Silver(I) Isocyanide Complexes: Spectroscopic Features and Reactions with Neutral Ligands

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The silver(I) isocyanide complexes $[Ag(CNR)_4]ClO_4$ (R = Me, cyclo-C_6H_{11}, or Bu^t) and $[Ag(CNC_6H_{11})_2]ClO_4$ have been prepared, their i.r., Raman, ^1H and ^{13}C n.m.r. spectra recorded, and assignments proposed. Particular emphasis has been placed on an assignment of the vibrational spectrum of $[Ag(CNMe)_4]ClO_4$. Some reactions of $[Ag(CNC_6H_{11})_2]ClO_4$ and $[Ag(CNBu^t)_4]ClO_4$ with neutral Group 5 donor ligands have been examined. Complete isocyanide displacement leads to the complexes $[AgL_4]ClO_4$ [L = PPh_3, $AsPh_3$, or $P(OMe)_3$]. The mixed-ligand complexes $[Ag(CNR)(bipy)]ClO_4$ (R = C_6H_{11} or Bu^t; bipy = 2,2′-bipyridyl), $[Ag(CNC_6H_{11})_2(py)]ClO_4$ (py = pyridine), and $[Ag(CNC_6H_{11})L_3]ClO_4$ [L_3 = $(Ph_2PCH_2)_3CMe$, L = $P(OMe)_3$] have also been prepared. The complexes involving nitrogen donors appear to contain three-co-ordinate silver(I) whereas those involving phosphorus donors contain four-co-ordinate silver(I).

It has been known since 1869 that alkyl isocyanides can be prepared by alkylation of silver cyanide,[1] both $AgX(CNR)$ (X = halide) and $Ag(CN)(CNR)$ being intermediates in these reactions. The cyano-complexes may also be formed by alkylation of $K[Ag(CN)_2]$ or by reaction of alkyl isocyanides with silver cyanide.

Direct reactions of silver salts with isocyanides are known to lead to $[Ag(CNC_6H_4Me\text{-}p)_4]NO_3{\cdot}H_2O$,[2] $[Ag(CNC_6H_4Me\text{-}p)_2]NO_3$,[2,3] $[Ag(CNC_6H_4Me\text{-}p)_4]ClO_4$,[3,4] $[Ag(CNCH_2SO_2C_6H_4Me\text{-}p)_2]BF_4$,[5] and polymeric $[AgCl(CNR)]_n$ (R = p-MeC_6H_4 or cyclo-C_6H_{11}).[6] Very recently some complexes involving very bulky isocyanides have been reported,[7] namely $[Ag(CNR)_2(PF_6)]$ (R = 2,4-Bu^t_2-6-MeC_6H_2, 2,4,6-$Bu^t_3C_6H_2$, or 2,6-$Me_2C_6H_3$) and $[Ag(CNR)_3(PF_6)]$ (R = 2,4-Bu^t_2-6-MeC_6H_2 or 2,6-$Me_2C_6H_3$). This work included the only report of an *X*-ray crystal structure determination of a silver isocyanide complex and, interestingly, $[Ag(CNC_6H_2Bu^t_3)_2(PF_6)]$ did not contain the expected linear $[Ag(CNC_6H_2Bu^t_3)_2]^+$ cation but rather a highly distorted tetrahedral species resulting from co-ordination of a bidentate PF_6 ligand.

Spectroscopic information on silver isocyanide complexes has been limited to i.r. ν(NC) frequencies [3,5-7] and ^1H n.m.r. data,[7] so we have prepared four new complexes and examined their i.r., Raman, ^1H and ^{13}C n.m.r. spectra. We were also aware that the only reactions of silver isocyanides reported to date [8] were those between $[AgCl(CNR)]_n$ and potassium hydroxide in alcohols R′OH leading to the trimeric $\{Ag[C(=NR)(OR')]\}_3$ species (R = p-MeC_6H_4, R′ = Me, Et, Pr^n, or Bu^n; R = C_6H_{11}, R′ = Me). We have therefore also examined the reactions of the isocyanide complexes with several neutral ligands. Some of these reactions lead to the complete displacement of the isocyanide ligands, others to the isolation of mixed-ligand complexes.

Experimental

All reactions were carried out in solvents deoxygenated prior to use by purging with nitrogen. Methyl isocyanide was prepared by a literature method,[9] other isocyanides and reagents being used as received from commercial sources.

