

Raman, infrared and proton magnetic spectra of silver(I) complexes of dimethyl sulfide and thiourea

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(Received January 29, 1991; revised May 13, 1991)

Abstract

The silver complexes of dimethyl sulfide (Me_2S), including the 1:1 complex, $\text{Ag}(\text{SMe}_2)\text{NO}_3$, and the 1:2 complex, $[\text{Ag}(\text{SMe}_2)_2]\text{PF}_6$, were isolated and characterized, in addition to the complex, bis(thiourea)silver(I) nitrate, $\text{Ag}(\text{Tu})_2\text{NO}_3$. Crystalline $\text{Ag}(\text{SMe}_2)\text{NO}_3$ and $\text{Ag}(\text{Tu})_2\text{NO}_3$ were characterized using Raman, IR and ^1H NMR spectroscopy, while the photosensitive $[\text{Ag}(\text{SMe}_2)_2]\text{PF}_6$ was characterized only by IR. The Raman spectra of 2.0 M AgNO_3 solution in neat Me_2S and an aqueous solution of $\text{Ag}(\text{Tu})_2\text{NO}_3$ were also examined to further support assignments. Vibrational assignments of most vibrational bands have been made and compared to the literature. Diagnostic bands for thiourea indicate that it is coordinated to silver through the sulfur atom.

Introduction

Characterization of Ag(I) complexes containing small ligands provides a basis for understanding and predicting the interactions with more complex ligands. The silver complexes very frequently exhibit a linear geometry about the silver and therefore provide attractive systems for vibrational characterization, including the assignment of silver–ligand stretching modes. Complex formation with ambidentate ligands, such as thiourea, also provides a model system to evaluate the electronic control of binding in the absence of steric factors. In addition, these complexes have been of great interest to the field of surface enhanced Raman scattering (SERS) and especially for probing the electrode surface [1–3]. Relatively few reports, however, have appeared in the literature on laser Raman and IR vibrational analyses of well-defined silver(I) complexes, especially those with sulfur-containing ligands. This is due, in part, to the instability of the complexes, many being especially photosensitive. In a previous report, Fleischmann *et al.* [1] successfully analyzed the S-bonded complex, $\text{Ag}(\text{Tu})_3\text{NO}_3$, using laser Raman spectroscopy. The tricoordinate $\text{Ag}(\text{Tu})_3\text{NO}_3$ was chosen for study instead of the dicoordinate $\text{Ag}(\text{Tu})_2\text{NO}_3$ complex because of its unusual stability in the solid state and to exposure to laser irradiation [1]. Although the structure of the 1:3 complex $\text{Ag}(\text{Tu})_3\text{NO}_3$ was not

addressed by the authors [1], it is possible that the complex may adopt a similar structure to that of ionic $\text{Ag}(\text{Tu})_3\text{ClO}_4$ [4]. The latter complex has been shown by X-ray crystallography to be dimeric $[\text{Ag}_2(\text{Tu})_6][\text{ClO}_4]_2$, in which each Ag(I) ion is surrounded by two bridging and two terminal S-bonded thiourea ligands. In this work, we report the comparative vibrational spectra of the 1:1 and the 1:2 complexes of Ag(I) with Me_2S , in addition to the ionic $\text{Ag}(\text{Tu})_2\text{NO}_3$ complex, in which it is concluded that the thiourea is terminally coordinated via the sulfur atom.

Experimental

The elemental analysis was performed by Galbraith Microanalytical Laboratories, Knoxville, TN. Dimethyl sulfide was obtained from Eastman Kodak Company. The IR spectra were recorded with a Beckman IR-12 spectrometer using the split Nujol–Halocarbon mull technique with KBr windows. The far-IR spectra ($200\text{--}400\text{ cm}^{-1}$) were obtained as Nujol mulls between polyethylene windows. Calibration of the instrument was effected by using a polystyrene film. The frequencies of sharp bands are believed accurate to 2 cm^{-1} , while those of broad bands should be within 5 cm^{-1} . Raman spectra were obtained as previously described [5], using 514.5 nm excitation, at a power of 300–1200 mW and a resolution of 8 cm^{-1} . The proton NMR spectra of

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$\text{Ag}(\text{SMe}_2)\text{NO}_3$ in D_2O and $\text{Ag}(\text{Tu})_2\text{NO}_3$ in DMSO-d_6 were obtained by using a Varian A-60 spectrometer.

