Notes

Infrared and Raman Spectra of Some Bis(thiocyanato)cuprate(I) and Bis(thiocyanato)aurate(I) Complexes

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The complexes $[\mathrm{AsPh_4}][\mathrm{M(SCN)_2}]$, $[\mathrm{N(PPh_3)_2}][\mathrm{M(SCN)_2}]$ (M = $\mathrm{Cu^I}$ or $\mathrm{Au^I}$), and $[\mathrm{NBu_4}][\mathrm{Au(SCN)_2}]$ have been prepared and studied by i.r. and Raman spectroscopy. The vibrational spectra indicate that the copper compounds do not contain discrete $[\mathrm{Cu(SCN)_2}]^-$ ions, although these are probably present in solutions of the above copper complexes, and in NaSCN–CuSCN solutions. The copper n.q.r. frequencies of $[\mathrm{N(PPh_3)_2}][\mathrm{Cu(SCN)_2}]$ lie in the region expected for digonal or trigonal co-ordination of copper. The vibrational spectra of the gold compounds indicate discrete $[\mathrm{Au(SCN)_2}]^-$ ions. The vibrational frequencies of $[\mathrm{Au(SCN)_2}]^-$ are very similar to those of the isoelectronic $\mathrm{Hg(SCN)_2}$ molecule.

In the course of our vibrational spectroscopic studies of halogeno- and thiolato-metallate(I) complexes of the Group 1B metals [1–5] we have noted that the corresponding thiocyanato-complexes have been studied to only a limited extent. Most of the published data concern the silver(I)–thiocyanate system. In one recent study of this system in a number of different solvents, Gans *et al.*[6] found i.r. and Raman evidence in the ν(CN) region for species such as $[\mathrm{Ag_2(SCN)}]^+$, AgSCN, $[\mathrm{Ag(SCN)_2}]^-$, and $[\mathrm{Ag_2(SCN)_3}]^-$. The wavenumbers for the $[\mathrm{Ag(SCN)_2}]^-$ ion in solution are 2 086 (i.r.) and 2 093 $\mathrm{cm^{-1}}$ (Raman). The crystal structure of $[\mathrm{NH_4}][\mathrm{Ag(SCN)_2}]$ has been determined, and has been described as containing AgSCN molecules, $\mathrm{NH_4}^+$ ions, and SCN^- ions.[7] The i.r. spectrum of this compound shows ν(CN) bands at 2 120 and 2 090 $\mathrm{cm^{-1}}$ and ν(CS) bands at 738 and 722 $\mathrm{cm^{-1}}$, and the presence of two bands for each mode has been attributed to the presence of two kinds of thiocyanate group in the complex.[8] Ellestad *et al.*[9] prepared $[\mathrm{NMe_4}][\mathrm{Ag(SCN)_2}]$ and studied its vibrational spectra. Mutual exclusion between the i.r. and Raman spectra was observed, and it was postulated that this compound contains centrosymmetric $[\mathrm{Ag(SCN)_2}]^-$ ions (C_{2h} or $D_{\infty h}$ symmetry).

No corresponding studies of thiocyanatocuprates(I) appear to have been reported to date, although i.r. studies of solutions of CuSCN in molten tetra-n-propylammonium thiocyanate have led to the postulate that bridged polymeric species $[\mathrm{Cu_2(SCN)_6}]^{4-}$ and $[\{\mathrm{Cu(SCN)_2}\}_n]^{n-}$ are present in these solutions.[10] No vibrational spectra have been reported for thiocyanatoaurates(I), although the salts $\mathrm{K}[\mathrm{Au(SCN)_2}]$ and $[\mathrm{NH_4}][\mathrm{Au(SCN)_2}]$ have been known for a long time.[11,12]

In the present work we have prepared several bis(thiocyanato)metallates of the type [cation]$[\mathrm{M(SCN)_2}]$ [cation = $\mathrm{AsPh_4}^+$ or $\mathrm{N(PPh_3)_2}^+$, M = Cu or Au; cation = $\mathrm{NBu_4}^+$, M = Au] and have recorded their vibrational spectra in the solid state and in solution. In the case of $[\mathrm{N(PPh_3)_2}][\mathrm{Cu(SCN)_2}]$ the copper n.q.r. spectrum of the solid has also been measured. These studies allow further vibrational assignments to be made for the $\mathrm{M(SCN)_2}^-$ ions, and give some information about the structure of the ions in the solid state.