Infrared spectra of Nujol and hexachlorobutadiene mulls were recorded on Perkin-Elmer 597 and 599B spectrophotometers. Far-i.r. spectra were obtained using a Beckman-R.I.I.C. FS720 interferometer with samples dispersed in pressed polyethylene discs. Raman spectra were obtained from samples sealed in capillary tubes using a Spex 1401 double monochromator in conjunction with either a Spectra-Physics 125 He–Ne laser or a Lexel 81 Ar^+ laser (514.5 nm line). A photomultiplier cooled to −15 °C and photon-counting detection were employed. The spectrometer was calibrated by reference to indene and emission bands of neon. A JEOL PS 100 spectrometer was used to obtain ^1H and ^{31}P n.m.r. spectra and a JEOL FX-90Q spectrometer for ^{13}C n.m.r. spectra.

Tetrakis(methyl isocyanide)silver(I) *Perchlorate*.—Silver perchlorate (0.13 g) was added to a stirred solution of methyl isocyanide (0.51 g) in ethanol (20 cm^3) and the reaction allowed to proceed for 3 h at room temperature. Evaporation left a colourless, crystalline solid which was collected by filtration, recrystallised from ethanol, washed with light petroleum, and vacuum dried. Yield 34% (Found: C, 25.2; H, 3.2; N, 14.9. Calc. for $C_8H_{12}AgClN_4O_4$: C, 25.9; H, 3.2; N, 15.1%).

Tetrakis(t-butyl isocyanide)silver(I) *Perchlorate*.—Silver perchlorate (0.50 g) and t-butyl isocyanide (1.64 cm^3) were added with stirring to ethanol (20 cm^3) and the mixture allowed to stand for 4 h at room temperature. After evaporation to low volume, light petroleum (b.p. 60—80 °C) was added to precipitate a colourless, crystalline, solid which was collected by filtration, washed with light petroleum, and vacuum dried. Yield 75% (Found: C, 44.3; H, 6.6; N, 10.1. Calc. for $C_{20}H_{36}AgClN_4O_4$: C, 44.5; H, 6.7; N, 10.4%). ν(NC): i.r. 2 188s, 2 172s, and 2 145w(sh); Raman 2 193s and 2 180(sh) cm^{-1}. Perchlorate: i.r., ν_3 at 1 085vs,br and ν_4 625vs; Raman, ν_1 at 930m, ν_2 at 458vw, ν_3 at 1 103vw, and ν_4 at 617w cm^{-1}.

Bis(cyclohexyl isocyanide)silver(I) *Perchlorate*.—Silver perchlorate (0.50 g) and cyclohexyl isocyanide (0.51 cm^3) were stirred together in ethanol (20 cm^3) for 3 h at room temperature. Evaporation of the ethanol left a viscous oil which afforded translucent waxy crystals after overnight refrigeration. These were collected, washed with light petroleum and diethyl ether, and vacuum dried. Yield 90% (Found: C, 38.2; H, 5.2; N, 6.5. Calc. for $C_{14}H_{22}AgClN_2O_4$: C, 39.5; H, 5.2; N, 6.6%). ν(NC): i.r., 2 215s and 2 190vs; Raman, 2 232s cm^{-1}. Perchlorate: i.r., ν_3 at 1 075vs,br and ν_4 at 622vs; Raman, ν_1 at 929s, ν_2 at 464w, and ν_4 at 623w cm^{-1}.

Tetrakis(cyclohexyl isocyanide)silver(I) *Perchlorate*.—Silver perchlorate (0.40 g) was dissolved in the minimum volume of ethanol and cyclohexyl isocyanide (1.50 cm^3) added. The mixture was stirred for 1 h at room temperature before removing ethanol and excess of isocyanide by rotary evaporation. The resulting colourless solid was filtered off, washed with light petroleum, and vacuum dried. Yield 75% (Found: C, 51.5; H, 6.7; N, 8.4. Calc. for $C_{28}H_{44}AgClN_4O_4$: C, 52.2; H, 6.8; N, 8.7%). ν(NC): i.r., 2 182vs and 2 150(sh); Raman, 2 193s cm^{-1}. Perchlorate: i.r., ν_3 at 1 080vs,br and ν_4 at 621s; Raman, ν_1 at 928s cm^{-1}.

Reactions of Bis(cyclohexyl isocyanide)silver(I) *Perchlorate.*—(*a*) *With triphenylphosphine.* Various molar ratios of $[Ag(CNC_6H_{11})_2]ClO_4$ and triphenylphosphine (1 : 1 to 1 : 20) were allowed to react in dichloromethane for 6 h at room temperature. Removal of the solvent under reduced pressure left a colourless viscous oil which could be induced to crystallise on addition of ethanol with stirring. The colourless solid was filtered off, washed with ethanol and diethyl ether, and vacuum dried. Yields of $[Ag(PPh_3)_4]ClO_4$ varied from 36 to 61% depending on the molar ratios of the reactants (Found: C, 68.9; H, 4.9. Calc. for $C_{72}H_{60}AgClO_4P_4$: C, 68.8; H, 4.8%). I.r.: perchlorate, ν_3 at 1 085vs,br and ν_4 at 625vs cm^{-1}.