Synthesis of complexes

$\text{Ag}(\text{SMe}_2)\text{NO}_3$

The complex was prepared by a modification of general methods [6, 7]. Dimethyl sulfide (1.7 ml, 10.0 mmol) was slowly added to a stirred aqueous solution of silver nitrate (0.68 g, 4.0 mmol). The solution, containing the highly soluble complex, was warmed to 50 °C and then the temperature lowered to 4 °C to produce glistening white crystals which were filtered, washed with absolute ethanol and finally recrystallized from water–ethanol mixture. Yield 50% (0.32 g); m.p. 98–100 °C. *Anal.* Calc. for $\text{C}_2\text{H}_6\text{AgNO}_3\text{S}$: C, 10.34; H, 2.59; Ag, 46.55. Found: C, 10.16; H, 2.52; Ag, 46.60%.

$[\text{Ag}(\text{SMe}_2)]_2\text{PF}_6$

Addition of Me_2S (1 ml, 6.6 mmol) to a stirred aqueous solution of silver nitrate (0.34 g, 2.0 mmol), followed by addition of aqueous $\text{NaPF}_6 \cdot \text{H}_2\text{O}$ (0.41 g, 2.2 mmol) produced a white precipitate. The product was recrystallized from water–ethanol mixture. The crystals were filtered, washed with H_2O and dried over P_4O_{10} . To minimize decomposition of this compound during even short-term storage, the crystals were stored desiccated at 4 °C. Yield 40% (0.33 g); m.p. 160 °C (dec.). *Anal.* Calc. for $\text{C}_4\text{H}_{12}\text{Ag}_2\text{F}_6\text{PS}_2$: Ag, 28.60. Found: Ag, 29.85%.

$\text{Ag}(\text{Tu})_2\text{NO}_3$

A solution of AgNO_3 (0.34 g, 2.0 mmol) was added dropwise to a stirred aqueous solution containing slightly over two equivalents of thiourea (0.32 g, 4.2 mmol). White crystals precipitated immediately, were filtered and washed with absolute methanol. The product was recrystallized from hot water, filtered and finally dried over P_4O_{10} under vacuum. Yield 50% (0.32 g); m.p. 162–164 °C. *Anal.* Calc. for $\text{C}_2\text{H}_8\text{AgN}_5\text{O}_3\text{S}_2$: C, 7.45; H, 2.50; Ag, 33.48. Found: C, 7.37; H, 2.80; Ag, 33.21%.

Results and discussion

Vibrational spectra of silver(I) complexes of dimethyl sulfide

The IR spectra of $\text{Ag}(\text{SMe}_2)\text{NO}_3$ (not shown) and the 1:2 complex $[\text{Ag}(\text{SMe}_2)_2]\text{PF}_6$, exhibit expected bands due to Me_2S , with the most prominent changes associated with the (C–S) stretching vibrations and the methyl rocking modes (see Table 1; and ‘Sup-

plementary material’). The $\nu_s(\text{CS})$ at 695 cm^{-1} in the spectrum of Me_2S decreased to 685 for the 1:1 complex and to 680 cm^{-1} for the 1:2 complex, with an accompanying large decrease in band intensity. The weak IR band at 740 cm^{-1} , assigned to $\nu_a(\text{CS})$, is shifted to 722 cm^{-1} , with a weak shoulder at 736 cm^{-1} for the 1:1 complex and to 732 cm^{-1} for the 1:2 complex. Both shifts are consistent with the drain of electron density from the (SC) bonds and the lowering of the bond order upon coordination to the silver. The methyl rocking mode, observed as a weak IR band at 900 cm^{-1} , is significantly increased in frequency to 930 for the 1:1 complex and to 940 cm^{-1} for the 1:2 complex. The IR spectrum of Me_2S showed two intense bands at 975 and 1030 cm^{-1} , which were also assigned to $\delta(\text{CH}_3)$ rocking modes. The band at 975 cm^{-1} is increased to 987 cm^{-1} with a weak shoulder at 964 cm^{-1} for the 1:1 complex, and to 998 cm^{-1} for the 1:2 complex. The band at 1030 cm^{-1} for Me_2S is significantly reduced in intensity with a concomitant (similar) increase in frequency to 1045 cm^{-1} for both the 1:1 complex and the 1:2 complex. An analogous frequency increase to 1045 cm^{-1} has been reported for the gold(I) complex, $[\text{Au}(\text{SMe}_2)(\text{PET}_3)]\text{PF}_6$ [8].

