea, its complexes and their thiourea analogues are given in Table 1.

The spectral conditions for the CPMAS reported here have already been discussed recently (6). The carbon chemical shifts were referenced to TMS by setting the high frequency isotropic peak of solid adamantane to 38.56 ppm. The chemical shift of nitrogen was initially referenced with respect to liquid NH₃ by setting the ¹⁵N peak in enriched solid ¹⁵NH₄Cl to 40.73 ppm(8), and then converted to the standard nitromethane by a shift

of -380.0 ppm (9) for ammonia. Selenium chemical shifts were referenced using the secondary reference (NH₄)₂SeO₄, by setting the ⁷⁷Se peak to +1040.2 ppm relative to (CH₃)₂Se (10).

The ⁷⁷Se NMR for the Ag(I)-DMSeU complexes could not be recorded in solution because the complexes give black deposits in the solution after some time. However, we were able to obtain the ⁷⁷Se NMR of the ligand.

Results and Discussion

Table 1 shows the chemical shift data obtained for the complexes in solution (7,11). The ¹³C chemical shift of the >C=Se resonance of SeU in Ag(SeU)NO₃ was found 12 ppm upfield compared to free SeU ligand, while in Ag(SeU)₂NO₃, the upfield shift was 7 ppm. The upfield shift is attributed to a lowering of >C=Se bond order upon coordination and a shift of N→C electron density producing a partial double bond character in the C-N bond, as observed in metal complexes of thiourea (11,12). The ¹⁵N NMR signal in all the complexes shifted downfield consistently with an increase in double bond character of the C-N bond. This trend observed in ¹⁵N NMR of the complexes is opposite to that observed in ¹³C NMR. The metal binding through nitrogen would involve an upfield shift of at least 50 ppm as it is observed in some Pt(II) complexes (13,14). A smaller downfield, instead of a large upfield shift, in ¹⁵N NMR rules out the binding of SeU to silver (I) via nitrogen.

The ¹⁰⁷Ag NMR chemical shifts for the complexes are comparable to the reported complexes of other thiones with the same stoichiometries (15,16). As shown in Table 1, when the ¹⁰⁷Ag NMR of AgNO₃ is recorded in DMSO-d₆ instead of D₂O, the signal is shifted by 166 ppm showing that the ¹⁰⁷Ag chemical shift is not only sensitive to the nature of ligands but is also affected by changing

Table 1. ¹³C, ¹⁵N and ¹⁰⁷Ag NMR chemical shifts (in ppm) of various species in DMSO-d₆.

Species ^a	δ (¹³ C)	δ (¹⁵ N)	¹ J _{CN} (Hz)	δ (¹⁰⁷ Ag)
TU	183.81	-271.1	14.0	-
AgNO ₃	-	-	-	165.96
[Ag(TU) ₁]NO ₃	176.53	-263.0	17.1	685.93
[Ag(TU) ₂]NO ₃	179.10	-266.3	16.5	671.77
[Ag(TU) ₃]NO ₃	180.44	-267.0	15.0	797.38
[Ag(TU) ₄]NO ₃	181.05	-268.2	16.0	835.51
SeU	179.99	-262.2	13.6	-
Ag(SeU) ₁ NO ₃	167.16	-254.4	16.7	810.46
Ag(SeU) ₂ NO ₃	172.07	-258.6	15.2	784.34

* This table is extracted from Refs. 7, 8, 11, 13.

the solvent. Upon complexation with TU, ^{107}Ag NMR silver resonances are deshielded by as much as 700 ppm depending upon the number of TU ligands. This very large reduction in shielding appears to be a characteristic of silver (I) bonding to sulfur (17). An increase in the downfield shift is observed as the number of coordinating TU ligands increases, however, $\text{Ag}(\text{TU})_2\text{NO}_3$ deviates from this trend. The deviation shown by $\text{Ag}(\text{TU})_2\text{NO}_3$ can be attributed to its solid-state structure. Crystal structures have been determined for 2:1 and 3:1 (TU:Ag) complexes such as $\text{Ag}(\text{TU})_2\text{Cl}$ (18) and $\text{Ag}(\text{TU})_3\text{ClO}_4$ (19), respectively. The 3:1 complex is dimeric with two bridging TU groups, connecting 4-coordinate silver ions, while the 2:1 complex is polymeric with an equal number of bridging and terminal groups and the Cl^- fills the 4th coordination site around silver(I). In the $\text{Ag}(\text{TU})_2\text{NO}_3$ complex, the fourth site is assumed to be filled by the NO_3^- ion. It is already known that the C=S carbon is less shielded than are carbonyl carbons. Carbonyl carbons are less shielded than are carbons which are doubly bonded to nitrogen (20). Similarly, silver will be more shielded if it is bonded to nitrogen or oxygen rather than to sulfur. Thus, in $\text{Ag}(\text{TU})_2\text{NO}_3$ where one coordination is occupied by NO_3^- ion instead of sulfur in TU, the Ag signal is shifted upfield instead of downfield. The ^{107}Ag chemical shifts for $\text{Ag}(\text{TU})_2\text{NO}_3$ and $\text{Ag}(\text{TU})_3\text{NO}_3$ are comparable to the reported complexes of the thiones with the same stoichiometries (15).