(*b*) *With triphenylarsine.* A solution of triphenylarsine (0.58 g) in the minimum volume of chloroform was added to a solution of $[Ag(CNC_6H_{11})_2]ClO_4$ (0.20 g) in ethanol (10 cm^3). The colourless solid that precipitated was filtered off, washed with ethanol and diethyl ether, and vacuum dried. Yield of $[Ag(AsPh_3)_4]ClO_4$, 64% (Found: C, 60.1; H, 4.2. Calc. for $C_{72}H_{60}AgAs_4ClO_4$: C, 60.3; H, 4.2%). I.r.: perchlorate, ν_3 at 1 085vs,br and ν_4 at 625vs cm^{-1}.

(*c*) *With* 2,2′-*bipyridyl.* 2,2′-Bipyridyl (0.146 g) was added to a solution of $[Ag(CNC_6H_{11})_2]ClO_4$ (0.20 g) in ethanol (10 cm^3) and the mixture stirred for 2 h at room temperature. Removal of the solvent left a very pale pink oil which was triturated with diethyl ether to remove any excess of 2,2′-bipyridyl (bipy). On refrigeration overnight the oil afforded a very pale pink solid which was recrystallised from chloroform. Yield of $[Ag(CNC_6H_{11})(bipy)]ClO_4$, 90% (Found: C, 43.6; H, 4.7; N, 8.7. Calc. for $C_{17}H_{19}AgClN_3O_4$: C, 43.2; H, 4.0; N, 8.9%). I.r.: ν(NC) at 2 252vs; perchlorate, ν_3 at 1 080vs,br and ν_4 at 623vs cm^{-1}.

(*d*) *With pyridine.* A mixture of $[Ag(CNC_6H_{11})_2]ClO_4$ (0.25 g) and pyridine (5.0 cm^3) was allowed to react overnight at room temperature. Removal of excess of pyridine under reduced pressure left a colourless viscous oil. Stirring the oil several times with diethyl ether served to remove the last traces of pyridine (py), but it could not be induced to crystallise. Yield of $[Ag(CNC_6H_{11})_2(py)]ClO_4$, 45% (Found: C, 45.2; H, 5.0; N, 8.1. Calc. for $C_{19}H_{27}AgClN_3O_4$: C, 45.2; H, 5.4; N, 8.3%). I.r.: ν(NC) at 2 195vs; perchlorate, ν_3 at 1 090vs,br and ν_4 at 625 vs cm^{-1}.

(*e*) *With* 1,1,1-*tris(diphenylphosphinomethyl)ethane* (*tppme*). A mixture of $[Ag(CNC_6H_{11})_2]ClO_4$ (0.40 g) and tppme (0.588 g) were stirred together in ethanol (20 cm^3) for 3 h at room temperature. Removal of ethanol under reduced pressure left a colourless viscous oil which rapidly afforded fluffy colourless crystals on stirring in diethyl ether. The product was filtered off, washed with diethyl ether, and vacuum dried. Yield of $[Ag(CNC_6H_{11})(tppme)]ClO_4$, 89% (Found: C, 62.7; H, 5.5. Calc. for $C_{48}H_{50}AgClNO_4P_3$: C, 61.2; H, 5.3%). I.r.: ν(NC) at 2 185vs; perchlorate, ν_3 at 1 080vs,br and ν_4 at 625vs cm^{-1}.

(*f*) *With trimethyl phosphite.* A solution of $[Ag(CNC_6H_{11})_2]ClO_4$ (0.40 g) in methanol or chloroform (15 cm^3) was treated with trimethyl phosphite (0.44 cm^3) for 3 h at room temperature. Removal of the solvent under reduced pressure left a colourless viscous oil which was stirred several times with light petroleum and diethyl ether. Although the oil solidified on cooling to *ca.* −60 °C, it always reformed on warming to room temperature. Yield of $[Ag(CNC_6H_{11})\{P(OMe)_3\}_3]ClO_4$, 62% (Found: C, 28.0; H, 5.5; N, 2.1. Calc. for $C_{16}H_{38}AgClNO_{13}P_3$: C, 27.9; H, 5.5; N, 2.0%). I.r.: ν(NC) at 2 188vs; perchlorate, ν_3 at 1 080vs,br and ν_4 at 627vs cm^{-1}.