In the far-IR, Me_2S has a medium band at 285 cm^{-1} due to $\delta(\text{SC}_2)$. This band increased to 305 cm^{-1} for the 1:1 complex, while it appears very weak at 300 cm^{-1} for the 1:2 complex. Additionally, the IR spectrum of the 1:1 complex also shows a band of medium intensity at 255 cm^{-1} , with a prominent shoulder at 240 cm^{-1} . These bands can be tentatively assigned to the $\nu(\text{AgS})$, in line with the assignment of $\nu(\text{AgS})$ at 240 cm^{-1} (IR) for the 1:1 polymeric complex, $\text{Ag}(\text{SBU})$, containing bridging 2-methylpropane-2-thiolate (SBU) [9]. The $\nu(\text{AgS})$ stretch, however, is not observed in the far-IR spectrum of $[\text{Ag}(\text{SMe}_2)_2]\text{PF}_6$. In many cases, it appears that (AgL) stretching vibrations are not especially sensitive to the nature of the donor ligand. For example, the $\nu(\text{AgN})$ for crystalline $\text{Ag}(\text{pyridine})_2\text{NO}_3$ occurs in this same region at 225 (Raman) and 240 (IR) cm^{-1} [10]. The $\nu(\text{AgO})$ has also been assigned at 240 cm^{-1} (IR) for the 1:1 dicoordinate nitrate complex, $\text{Ag}\{\text{P}(\text{t-Bu})_3\}\text{NO}_3$ [11]. The $\nu(\text{AgS})$ for $\text{Ag}(\text{SMe}_2)\text{NO}_3$ is significantly lower than the assigned $\nu(\text{AuS})$ at 368 cm^{-1} (IR) for $[\text{Au}(\text{SMe}_2)(\text{PET}_3)]\text{PF}_6$ [8], and for the $\nu(\text{Hg–S})$ at 302 cm^{-1} (Raman) for $\text{Hg}(\text{Me})(\text{SMe}_2)\text{NO}_3$ [12]. The reasons for the discrepancies are not very clear; however, the higher frequencies for $\nu(\text{AuS})$ and $\nu(\text{HgS})$ may be due to coupling factors and/or to a stronger metal–sulfur bond since Au(I) and Hg(II) metal ions are much softer Lewis acids than Ag(I).

The Raman spectrum of crystalline $\text{Ag}(\text{SMe}_2)\text{NO}_3$ is shown in Fig. 1. The assignments of the Raman frequencies are given in Table 1, together with those for Me_2S and the 2.0 M AgNO_3 solution in neat Me_2S . The $\delta(\text{SC}_2)$ vibration for Me_2S in the Raman spectrum is observed at 285 cm^{-1} . In the Raman spectrum of crystalline $\text{Ag}(\text{SMe}_2)\text{NO}_3$, this band increased to 300 cm^{-1} , with a significant intensity enhancement. For the 2 M solution of $\text{AgNO}_3/\text{Me}_2\text{S}$, the intensity but not the frequency of the analogous polarized, Raman band observed at 285 cm^{-1} also increased, upon complexation. The $\nu_s(\text{CS})$ at 692 cm^{-1} in the Raman spectrum of Me_2S decreased upon coordination to 685 cm^{-1} , with a shoulder at 716 cm^{-1} in that of crystalline $\text{Ag}(\text{SMe}_2)\text{NO}_3$. A smaller decrease to 688 (p) cm^{-1} was also observed in 2 M AgNO_3 in Me_2S . Similarly, the weak Raman band at 743 cm^{-1} assigned to $\nu_a(\text{CS})$ for free Me_2S decreased with a significant increase in intensity, upon complexation. It decreased to 736 cm^{-1} for crystalline $\text{Ag}(\text{SMe}_2)\text{NO}_3$ and to 737 cm^{-1} for the $\text{AgNO}_3/\text{Me}_2\text{S}$ solution. The Raman spectrum of crystalline $\text{Ag}(\text{SMe}_2)\text{NO}_3$ shows a weak band at 236 cm^{-1} , in the region expected for a $\nu(\text{AgS})$ stretch. Perhaps a surprising result of this work was the absence of $\nu(\text{AgS})$ for $\text{AgNO}_3/\text{Me}_2\text{S}$ solution. In a previous report, we commented on the absence of a (AgN) stretching mode in the Raman spectrum of AgNO_3 in neat pyridine [10]. Solutions of silver(I) perchlorate in pyridine are reported to contain the $\text{Ag}(\text{Py})_4^+$ complex in which the $\text{Ag}(\text{I})$ ion is tetrahedrally coordinated by four pyridine molecules [13]. This may likewise be the case for the solution complex for Me_2S , where the formation of tetrahedral $\text{Ag}(\text{SMe}_2)_4^+$ may explain the weak polarizability of the silver-sulfur bond. This proposed geometry can be supported from the finding that solutions of AgX