The complexation with SeU shifts the ^{107}Ag NMR signal downfield by more than 600 ppm relative to AgNO_3 . This very large reduction in shielding appears to be the characteristic of silver (I) binding to the selenium of SeU. The nitrogen-bonded complexes possess a shift of around 100 ppm in ^{107}Ag NMR (20). This provides a clear evidence that SeU binds to silver (I) only through the selenium atom. The ^{107}Ag chemical shifts for SeU complexes are found approx. 100 ppm downfield than the corresponding TU complexes. This greater shift can be attributed to the more polarizable nature of Se compared to sulfur. For TU complexes, which exist in the form of polymers, it was observed that the ^{107}Ag resonance for $\text{Ag}(\text{TU})_2\text{NO}_3$ appears upfield compared to that for $\text{Ag}(\text{TU})\text{NO}_3$ (17,21). A similar trend is observed for SeU complexes, which suggests that these compounds should also be polymeric. Further confirmation of their polymeric nature comes from their solubility; when dissolved in DMSO, they give black deposits indicating the breakage of polymers.

Table 2 shows the solid state ^{13}C and ^{15}N chemical shifts of Ag-thiourea complexes. The complexes con-

taining 1:1 and 1:4 ratios provide only one set of ^{13}C resonance at 177.6 ppm and 167.2 ppm respectively, indicating that these complexes are of single type. However, for 1:2 and 1:3 ratios there are two sets of ^{13}C resonances showing two types of complexes present which are closer to 1:1 and 1:4 ratios. The 167.2 ppm resonance is present in 1:2, 1:3 and 1:4 ratios. Hence, the 1:2 and 1:3 composition of Ag (I):TU seem to be mixtures of 1:4 ratio and 1:1 ratio composition. This observation also indicates that 1:4 ratio complex has a more stable structure in the solid state, on account of the larger shielding of the >C=S carbon, compared to the 1:1 ratio complex.

The ^{15}N solid state (Table 2) NMR indicates the difference of 6 ppm between free and bound TU to Ag (I) at a 1:1 ratio. The rest of the ratios have similar chemical shifts. Since ^{15}N is farther away from the S bonding site, the chemical shifts fall within the same range for all the remaining, 1:2, 1:3 and 1:4 ratios.

The ^{77}Se CPMAS spectra of *N,N*-dimethyl selenourea and its complexes with silver are shown in Figures 1 and 2, respectively. The ^{77}Se solid state chemical shift data for the dimethyl selenourea complexes studied are given in Table 3. The data for the free ligand is also determined and added, along with data (10) for selenourea for comparison. The solid state data for both complexes show two chemically distinct selenium signals, presumably due to the presence of two crystallographically inequivalent Se in the unit cell. (The two distinct resonances observed in the ^{13}C spectra for the two complexes corroborate this). The selenium nucleus in the complexes is more shielded than the selenium in the free ligand. This has been interpreted using electron density arguments that the lowest unoccupied orbitals on Se are the 5s and 4d electron shells, and these are the orbitals that are being filled in second-row transition metal Ag. One expects silver is able to provide the good overlap, according to this simple picture; hence, Se in the complex is more shielded relative to free ligand. The most shielded tensor element can be aligned orthogonal to the Ag-Se bond axis, due to possible π bonding between Ag and Se (22). In these complexes, all three tensor elements show shielding to different degrees when compared to the free ligand; hence it is not possible to assign the molecular axis containing the Ag-Se axis to any particular principal axis of the tensors. The asymmetry factor, η , for the complexes are lower than that for the free ligand, indicating an increase in the point symmetry around Se in the complexes relative to the free ligand.