Table 1. Proton n.m.r. data for the silver isocyanide complexes in $CDCl_3$ solution

Compound	δ/p.p.m., multiplicity, assignment, *J*/Hz
MeNC	2.72, t, CH_3, $J(^{14}N-^{1}H)$ 2.4
$[Ag(CNMe)_4]ClO_4$	3.38, t, CH_3, $J(^{14}N-^{1}H)$ 2.5
Bu^{t}NC	1.17, t, $C(CH_3)_3$, $J(^{14}N-^{1}H)$ 2.4
$[Ag(CNBu^t)_4]ClO_4$	1.59, s, $C(CH_3)_3$
$C_6H_{11}NC$	3.58, br m, $(CH_2)_5$ and CH
$[Ag(CNC_6H_{11})_2]ClO_4$	1.70, m, $(CH_2)_5$; 3.95, m, CH
$[Ag(CNC_6H_{11})_4]ClO_4$	1.70, m, $(CH_2)_5$; 3.87, m, CH
$[Ag(CNC_6H_{11})(bipy)]ClO_4$	1.70, m, $(CH_2)_5$; 4.00, m, CH; 7.4—8.9, m, bipy
$[Ag(CNBu^t)(bipy)]ClO_4$	1.60, s, $C(CH_3)_3$; 7.4—8.9, m, bipy
$[Ag(CNC_6H_{11})_2(py)]ClO_4$	1.70, m, $(CH_2)_5$; 4.00, m, CH; 7.3—8.7, m, py
$[Ag(CNC_6H_{11})(tppme)]ClO_4$	1.60, m, $(CH_2)_5$ and tppme CH_3; 2.48, s, tppme CH_2; 3.94, m, CH; 7.8, m, tppme C_6H_5
$[Ag(CNC_6H_{11})\{P(OMe)_3\}_3]ClO_4$	1.65, m, $(CH_2)_5$; 3.68, d, OCH_3, *J*(PH) 12; 4.00, m, CH
$[Ag\{P(OMe)_3\}_4]ClO_4$	3.68, d, OCH_3, *J*(PH) 12

Reactions of Tetrakis(t-butyl isocyanide)silver(I) *Perchlorate.*—(*a*) *With* 2,2′-*bipyridyl.* 2,2′-Bipyridyl (0.138 g) was added to a solution of $[Ag(CNBu^t)_4]ClO_4$ (0.159 g) in ethanol (10 cm^3) and the mixture stirred for 2 h at room temperature. Removal of the solvent under reduced pressure left a very pale pink viscous oil which on stirring with light petroleum afforded a very pale pink solid. This was filtered off, washed with light petroleum, recrystallised from chloroform, and vacuum dried. Yield of $[Ag(CNBu^t)(bipy)]ClO_4$, 87% (Found: C, 40.5; H, 3.8; N, 9.4. Calc. for $C_{15}H_{17}AgClN_3O_4$: C, 40.3; H, 3.8; N, 9.4%). I.r.: ν(NC) at 2 212vs; perchlorate, ν_3 at 1 075vs,br and ν_4 at 625vs cm^{-1}.

(*b*) *With trimethyl phosphite.* A mixture of $[Ag(CNBu^t)_4]ClO_4$ (0.40 g) and trimethyl phosphite (0.53 cm^3) was stirred in chloroform (15 cm^3) for 3 h at room temperature. Removal of the solvent left a colourless oil which on stirring with diethyl ether afforded flaky colourless crystals. These were filtered off, washed with diethyl ether, and vacuum dried. Yield of $[Ag\{P(OMe)_3\}_4]ClO_4$, 50% (Found: C, 20.3; H, 5.3. Calc. for $C_{12}H_{36}AgClO_{16}P_4$: C, 20.5; H, 5.1%). I.r.: perchlorate, ν_3 at 1 090vs,br and ν_4 at 625vs cm^{-1}.