($\text{X} = \text{I}, \text{Br}$ or ClO_4) in tetrahydrothiophene ($\text{C}_4\text{H}_8\text{S}$), a small cyclic thioether, have been shown by large angle X-ray scattering (LAXS) to contain the tetrahedral $\text{Ag}(\text{SC}_4\text{H}_8)_4^+$ complex [14].

The crystalline $\text{Ag}(\text{SMe}_2)\text{NO}_3$ complex showed an intense single band at 1037 cm^{-1} in the Raman and a weak, but very sharp IR band at 1038 cm^{-1} for the nitrate. This is evidence for the ionic nature of the nitrate in the solid state complex [6]. In addition, the strong IR bands at 820 and 1355 cm^{-1} in the solid $\text{Ag}(\text{SMe}_2)\text{NO}_3$ also support the conclusion of an ionic nitrate complex. The intense single band at 1035 cm^{-1} in the Raman spectrum of $\text{AgNO}_3/\text{Me}_2\text{S}$ solution is also consistent with this conclusion and not inconsistent with the formation of a tetrahedral $[\text{Ag}(\text{SMe}_2)_4]^+$ complex.

Attempts to determine the exact structure of crystalline $\text{Ag}(\text{SMe}_2)\text{NO}_3$ by X-ray crystallographic methods have not been successful due to the instability of the complex. The Raman and IR data, however, are consistent with the ionic character of the nitrate anion [6]. The multiplicity of the $\nu(\text{AgS})$ and $\nu_{\text{as}}(\text{CS})$ modes in the IR also suggests that this complex is present as polynuclear species in the solid state. This agrees with the earlier suggestion that for the $\text{Ag}(\text{I})$ in the solid 1:1 complex $\text{Ag}(\text{SR}_2)\text{NO}_3$ ($\text{R} = \text{alkyl}$) to have a coordination number of two (or greater), the ligand Me_2S must serve as a bridge between silver(I) ions [6]. Indeed, the observation of three IR active modes associated with the symmetric and asymmetric $\nu(\text{CS})$ in solid $\text{Ag}(\text{SMe}_2)\text{NO}_3$ and four in the Raman suggests that the 1:1 complex has C_{2v} symmetry as would be expected if Me_2S served as a bridging ligand. It is also possible that the solid $\text{Ag}(\text{SMe}_2)\text{NO}_3$ may adopt an associated structure in which the silver ions are tetrahedrally coordinated by four bridging Me_2S as proposed earlier for other 1:1 $\text{Ag}(\text{PR}_3)\text{NO}_3$