Experimental

Preparation of Compounds.—Copper(I) thiocyanate was prepared by a method similar to that for copper(I) chloride [13] by using sodium thiocyanate instead of sodium chloride. Silver(I) thiocyanate was obtained by precipitation from silver nitrate with sodium thiocyanate. Bis(triphenylphosphine)iminium chloride [14] and tetrabutylammonium dichloroaurate(I) and dibromoaurate(I) [3] were prepared by literature methods. Tetraphenylarsonium thiocyanate (m.p. 272—274 °C) and bis(triphenylphosphine)iminium thiocyanate (m.p. 191—194 °C) were prepared by adding aqueous solutions containing an excess of KSCN to an aqueous solution of the corresponding chloride.

Bis(triphenylphosphine)iminium dichlorocuprate(I), $[\mathrm{N(PPh_3)_2}][\mathrm{CuCl_2}]$ (m.p. 213—215 °C), was prepared by dissolving copper(I) chloride in a solution of $[\mathrm{N(PPh_3)_2}]\mathrm{Cl}$ in ethanol. Tetraphenylarsonium dichloroaurate(I), $[\mathrm{AsPh_4}][\mathrm{AuCl_2}]$ (m.p. 162—168 °C), and bis(triphenylphosphine)iminium dichloroaurate(I), $[\mathrm{N(PPh_3)_2}][\mathrm{AuCl_2}]$ (m.p. 185—192 °C), were prepared by adding tetrabutylammonium dichloroaurate(I) to a solution of $[\mathrm{AsPh_4}]\mathrm{Cl}$ or $[\mathrm{N(PPh_3)_2}]\mathrm{Cl}$ in ethanol.

Tetraphenylarsonium bis(thiocyanato)cuprate(I), $[\mathrm{AsPh_4}][\mathrm{Cu(SCN)_2}]$. Tetraphenylarsonium thiocyanate (0.59 g, 1.39 mmol) was added to deoxygenated acetonitrile (40 $\mathrm{cm^3}$) under nitrogen. When all the solid had dissolved, copper(I) thiocyanate (0.10 g, 0.85 mmol) was added. The solution was then heated and stirred under nitrogen for 10 h, to ensure complete dissolution of the CuSCN. The volume was reduced to 10 $\mathrm{cm^3}$, stirring and heating stopped, and the solution was allowed to cool overnight. The white crystalline solid which separated out was filtered off and dried *in vacuo*. Yield, 0.15 g (32.2%), m.p. 163—165 °C (Found: C, 55.9; H, 3.7; N, 4.9. Calc. for $\mathrm{C_{26}H_{20}AsCuN_2S_2}$: C, 55.5; H, 3.6; N, 5.0%).

Bis(triphenylphosphine)iminium bis(thiocyanato)cuprate(I), $[\mathrm{N(PPh_3)_2}][\mathrm{Cu(SCN)_2}]$. The salt $[\mathrm{N(PPh_3)_2}][\mathrm{CuCl_2}]$ (0.42 g, 0.64 mmol) was dissolved in absolute ethanol (15 $\mathrm{cm^3}$) and water (3 $\mathrm{cm^3}$) by gentle heating. Sodium thiocyanate (1.03 g, 12.8 mmol) was dissolved in absolute ethanol (25 $\mathrm{cm^3}$). On adding the $[\mathrm{N(PPh_3)_2}][\mathrm{CuCl_2}]$ solution to the sodium thiocyanate solution, a brown colouration developed. This solution was chilled in ice. The white rectangular crystals which separated out were filtered off and dried over silica gel. Yield = 0.31 g (69.7%), m.p. 165 °C (Found: C, 63.0; H, 4,2; N, 5.6. Calc. for $\mathrm{C_{38}H_{30}CuN_3P_2S_2}$: C, 63.5; H, 4.2; N, 5.8%).