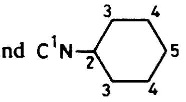
Results and Discussion

Four new silver(I) isocyanide complexes, $[Ag(CNC_6H_{11})_2]ClO_4$ and $[Ag(CNR)_4]ClO_4$ (R = Me, C_6H_{11}, or Bu^t), have been prepared by addition of isocyanide to silver perchlorate in ethanol, a method previously used[4] to prepare $[Ag(CNC_6H_4Me\text{-}p)_4]ClO_4$. Analytical data and i.r. and Raman ν(NC) and perchlorate band positions {apart from those of $[Ag(CNMe)_4]ClO_4$ which are discussed later} are given in the Experimental section. The ν(NC) frequencies lie in the range 2 150—2 250 cm^{-1} as expected for terminal isocyanide ligands[1,3] and the perchlorate frequencies are typical of the unco-ordinated anion.[10]

N.M.R. Spectroscopy.—The ^1H n.m.r. spectral data of the four complexes and of the free isocyanides are listed in Table 1. Whereas the free alkyl isocyanides display long-range $^{14}N-^{1}H$ coupling, metal isocyanide complexes do not normally show

Table 2. ^{13}C N.m.r. data for the silver isocyanide complexes in $CDCl_3$ solution

Compound [a]	δ/p.p.m., assignment, J/Hz
Bu^{t}NC	153.2, C^1, $J(^{14}N-^{13}C)$ 4.4; 54.1, C^2, $J(^{14}N-^{13}C)$ 5.0; 30.3, C^3
$[Ag(CNBu^t)_4]ClO_4$	138.3, C^1; 57.8, C^2; 30.0, C^3
$[Cu(CNBu^t)_4]BF_4$ [b]	137.7, C^1; 57.1, C^2; 29.4, C^3
$C_6H_{11}NC$	154.7, C^1, $J(^{14}N-^{13}C)$ 4.5; 51.7, C^2, $J(^{14}N-^{13}C)$ 5.8; 32.8, C^3; 22.8, C^4; 25.1, C^5
$[Ag(CNC_6H_{11})_2]ClO_4$	138.6, C^1; 54.2, C^2; 31.7, C^3; 22.6, C^4; 24.6, C^5
$[Ag(CNC_6H_{11})_4]ClO_4$	142.9, C^1; 53.5, C^2; 32.1, C^3; 22.8, C^4; 24.9, C^5

[a] Carbon atoms labelled $C^1NC^2(C^3H_3)_3$ and 

respectively.

[b] Data from ref. 16 (dimethyl sulphoxide solution).

this feature. However, such coupling has been observed for $[AuCl(CNBu^t)]$ (J *ca.* 1 Hz)[11] and $[Mo(CO)_5(CNBu^t)]$ (J = 2 Hz).[12] Only $[Ag(CNMe)_4]ClO_4$ of the silver complexes studied here retains detectable $^{14}N-^{1}H$ coupling (J = 2.5 Hz).

Whereas the unique proton of free cyclohexyl isocyanide is not separately identifiable, in $[Ag(CNC_6H_{11})_n]ClO_4$ (n = 2 and 4) the unique proton of each cyclohexyl group appears downfield of the methylene protons. In the silver complexes all protons, except the methylene cyclohexyl protons, are found downfield of their free-ligand positions, in agreement with increasing positive charge on the isocyanides with co-ordination.

The ^{13}C n.m.r. data for t-butyl and cyclohexyl isocyanides and their silver complexes are listed in Table 2. Isocyanides have posed problems for routine ^{13}C n.m.r. studies.[13,14] However, useful studies have been reported for some isocyanide-substituted metal carbonyls and Group 8 metal complexes,[15] and, particularly relevant to this work, for $[Cu(CNBu^t)_4]BF_4$.[16]

For the silver complexes, all expected ^{13}C resonances have been detected and assigned, including the very weak isocyanide carbon signals. The C^1NR and CNC^2 resonances, which appear as triplets in the free ligands because of $^{14}N-^{13}C$ coupling, are observed as broadened singlets in the complexes. The most significant feature of the spectra is an *upfield* shift of *ca.* 15 p.p.m. for the C^1NR resonance on co-ordination to silver, the chemical shift values for the carbons of $[Ag(CNBu^t)_4]^+$ being almost identical to those of $[Cu(CNBu^t)_4]^+$.[16] The increase in shielding of C^1NR with increasing metal size observed[15] in a series such as $[M(CO)_5(CNR)]$ (M = Cr, Mo, or W) obviously does not occur for copper(I) and silver(I).

It is also instructive to compare i.r. or Raman $[\nu(NC)_{complex} - \nu(NC)_{free\ ligand}]$ differences with ^{13}C n.m.r. $[\delta(C^1NR)_{complex} - \delta(C^1NR)_{free\ ligand}]$ differences for the silver complexes. For each of the three cations the increased ν(NC) frequencies on co-ordination are matched by upfield C^1NR n.m.r. co-ordination shifts. Further, the greatest ν(NC) increase {for $[Ag(CNC_6H_{11})_2]ClO_4$}, is paired with the greatest upfield C^1NR shift. An increase of ν(NC) on co-ordination must imply an increased NC bond order, presumably by strong C → Ag σ bonding with little or no Ag → C π-back bonding. The increased NC bond order has been rationalised by delocalisation of the nitrogen lone pair into the carbon p_z orbital. Should electron density on C^1NR be increased by co-ordination in this manner, the result will be a more shielded C^1 and so an upfield shift as observed.