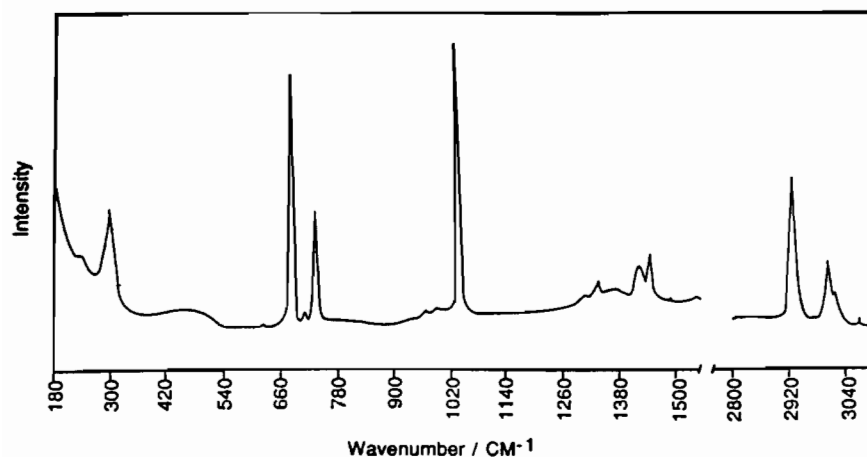


Fig. 1. Laser Raman spectrum ($180\text{--}1500, 2900\text{--}3040\text{ cm}^{-1}$) of crystalline $\text{Ag}(\text{SMe}_2)\text{NO}_3$.

TABLE 1. Vibrational spectra (cm^{-1}) of Me_2S , crystalline $\text{Ag}(\text{SMe}_2)\text{NO}_3$, $[\text{Ag}(\text{SMe}_2)_2]\text{PF}_6$ and a 2.0 M AgNO_3 in Me_2S solution

Me_2S		Crystalline $\text{Ag}(\text{SMe}_2)\text{NO}_3$		$\text{AgNO}_3/\text{Me}_2\text{S}$	$[\text{Ag}(\text{SMe}_2)_2]\text{PF}_6$	Assignment
(IR)	Raman	(IR)	Raman	Raman	(IR)	
285m,b	285s,p	240m, 255m 305m	236w,b 300s	285s,p	300vw,b 562vs	$\nu(\text{Ag-S})$ $\delta(\text{SC}_2)$ $\nu(\text{PF}_6^-)$
695s 740w,sh	692vs,p 743w,dp	685m 722s, 736w,sh 820s,sp 930w	620vw, 685vs 716w,sh, 736vs	688vs, p 737m,dp	680s 732m,sh	$\nu_s(\text{C-S})$ $\nu_a(\text{C-S})$ $\delta(\text{NO}_3^-)$
900w					940w 840vs	$\rho(\text{CH}_3)$ $\nu(\text{PF}_6^-)$
975vs		987vs	1037vs	1035vs	998s	$\rho(\text{CH}_3)$ $\nu_s(\text{NO}_3^-)$
1030vs		1045s 1038w,sh,sp			1045s	$\rho(\text{CH}_3)$ $\delta(\text{NO}_2)$

Abbreviations (Tables 1 and 2): vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; b, broad; ν , stretching; ρ , rocking; δ , bending or deformation; δ_{ip} , in-plane bend; β , out-of-plane deformation; s, symmetric; a, asymmetric; sp, sharp; IR, infrared; p, polarized, dp, depolarized.

complexes, such as ionic $\text{Ag}(\text{PMe}_3)\text{NO}_3$ [11, 15]. The polymeric $\text{Ag}(\text{PMe}_3)\text{NO}_3$ has been reported to exist as a tetramer in benzene [15].