Tetraphenylarsonium bis(thiocyanato)aurate(I), $[\mathrm{AsPh_4}][\mathrm{Au(SCN)_2}]$. Sodium thiocyanate (0.58 g, 7.10 mmol) was dissolved in absolute ethanol (10 $\mathrm{cm^3}$) and water (5 $\mathrm{cm^3}$) and added to a suspension of $[\mathrm{AsPh_4}][\mathrm{AuCl_2}]$ (0.23 g, 0.36 mmol) in absolute ethanol (10 cm^3). The suspension dissolved with stirring, and the clear solution which resulted was filtered. Water was added until a cloudy precipitate lingered and the solution was allowed to stand in a freezer at −40 °C. The white needles which formed were filtered off and dried over silica gel *in vacuo*. Yield = 0.17 g (69.4%), m.p. 99—102 °C (Found: C, 45.4; H, 3.1; N, 3.5; S, 9.1. Calc. for $C_{26}H_{20}AsAuN_2S_2$: C, 44.8; H, 2.9; N, 4.0; S, 9.2%).

Bis(triphenylphosphine)iminium bis(thiocyanato)aurate(I), $[N(PPh_3)_2][Au(SCN)_2]$. Sodium thiocyanate (0.71 g, 8.70 mmol), dissolved in absolute ethanol (10 cm^3) and water (5 cm^3), was added to a suspension of $[N(PPh_3)_2][AuCl_2]$ (0.35 g, 0.44 mmol) in absolute ethanol (40 cm^3). The solution was stirred with gentle heating, for 2 h. The resulting clear solution was filtered, water was added until a cloudy precipitate lingered, and the solution was placed in a freezer at −40 °C. The white crystalline needles which formed were filtered off and dried over silica gel *in vacuo*. Yield = 0.30 g (81.4%), m.p. 130—131 °C (Found: C, 53.9; H, 3.9; N, 5.2. Calc. for $C_{38}H_{30}AuN_3P_2S_2$: C, 53.6; H, 3.6; N, 4.9%).

Tetrabutylammonium bis(thiocyanato)aurate(I), $[NBu_4][Au(SCN)_2]$. Sodium thiocyanate (1.33 g, 16.4 mmol) was dissolved in absolute ethanol (15 cm^3) and to this was added a suspension of $[NBu_4][AuBr_2]$ (0.57 g, 1.05 mmol) in absolute ethanol (70 cm^3). Stirring was continued for 10 min. The resulting clear solution was filtered, dry diethyl ether (30 cm^3) was added, and a red oil formed. On evaporation and stirring a pinkish white solid formed. This was filtered off and dried *in vacuo*. The dark brown-red solid which formed on drying melted at 28—32 °C. Yield = 0.18 g (30.9%) (Found: C, 39.1; H, 6.5; N, 7.8. Calc. for $C_{18}H_{36}AuN_3S_2$: C, 38.9; H, 6.5; N, 7.6%).

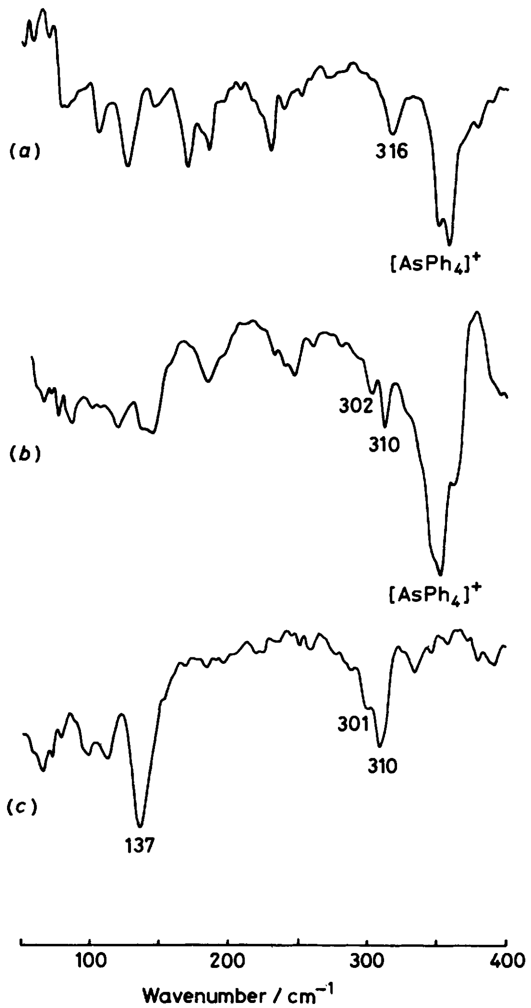

Figure 1. Far-i.r. spectra (at *ca.* 120 K) of (*a*) $[AsPh_4][Cu(SCN)_2]$, (*b*) $[AsPh_4][Au(SCN)_2]$, and (*c*) $[NBu_4][Au(SCN)_2]$

Microanalyses.—Microanalyses were carried out by Professor A. D. Campbell at the University of Otago, Dunedin.