Table 4 shows the solid state ^{13}C chemical shifts of the selenone and *N*-methyl carbons of *N*-dimethyl selenourea

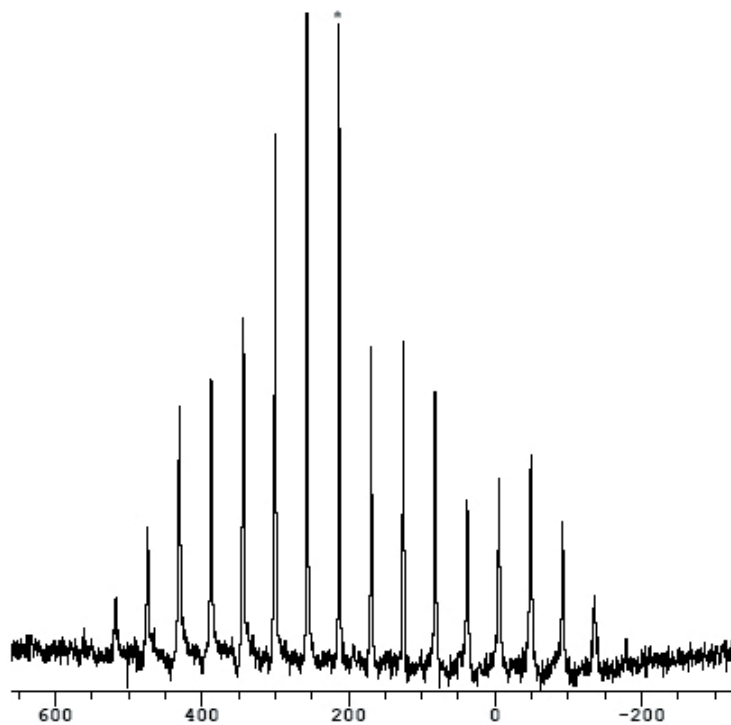


Figure 1. ^{77}Se CPMAS spectrum dimethylselenourea
* indicates the isotropic peak

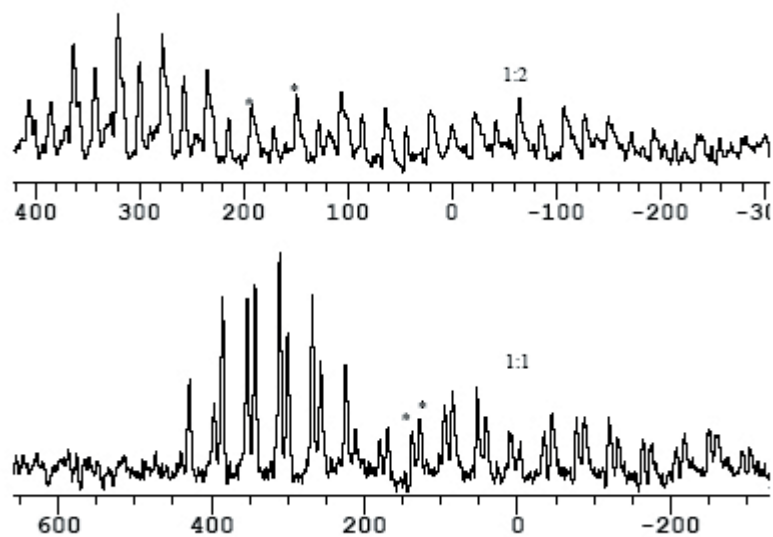


Figure 2. ^{77}Se CPMAS spectra of AgNO_3 :dimethyl selenourea complexes.
* indicates isotropic peaks

Table 2. ^{13}C and ^{15}N solid NMR chemical shifts of (^{13}C , ^{15}N -TU_nAgNO₃, where n = 1 to 4).

	$^{13}\text{C}^{\text{b}}$	$^{15}\text{N}^{\text{a}}$
TU	181.6	-270.3
Ag:TU 1:1	177.6	-264.3
Ag:TU 1:2	178.1, 166.2	-269.0
Ag:TU 1:3	178.0, 167.2	-268.3
Ag:TU 1:4	167.2	-268.8

^a relative to nitromethane; ^b relative to TMS

Table 3. ^{77}Se isotropic chemical shifts (δ_{iso}) and principle shielding tensors (σ_{xx})^a

Compound	δ_{iso}	σ_{11}	σ_{22}	σ_{33}	$\Delta\sigma$	η
Selenourea ^b	180.4	-300	-230	529	829	0.83
DMSeU	213.1	-501	-260	122	502	0.72
Ag(DMSeU) ₁ NO ₃	(i) 180.0	-382	-304	146	490	0.24
	(ii) 169.8	-398	-322	210	570	0.20
Ag(DMSeU) ₂ NO ₃	(i) 192.2	-417	-305	146	507	0.33
	(ii) 128.7	-382	-329	325	681	0.12

^a isotropic shielding, $\sigma_{\text{i}} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$; $\Delta\sigma = \sigma_{33} - 0.5(\sigma_{11} + \sigma_{22})$; $\eta = 3(\sigma_{22} - \sigma_{11})/2\Delta\sigma$

^b From ref. 10, δ_{iso} is the weighted average position of the 5 different crystallographic sites.