The ^1H NMR spectrum of the 1:1 complex $\text{Ag}(\text{SMe}_2)\text{NO}_3$ in D_2O showed only a single peak at $\delta=2.50$ ppm for coordinated Me_2S , downfield from $\delta=2.13$ for free Me_2S . The addition of excess Me_2S to the $\text{Ag}(\text{SMe}_2)\text{NO}_3$ solution shifted the peak to $\delta=2.42$ ppm due to rapid ligand exchange. Nonetheless, the chemical shift to 2.50 ppm observed for coordinated Me_2S in $\text{Ag}(\text{SMe}_2)\text{NO}_3$ is comparable to, but slightly lower than, that observed for terminally coordinated Me_2S in $[\text{Au}(\text{SMe}_2)(\text{PEt}_3)]\text{PF}_6$ (2.68 ppm) [8], $\text{AuCl}(\text{SMe}_2)$ (2.68 ppm) [16], $\text{AuBr}(\text{SMe}_2)$ (2.69 ppm) [16], $[\text{Au}(\text{Me})_2(\text{SMe}_2)_2]\text{NO}_3$ (2.57 ppm) [17] and anionic $\text{Pt}_2\text{Cl}_5(\text{SMe}_2)_2^-$ (2.58 ppm) [18]. The higher chemical shift for terminally coordinated Me_2S in $\text{Au}(\text{I})$ complexes is consistent with the expected increase in (M-S) bond strength on going from $\text{Ag}(\text{I})$ to the isoelectronic, but softer $\text{Au}(\text{I})$. Nonetheless, the ^1H NMR data suggest that such an associated structure in solid $\text{Ag}(\text{SMe}_2)\text{NO}_3$ may be disrupted in aqueous solutions since the ^1H NMR resonance for bridging Me_2S in transition metal complexes is expected to occur at lower field compared to those for terminal Me_2S [18]. For example, in addition to the single proton peak at 2.58 ppm for a terminal Me_2S in anionic $\text{Pt}_2\text{Cl}_5(\text{SMe}_2)_2^-$, a second peak observed at a lower field of 3.24 ppm was attributed to the other Me_2S , believed to be bridging between $\text{Pt}(\text{II})$ metal ions [18]. Although the 1:2 complex, $[\text{Ag}(\text{SMe}_2)_2]\text{NO}_3$, could not be isolated, that of $[\text{Ag}(\text{SMe}_2)_2]\text{PF}_6$ is expected to involve

the linear $\text{Ag}(\text{SMe}_2)_2^+$ complex, in which the thioether, Me_2S , is terminally coordinated via the sulfur atom.

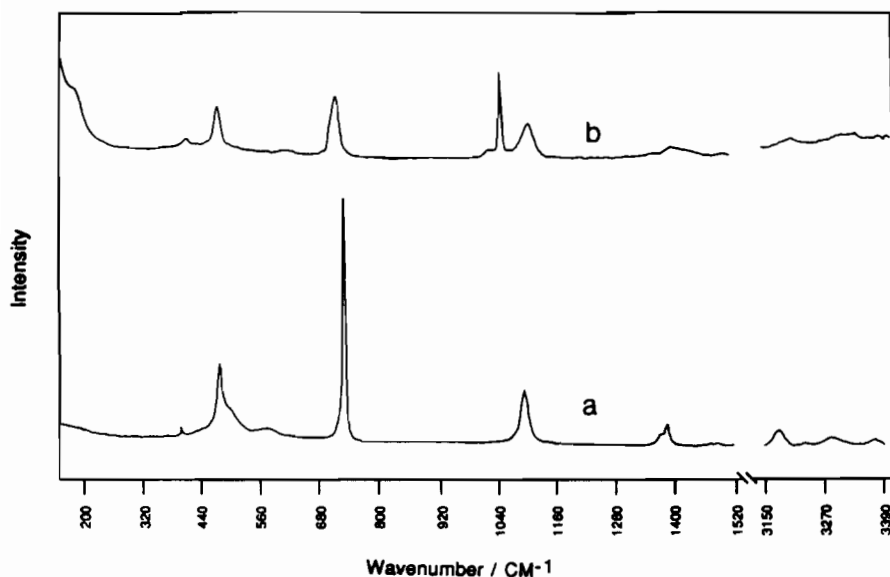
$\text{Ag}(\text{TU})_2\text{NO}_3$

Thiourea, $\text{SC}(\text{NH}_2)_2$, is a classic ambidentate ligand, capable of bonding to transition metals via the sulfur or nitrogen atom. There are at least three major IR bands, including $\nu(\text{C}=\text{S})$, $\nu(\text{CN})$ and $\nu(\text{NH}_2)$, which are considered diagnostic of the mode of binding of thiourea to metals. Upon coordination via the sulfur atom, the (CS) double bond character is expected to be reduced, while the electron density in the (CN) bond increases to produce partial double bond character. As a result, a decrease in the frequency for the $\nu(\text{C}=\text{S})$ mode is expected, with a concomitant increase in the $\nu(\text{CN})$ and the $\nu(\text{NH}_2)$ modes. The opposite would be observed if thiourea were coordinated via the nitrogen.