Spectroscopy.—Infrared spectra in the range 400—4 000 cm^{-1} were obtained on a Perkin-Elmer 397 spectrometer as Nujol mulls between KBr plates, and were calibrated by using the spectrum of polystyrene. The far-i.r. spectra (50—400 cm^{-1}) were recorded on a Grubb-Parsons Cube Mk II interferometer fitted with a 6.25-μm Mylar-film beam splitter. They were run on petroleum jelly mulls between Polythene plates, and were calibrated by using the spectrum of water vapour. Far-i.r. spectra at *ca.* 125 K were recorded in a Grubb-Parsons GRM 01 low-temperature cell cooled with liquid nitrogen. Raman spectra were obtained on a Jasco R300 Raman spectrometer and were excited with a Control 540 argon-ion laser (488.0 nm line) or a Coherent CR4 argon-ion laser. The spectra of the solids were run on polycrystalline samples in glass capillary tubes; those of solution were run in glass cells.

N.q.r. spectra were obtained at the University of Tasmania on a Wilks NQR-1A spectrometer, and the frequencies were measured with a Hewlett-Packard model 5345A frequency meter.

Results and Discussion

The i.r. and Raman bands which can be unambiguously assigned to the anions are given in the Table, and representative spectra in the low-wavenumber region are shown in Figures 1 and 2.

The copper compounds show two well separated ν(CN) bands at about 2 105 and 2 080 cm^{-1} in both the i.r. and Raman spectra. On dissolution of these compounds in chloroform or acetonitrile, the higher-wavenumber band in the i.r. spectrum disappears and a single strong band is observed at 2 080 cm^{-1}. This is near the wavenumber 2 086 cm^{-1} assigned to the $[Ag(SCN)_2]^-$ ion in solution,[6] and it seems reasonable to assign this band to the $[Cu(SCN)_2]^-$ ion in solution. The appearance of the extra band at 2 105 cm^{-1} in the solid

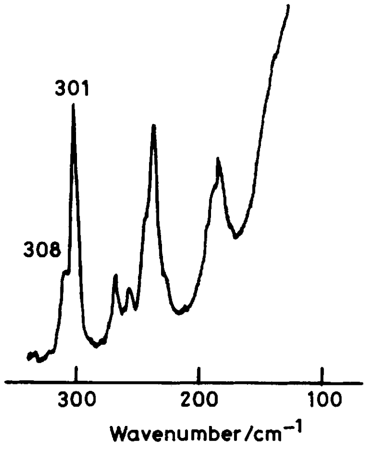

Figure 2. Raman spectrum of $[AsPh_4][Au(SCN)_2]$

Table. Vibrational bands (cm^{-1}) [a] assigned to the anions in some bis(thiocyanato)metallates(I), and related compounds

Compound	I.r.	Raman	Assignment
$[AsPh_4][Cu(SCN)_2]$	2 105s, 2 080s	2 111m, 2 084vs	ν(CN)
	812mw, 781w	814ms, 778w	ν(CS)
		470m, 457w	δ(SCN)
$[N(PPh_3)_2][Cu(SCN)_2]$	2 105ms, 2 084s	2 109ms, 2084s	ν(CN)
	821mw, 781w	820w, 781vw	ν(CS)
$[AsPh_4][Au(SCN)_2]$	2 122ms, 2 118s	2 118 (sh), 2 114s	ν(CN)
	310w, 302vw	308 (sh), 301s	ν(AuS)
	144w, 136 (sh)		δ(AuSC)
$[N(PPh_3)_2][Au(SCN)_2]$	2 125 (sh), 2 120s	2 118s	ν(CN)
	320m, 312mw	307m	ν(AuS)
	152w		δ(AuSC)
$[NBu_4][Au(SCN)_2]$	2 109vs, 2 082ms		ν(CN)
	691w		ν(CS)
	310m, 301 (sh)		ν(AuS)
	137s		δ(AuSC)
$Hg(SCN)_2$ [b]	2 110vs	2 112vs	ν(CN)
	720w	721s	ν(CS)
	461m, 430s	461m	δ(SCN)
	313s, 309m	270vs	ν(HgS)
		148w	δ(HgSC)
$[NBu_4][Au(SMe)_2]$ [c]	342	334	ν(AuS)
$Hg(SMe)_2$ [d]	337	297	ν(HgS)