Table 3. Vibrational spectra (cm^{-1}) of solid $[Ag(CNMe)_4]ClO_4$

Class	Description	Activity	I.r.	Raman
ClO_4^- Fundamentals (T_d)				
A_1	ν_1 ClO sym. str.	Raman		930s
E	ν_2 OClO deg. def.	Raman		455mw
T_2	ν_3 ClO deg. str.	I.r., Raman	1 085vs,br	1 118vw
T_2	ν_4 OClO deg. def.	I.r., Raman	623s	623mw
CH_3 Fundamentals (C_{3v})				
A_1	CH_3 sym. str.	I.r., Raman	2 960w	2 953s
A_1	CH_3 sym. bend	I.r., Raman	1 412w 1 400w	1 415m 1 402m
E	CH_3 asym. str.	I.r., Raman	3 020w	3 024w
E	CH_3 asym. bend	I.r., Raman	1 438mw	1 441vw
E	CH_3 rock	I.r., Raman	1 168w(sh)	
$Ag(CNC)_4$ Fundamentals (T_d)				
A_1	C≡N str.	Raman		2 224s, br
A_1	AgC str.	Raman		341vw
A_1	N–C str.	Raman		*
E	AgCN def.	Raman		303mw
E	CAgC def.	Raman		
E	CNMe bend	Raman		237w
T_2	C≡N str.	I.r., Raman	2 240(sh) 2 212vs	2 218(sh)
T_2	AgCN def.	I.r., Raman	313mw	
T_2	AgC str.	I.r., Raman	332m	334m
T_2	CAgC def.	I.r., Raman	150m,br	
T_2	CNMe bend	I.r., Raman	202m,br	
T_2	N–C str.	I.r., Raman	942m 932(sh) 925m	
T_1	AgCN def.	Inactive		
T_1	CNMe bend	Inactive		

* 909vw cm^{-1} or masked by the ν_1 perchlorate band.

Vibrational Spectroscopy.—Apart from the routine listing of ν(NC) frequencies there have been few reports[17–20] of vibrational spectroscopic studies for metal isocyanide complexes. The i.r. and Raman spectra of the silver(I) complexes prepared here have been examined. Most attention has been focused on $[Ag(CNMe)_4]ClO_4$ because of the relative simplicity of the spectra and the firmly established assignment of the vibrational spectrum of free methyl isocyanide.[21] Since it is known that in the cation of the analogous $[Cu(CNMe)_4]BF_4$ the copper is tetrahedrally co-ordinated by essentially linear methyl isocyanide ligands,[22] we have assumed that, to a first-approximation, the spectra can be regarded as arising from a combination of the vibrations of an isolated T_d ClO_4^- anion, a $[Ag(CNC)_4]^+$ skeleton with local T_d symmetry, and methyl groups with local C_{3v} symmetry. The T_d $[Ag(CNC)_4]^+$ skeleton will possess $3A_1 + 3E + 6T_2 + 2T_1$ normal modes, the A_1 and E modes being Raman-active, the T_2 modes i.r.- and Raman-active, and the T_1 modes inactive. The approximate descriptions of the normal modes and proposed band assignments are listed in Table 3.

Bands associated with the methyl stretching, bending, and rocking modes have been assigned by consideration of their frequencies in the vibrational spectrum of free methyl isocyanide.[21] The ν(N≡C) band assignments are based on the assumption that the A_1 mode will be higher in frequency than the T_2 mode and will give the more intense band in the Raman spectrum. A high-frequency shoulder in the i.r. spectrum points to the limitation inherent in considering the solid-state spectrum on the basis of a regular tetrahedral geometry. The T_2 ν(C–N) stretch appears in the i.r. spectrum as a split band (942, 925 cm^{-1}) but is masked by the intense ν_1 perchlorate band in the Raman spectrum. The Raman-active A_1 ν(C–N) stretch is either similarly hidden or could be assigned to a very weak band at 909 cm^{-1}.