Consistent with the conclusion of (Ag-S) bonding, the IR $\nu(\text{C}=\text{S})$ mode at 730 cm^{-1} for thiourea is simultaneously reduced in intensity and decreased in frequency to 724 cm^{-1} , with an accompanying weak shoulder 715 cm^{-1} in the complex (Table 2; see also 'Supplementary material'). The $\nu(\text{C}=\text{S})$ mode in the Raman at 734 cm^{-1} for crystalline thiourea (Fig. 2) is also both reduced in intensity and lowered in frequency to 722 cm^{-1} for $\text{Ag}(\text{TU})_2\text{NO}_3$. A smaller decrease to 727 cm^{-1} was found in the Raman spectrum of crystalline, S-bonded $\text{Ag}(\text{TU})_3\text{NO}_3$ [1]. In aqueous solution, the $\nu(\text{C}=\text{S})$ band at 729 cm^{-1} for thiourea is similarly decreased to 720 cm^{-1} for the S-bonded complex $\text{Ag}(\text{TU})_2\text{NO}_3$.

TABLE 2. Vibrational spectra (cm^{-1}) of thiourea and $\text{Ag}(\text{Tu})_2\text{NO}_3$ in crystalline state and in aqueous solution

Thiourea (Tu)			$\text{Ag}(\text{Tu})_2\text{NO}_3$			Assignment
IR	Raman		IR	Raman		
	Crystalline	aq. (1.0 M)		Crystalline	aq. (0.25 M)	
411m	420w	405w,dp	235m	196w,b		$\nu(\text{AgS})$
486s, 463sh	481s	479m,p	411w	420w		$\delta_{\text{ip}}(\text{SCN})$
630m			477s	482s		$\delta(\text{NCN})$
730s	734vs	729vs,p	630vw			$\beta(\text{SCNN})$
			715sh, 723s	722s	720vs,p	$\nu(\text{CS})$
			818m,sp			$\delta(\text{NO}_3^-)$
				1055vs	1046vs	$\nu_3(\text{NO}_3^-)$
1086m	1093s	1093s,p		1112s,b	1100s,p	$\nu_2(\text{NCN})$
1414s			1382s, 1400sh			$\nu(\text{NCN}), \rho(\text{NH}_2), \nu(\text{C}=\text{S})$
			1437sh			
1473s	1472w,b	1472w,b	1502m			$\nu_1(\text{NCN})$
1610s		1635w,b	1620s, 1640sh		1630b,p	$\delta(\text{NH}_2)$
			1653sh			

Fig. 2. Laser Raman spectrum ($150\text{--}1520, 3150\text{--}3390 \text{ cm}^{-1}$) of crystalline (a) thiourea (Tu) and (b) $\text{Ag}(\text{Tu})_2\text{NO}_3$.

Free thiourea has a band of medium intensity at 1086 cm^{-1} in the IR and a strong band at 1093 cm^{-1} in the Raman. This band, which is primarily assigned to the $\nu_2(\text{NCN})$ stretch, is markedly reduced in intensity in the IR spectra of transition metal complexes containing S-bonded thiourea [19]. This was also the case in the IR spectrum of $\text{Ag}(\text{Tu})_2\text{NO}_3$. On the other hand, this band retains its strong intensity and increases to 1112 cm^{-1} in the Raman spectrum of crystalline $\text{Ag}(\text{Tu})_2\text{NO}_3$. This increase in frequency is in accord with an increase in the (C–N) double bond character upon metal–sulfur bond formation. Similarly, this band also retains its strong

intensity in the Raman of crystalline, S-bonded $\text{Ag}(\text{Tu})_3\text{NO}_3$, but with a relatively smaller increase in frequency to 1102 cm^{-1} [1]. The latter frequency is essentially the same as that at 1100 cm^{-1} found in the Raman spectrum of 0.25 M solution of $\text{Ag}(\text{Tu})_2\text{NO}_3$ in H_2O . Furthermore, the strong IR band at 1413 cm^{-1} for thiourea is assigned to a combination mode involving $\nu(\text{NCN})$, $\delta(\text{NH}_2)$ and $\nu(\text{C}=\text{S})$. This mode is clearly split in the IR spectrum of the complex ($1382, 1400$ and 1437 cm^{-1}) in further support for the presence of thiourea being coordinated to silver via the sulfur atom [19]. Also in line with (Ag–S) bond formation is the significant