[a] Spectra obtained on polycrystalline samples. w = weak; m = medium; s = strong; sh = shoulder. No Raman spectrum could be obtained for $[NBu_4][Au(SCN)_2]$ due to the colour of this compound and its instability in the laser beam. [b] Ref. 20. [c] Ref. 5. [d] A. J. Canty, R. Kishimoto, G. B. Deacon, and G. J. Farquharson, *Inorg. Chim. Acta*, 1976, **20**, 161.

suggests that discrete $[Cu(SCN)_2]^-$ ions are not present in the solid. The situation is similar to that observed in $[NH_4][Ag(SCN)_2]$, which shows two ν(CN) i.r. bands at 2 120 and 2 090 cm^{-1} in the solid,[8] but only one at about 2 086 cm^{-1} in solution.[6]

Bands at about 780 and 820 cm^{-1} in the solid copper complexes are assigned to the ν(CS) modes, and these are above the range 690—760 cm^{-1} generally found for *S*-bonded thiocyanate.[15]

The salt $[N(PPh_3)_2][Cu(SCN)_2]$ gives a single strong ^{63}Cu ν($\frac{1}{2}\leftrightarrow\frac{3}{2}$) n.q.r. signal at 34.86 MHz at 301 K (the corresponding ^{65}Cu signal was observed at 32.26 MHz). This compares with the values 30.05 and 30.2 MHz found for digonally co-ordinated $[CuCl_2]^-$ and $[CuBr_2]^-$,[1] and the value 33.47 MHz found for $K[Cu(CN)_2]$.[16] The latter compound has been shown to contain infinite polymeric anions with both bridging and terminal cyanide groups, and a distorted trigonal planar co-ordination environment for the copper.[17] Thus the copper n.q.r. frequencies lie in the region expected for digonal or trigonal co-ordination of copper.

The uncertainty concerning the existence or otherwise of discrete $[Cu(SCN)_2]^-$ ions in the solids studied here arises mainly from the lack of information about the vibrational spectrum of the free ion. This problem did not exist in the study of similar halogenocuprate(I) compounds [1] because the frequencies of the free ions in tributyl phosphate solution were available.[18] In an attempt to obtain such data for the thiocyanate system, the i.r. and Raman spectra of NaSCN–CuSCN solutions in tributyl phosphate were obtained. The NaSCN–AgSCN system was also studied for comparison purposes. A solution with [NaSCN]/[AgSCN] = 3.1 showed bands at 2 090 (i.r.) and 2 092 cm^{-1} (Raman) in addition to the band at 2 055 cm^{-1} due to uncomplexed thiocyanate. These values agree well with those found previously for $[Ag(SCN)_2]^-$ in other solvents.[6] A solution with [NaSCN]/[CuSCN] = 2.2 showed bands due to complexed thiocyanate at 2 085 (i.r.) and 2 090 cm^{-1} (Raman). No other bands which could not be attributed to the solvent were observed in the i.r. or Raman spectra of either system, even though the solutions were as concentrated as possible. Thus it was not possible to obtain more vibrational data for the solution species.