Apart from the two perchlorate deformations, no bands have been detected in the i.r. and Raman spectra of $[Ag(CNMe)_4]ClO_4$ between 900 and 400 cm^{-1}. However, $[Mn(CNMe)_6]I$,[19,20] $[Co(CNMe)_5]ClO_4$,[18] $[Co_2(CNMe)_{10}][ClO_4]_4$,[18] and $[Mo(CNMe)_7][PF_6]_2$[23] all display often intense δ(MCN) deformations between 450 and 600 cm^{-1}. It would seem that the δ(AgCN) bands must be closely grouped with the ν(AgC) bands and appear below 400 cm^{-1}. Strong coupling will undoubtedly occur. A similar situation is known for other comparable d^{10} complexes, for example in $[Ni(CO)_4]$ all δ(NiCO) and ν(NiC) bands are found between 460 and 300 cm^{-1}.[24] It is also known that the δ(AgCN) bands of $[NMe_4][Ag(CN)_2]$ are found at 292 and 238 cm^{-1} with ν(AgC) at 389 and 350 cm^{-1}.[25] A number of medium-to-weak bands are observed in the i.r. and Raman spectra of $[Ag(CNMe)_4]ClO_4$ between 340 and 260 cm^{-1} and these are tentatively assigned to δ(AgCN) and ν(AgC) vibrations. The medium-intensity band in the i.r. at 332 cm^{-1} and the Raman at 334 cm^{-1} is assigned to the T_2 ν(AgC) stretch and the medium-weak i.r. band at 313 cm^{-1} to the T_2 δ(AgCN) degenerate deformation. These assignments could be reversed, but stretching modes are usually more intense in the Raman. Two weak Raman-active bands at 341 and 303 cm^{-1} may be assigned to the A_1 ν(AgC) and E δ(AgCN) modes.

There remains consideration of the δ(CNMe) and δ(CAgC) deformations. The δ(CNMe) bend is found at 288 cm^{-1} for the free isocyanide[21] and at 295 cm^{-1} for $[Mn(CNMe)_6]I$,[20] although other workers[19] assign δ(CNMe) bends to bands at 185 and 180 cm^{-1} for this complex. The expected frequency range for δ(CAgC) bends may be estimated from the knowledge that δ(CAgC) of $[Ag(CN)_2]^-$ is found[25] at 116 cm^{-1}. It seems reasonable to suggest that δ(CNMe) will be of higher frequency than δ(CAgC) for $[Ag(CNMe)_4]ClO_4$ and assignments for the T_2 modes are made accordingly. The increasing Rayleigh background prohibits the detection of more than one band in this region of the Raman spectrum, the weak band at 237 cm^{-1} being tentatively assigned to the E δ(CNMe) mode.

Although the i.r. and Raman spectra of $[Ag(CNBu^t)_4]ClO_4$ and $[Ag(CNC_6H_{11})_n]ClO_4$ (n = 2 and 4) have also been recorded, the presence of many alkyl bands makes assignments less assured. We therefore merely list the ν(NC) and perchlorate band positions in the Experimental section, noting that the i.r. and Raman ν(NC) bands appear some 30—40 cm^{-1} higher for $[Ag(CNC_6H_{11})_2]ClO_4$ than for $[Ag(CNC_6H_{11})_4]ClO_4$.

Reactions of $[Ag(CNC_6H_{11})_2]ClO_4$ *and* $[Ag(CNBu^t)_4]ClO_4$ *with Neutral Ligands.*—Apart from the synthesis[6,8] of trimeric $\{Ag[C(=NR)(OR')]\}_3$ (R = p-MeC_6H_4; R′ = Me, Et, Pr^n, or Bu^n; R = C_6H_{11}, R′ = Me) from $[AgCl(CNR)]_n$, no reactions of silver isocyanide complexes appear to have been reported. We have succeeded in isolating a number of mixed-ligand complexes containing isocyanide in combination with either nitrogen- or phosphorus-donor ligands from reactions of $[Ag(CNC_6H_{11})_2]ClO_4$ or $[Ag(CNBu^t)_4]ClO_4$ with neutral ligands. The major problem experienced was the formation of oils during work-up procedures. These oils could be induced to crystallise except for $[Ag(CNC_6H_{11})_2(py)]ClO_4$ and $[Ag(CNC_6H_{11})\{P(OMe)_3\}_3]ClO_4$. The products are not significantly air-, moisture-, or light-sensitive. Analytical and i.r. data are given in the Experimental section and ^{1}H n.m.r. data in Table 1. The i.r. spectra of all products show ν_3 and ν_4 perchlorate bands at *ca.* 1 080 and *ca.* 625 cm^{-1} respectively indicating[10] the presence of unco-ordinated perchlorate anions. Silver(I) assumes two-, three-, or four-co-ordination in many of its complexes and in the absence of definitive structural studies it seems that three-co-ordination is favoured for the complexes containing heterocyclic nitrogen donors, $[Ag(CNR)(bipy)]ClO_4$ (R = C_6H_{11} or Bu^t) and $[Ag(CNC_6H_{11})_2(py)]ClO_4$, whereas the complexes containing phosphorus donors, $[Ag(CNC_6H_{11})(tppme)]ClO_4$ and $[Ag(CNC_6H_{11})\{P(OMe)_3\}_3]ClO_4$, involve four-co-ordinate silver.