increase in $\nu_2(\text{NCN})$ upon coordination. It occurs at 1473 cm^{-1} in the IR spectrum of free thiourea and increases to 1500 cm^{-1} in the complex. In the Raman, the $\nu_2(\text{NCN})$ mode appeared as a weak broad band at 1474 cm^{-1} for free thiourea, but was absent for crystalline $\text{Ag}(\text{Tu})_2\text{NO}_3$. Furthermore, the strong IR band at 1610 cm^{-1} for thiourea due to the $\delta(\text{NH}_2)$ mode is split upon complexation into three bands of higher frequencies at 1620, 1653 and 1660 cm^{-1} . Also consistent with S-bonding is the increase to higher frequencies in the symmetric and asymmetric NH_2 stretches for thiourea upon complex formation. These bands, which occur in the IR at 3097, 3156, 3258 and 3365 cm^{-1} for thiourea are observed at 3120, 3180, 3270 and 3370 cm^{-1} , respectively, for the complex. An interesting feature in the Raman spectrum of crystalline $\text{Ag}(\text{Tu})_2\text{NO}_3$ is the appearance of a weak, broad band at 196 cm^{-1} which is tentatively assigned to $\nu(\text{Ag-S})$. Surprisingly, a band assignable to $\nu(\text{Ag-S})$ was not observed in the Raman spectrum of $\text{Ag}(\text{Tu})_2\text{NO}_3$ solution. However, a weak-to-medium band at 235 cm^{-1} is observed in the far-IR spectrum of the crystalline $\text{Ag}(\text{Tu})_2\text{NO}_3$ complex. The IR $\nu(\text{AgS})$ at 235 cm^{-1} is, unexpectedly, lower than that at 268 cm^{-1} for $\nu(\text{AuS})$ in $\text{Au}(\text{Tu})(\text{PET}_3)^+\text{Cl}^-$ [8], with possible reasons discussed earlier. The $\nu(\text{Ag-S})$ in the Raman spectrum of crystalline $\text{Ag}(\text{Tu})_3\text{NO}_3$ has not been observed; however, an intense band at 242 cm^{-1} was assigned to $\nu(\text{Ag-S})$ in the surface enhanced Raman spectrum (at -1.0 V versus SCE) of thiourea adsorbed on electrochemically roughened silver electrode [1]. In another study, a broad, weak band at 185 cm^{-1} in the surface enhanced Raman spectrum (at -1.4 V versus SCE) of thiourea adsorbed on silver electrode was assigned to $\nu(\text{Ag-S})$ [3]. The Raman spectrum of $\text{Ag}(\text{Tu})_2\text{NO}_3$ exhibited an intense, single band at 1055 cm^{-1} in the crystalline state and at 1046 cm^{-1} in solution. The frequency of this band, due to $\nu_3(\text{NO}_3^-)$ for an ionic nitrate, is essentially the same as that at 1052 cm^{-1} observed in the Raman spectrum of crystalline $\text{Ag}(\text{Tu})_3\text{NO}_3$ [1]. Meanwhile, a sharp band at 818 cm^{-1} in the IR spectrum of $\text{Ag}(\text{Tu})_2\text{NO}_3$ is also consistent with the presence of ionic nitrate.

Finally, the ^1H NMR spectrum of $\text{Ag}(\text{Tu})_2\text{NO}_3$ in DMSO-d_6 shows a single peak at $\delta=7.90\text{ ppm}$, downfield from that at $\delta=7.18\text{ ppm}$ for uncoordinated thiourea. This downfield shift for the NH_2 group in coordinated thiourea is comparable to that at 7.80 ppm found for the ionic gold(I) complex

$\text{Au}(\text{Tu})(\text{PET}_3)^+\text{Cl}^-$, containing terminally coordinated thiourea via the sulfur atom [8].

Supplemental material

Complete vibrational data are available from the authors on request.

Acknowledgement

This work was supported by a Bowling Green State University FRC grant.

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