Since Au^I generally shows a greater tendency to linear two-co-ordination than Cu^I or Ag^I, it might be expected that the bis(thiocyanato)aurate(I) compounds would contain mononuclear $[Au(SCN)_2]^-$ ions, and this expectation appears to be borne out by the vibrational spectra. The $AsPh_4^+$ and $N(PPh_3)_2^+$ salts show two ν(CN) bands at about 2 120 cm^{-1} with a much smaller splitting (*ca.* 4 cm^{-1}) than that in the corresponding copper compounds (*ca.* 20 cm^{-1}). The NBu_4^+ salt shows a larger splitting in this region (*ca.* 25 cm^{-1}). Solutions of these salts in CH_2Cl_2 show a single strong i.r. band at 2 120 cm^{-1}. This lies in the region expected for *S*-bonded thiocyanate, and is attributed to $[Au(SCN)_2]^-$ ions in solution. The close proximity of the wavenumbers of the ν(CN) bands of the $AsPh_4^+$ and $N(PPh_3)_2^+$ salts in the solid state to the solution value suggests that the same ions are present in the solids. For an isolated ion of C_{2h} symmetry, single non-coincident ν(CN) bands are expected in the i.r. and Raman spectra. The i.r. and Raman bands are not exactly coincident, so the observed splittings are probably due to site-group or factor-group effects. The larger splitting in the NBu_4^+ salt suggests that a different structure might be involved in this case, but the lower-wavenumber vibrational spectra argue against this. None of the gold compounds exhibits bands in the 780—820 cm^{-1} region, where ν(CS) bands were observed for the copper compounds. A single ν(CS) band is observed at 691 cm^{-1} for the NBu_4^+ salt. This is at the lower limit of the range expected for *S*-bonded thiocyanate, but is well below the ranges for bridging or *N*-bonded thiocyanate.[15] A corresponding band is possibly present, but obscured by cation bands, for the $AsPh_4^+$ and $N(PPh_3)_2^+$ salts.

The clearest evidence that all three gold compounds contain the same anion comes from the far-i.r. and low-wavenumber Raman spectra (Figures 1 and 2). These show bands (usually doublets) in the 300—310 cm^{-1} region which can be assigned as ν(AuS) modes; ν(AuS) has previously been assigned in the

290—300 cm^{-1} region in some AuSCN complexes.[19] The assignments for $[Au(SCN)_2]^-$ can be compared with those for the isoelectronic $Hg(SCN)_2$ molecule [20] (Table). The wavenumbers of corresponding bands of the mercury and gold species are very similar, and this lends further support to the assignments made for the gold compounds. The ν(CS) bands at 720 cm^{-1} in solid $Hg(SCN)_2$ lie within the range expected for *S*-bonded thiocyanate, but are higher than the value 691 cm^{-1} found for $[Au(SCN)_2]^-$. However, on dissolution of $Hg(SCN)_2$ in diglyme (2,5,8-trioxanonane), ν(CS) moves to 692 cm^{-1},[20] which is almost exactly the same as the value found for $[Au(SCN)_2]^-$. Solid $Hg(SCN)_2$ is known to contain C_{2h} $Hg(SCN)_2$ molecules, but the mercury atoms are involved in weak interactions with the nitrogen atoms of four neighbouring molecules to produce a distorted octahedral environment about the mercury atom.[21] This weak bridging interaction of the thiocyanate groups is probably responsible for the higher ν(CS) frequency observed for the solid, and is probably not present in the $[Au(SCN)_2]^-$ compounds. Although the ν(MS) wavenumbers for $Hg(SCN)_2$ and $[Au(SCN)_2]^-$ are almost identical in the i.r., the Raman values differ significantly. In $Hg(SCN)_2$ mutual exclusion between the i.r. and Raman ν(HgS) vibrations is quite obvious, whereas the i.r. and Raman ν(AuS) bands are nearly coincident for $[Au(SCN)_2]^-$. We believe that this coincidence is accidental, as we have found a similar situation in comparing ν(MS) wavenumbers of $[Au(SMe)_2]^-$ and $Hg(SMe)_2$ (Table). However this coincidence clearly renders less certain any conclusions regarding the structure of the $[Au(SCN)_2]^-$ ion based on its vibrational spectra. The splitting of the ν(AuS) bands is similar in magnitude to the factor-group splitting of ν(HgS) in the solid-state i.r. spectrum of $Hg(SCN)_2$.[20] The assignment of bands in the 135—150 cm^{-1} region of the $[Au(SCN)_2]^-$ compounds to δ(AuSC) vibrations was made by analogy with the corresponding assignment for $Hg(SCN)_2$.[20]

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