Table 4. ^{13}C chemical shifts^a from CPMAS spectra.

	C = Se	N-Me
SeU	181.1	-
Ag(SeU) ₁ NO ₃	168.2, 171.2	-
Ag(SeU) ₂ NO ₃	178.8, 174.5	-
DMSeU	175.0	47.1, 38.3
Ag(DMSeU) ₁ NO ₃	168.6, 166.6	48.0, 46.4, 40.2
Ag(DMSeU) ₂ NO ₃	164	47.1, 41.4

^a relative to TMS

and its silver complexes. As in the thiourea complexes, the selenone carbon in these complexes is shielded relative to the free ligand. We were not able to record Ag (SeU) solid state complexes because of the polymeric nature. Even after a 24 hours run, the resonances were still not resolved.

Conclusion

The study provides useful information about the nature of bonding in silver (I) complexes. The large ^{107}Ag NMR chemical shifts differences in different complexes presented here can be utilized to study silver (I) complexes with sulfur and selenium containing biological ligands. The solid state ^{13}C NMR for various species 1:1, 1:2, 1:3 and 1:4 ratios of Ag(I):TU indicate that TU

prefers to bind to Ag(I) in a tetrahedral symmetrical nature which is very stable compared to other ratios. The solid state NMR can distinguish various compositions from the heterogeneous mixture as demonstrated in this paper.

Acknowledgements

This research was supported by the King Fahd University of Petroleum & Minerals Research Committee under project No. SABIC 2004-01.

References

1. W. Eikens, C. Kienitz, P. G. Jones and C. Thone, *J. Chem. Soc. Dalton Trans.*, 83 (1994).

2. A. D. Al-Amri, M. Fettouhi, M. I. M. Wazeer and A. A. Isab, *Inorg. Chem. Comm.*, **8**, 1109 (2005).
3. M. I. M. Wazeer and A. A. Isab, *Spectro.Chim. Acta A*, **62**, 880 (2005).
4. C. Sasakura and K. T. Suzuki, *J. Inorg. Biochem.* **71**, 159 (1998).
5. C. J. Dollard and A. L. Tappel, *J. Inorg. Biochem.*, **28**, 13 (1986).
6. A. A. Isab and M. I. M. Wazeer, *J. Coord. Chem.*, **58**, 529 (2005).
7. S. Ahmad, A. A. Isab and H. P. Perzanowski, *Transit. Metal Chem.*, **27**, 782 (2002).
8. S. Hayashi, K. Hayamizu, *Bull. Chem. Soc. Jpn.* **64**, 688 (1991).
9. W. Kemp, *NMR in Chemistry*, Macmillan Education, London, (1986).
10. M. J. Collins, C. I. Ratcliffe, J. A. Ripmeester, *J. Magn. Reson.*, **68**, 172 (1986).
11. S. Ahmad and A. A. Isab, *Inorg. Chem. Comm.*, **5**, 355 (2002).
12. U. Bierbach, T. W. Hambly and N. Farrell, *Inorg. Chem.*, **37**, 708 (1998).
13. T. G. Appleton, J. R. Hall, S. T. Ralph, *Inorg. Chem.*, **24**, 673 (1985).
14. F. M. Macdonald, P. J. Sadler, *Magn. Res. Chem.*, **29**, S52 (1991).
15. J. S. Casas, E. G. Martinez, A. Sanchez, A. S. Gonzalez, J. Sordo, U. Casellato, R. Graziani, *Inorg. Chim. Acta*, **241**, 117 (1996).
16. S. Ahmed, A. A. Isab and M. Arab, *Polyhedron*, **21**, 1267 (2002).
17. P. M. Henrichs, J. J. H. Jackerman and G. E. Maciel, *Inorg. Chem.*, **16**, 2544 (1977).
18. E. A. Vizzini, I. F. Taylor and E. L. Amma, *Inorg. Chem.*, **7**, 1351 (1968).
19. M. R. Udupa and B. Krebs, *Inorg. Chim. Acta*, **7**, 271 (1973).
20. P. M. Henrichs, S. Sheard, J. J. H. Jackerman and G. E. Maciel, *J. Am. Chem. Soc.*, **101**, 3222 (1979).
21. M. R. Dupa, G. Henke and B. Krebs, *Inorg. Chim. Acta*, **18**, 173 (1976).
22. T.G. Oas, C. J. Hartzell, T. J. McMohan, G. P. Drobny, F. W. Dahlquist, *J. Am. Chem. Soc.*, **109**, 5956 (1987).