The only product isolated from reactions of $[Ag(CNC_6H_{11})_2]ClO_4$ and triphenylphosphine in molar ratios from 1 : 1 to 1 : 20 was the known[26] $[Ag(PPh_3)_4]ClO_4$. Attempts to identify intermediates retaining one or two isocyanide ligands were not successful. The analogous complex $[Ag(AsPh_3)_4]ClO_4$[27] arises from the reaction of $[Ag(CNC_6H_{11})_2]ClO_4$ with excess of triphenylarsine. Similarly, all four isocyanide ligands are displaced from $[Ag(CNBu^t)_4]ClO_4$ on the addition of trimethyl phosphite. The i.r. spectrum of this product showed bands characteristic of co-ordinated phosphite (strongest bands at 1 180, 780, 745, 520, 423, and 383 cm^{-1}) and the absence of a ν(NC) band. The ^{1}H n.m.r. spectrum of the product consists only of a doublet centred at δ 3.68 p.p.m. [J(PH) = 12 Hz], simplifying to a singlet on phosphorus decoupling. This information, taken with the analytical results, points to the formation of tetrahedral $[Ag\{P(OMe)_3\}_4]ClO_4$.

Reactions of $[Ag(CNC_6H_{11})_2]ClO_4$ and $[Ag(CNBu^t)_4]ClO_4$ with 2,2′-bipyridyl involve the loss of one and three isocyanide ligands respectively, the products being of the type $[Ag(CNR)(bipy)]ClO_4$ (R = C_6H_{11} or Bu^t) with probably three-co-ordinate cations. The ν(NC) bands are found *ca.* 40 cm^{-1} higher than for the $[Ag(CNR)_n]ClO_4$ reactants, following the trend mentioned previously of increasing ν(NC) as the number of isocyanide ligands decreases.

Reaction of $[Ag(CNC_6H_{11})_2]ClO_4$ with pyridine also produces a three-co-ordinate cation, but no isocyanide is displaced, the product being $[Ag(CNC_6H_{11})_2(py)]ClO_4$. A 20-cm^{-1} reduction in ν(NC) from that of $[Ag(CNC_6H_{11})_2]ClO_4$ probably reflects the increasing co-ordination number and hence enhanced electron density at the metal.

Two four-co-ordinate mixed-ligand complexes have also been isolated from reactions of $[Ag(CNC_6H_{11})_2]ClO_4$. One isocyanide ligand is displaced on reaction with tppme to give $[Ag(CNC_6H_{11})(tppme)]ClO_4$, the ν(NC) of which is 30 cm^{-1} *lower* than that of $[Ag(CNC_6H_{11})_2]ClO_4$. This lower frequency suggests a greater electron density at the metal after co-ordination of the three phosphorus-donor atoms. The ^{1}H n.m.r. spectrum provides evidence that all three phosphorus atoms are co-ordinated, the six methylene protons of the tppme ligand appearing as a singlet. The methyl protons are not found as a separate singlet but are hidden within the broad cyclohexyl-methylene proton multiplet, the composite signal integrating to the correct thirteen protons. Similarly, reaction of $[Ag(CNC_6H_{11})_2]ClO_4$ with trimethyl phosphite gives $[Ag(CNC_6H_{11})\{P(OMe)_3\}_3]ClO_4$ as an oil. The i.r. ν(NC) band is only 3 cm^{-1} different to that of the tppme complex and the bands of the co-ordinated trimethyl phosphite ligands match those of $[Ag\{P(OMe)_3\}_4]ClO_4$. The methyl-proton doublet in the ^{1}H n.m.r. spectrum at δ 3.68 p.p.m. [J(PH) = 12 Hz] gives a singlet on phosphorus decoupling. A proton-decoupled ^{31}P n.m.r. spectrum of the complex in $CDCl_3$ consists merely of a singlet at δ 132 p.p.m. relative to 85% phosphoric acid. Free trimethyl phosphite shows a proton-decoupled singlet at 139.5 p.p.m.

These mixed-ligand complexes of silver(I) are the first to contain isocyanide ligands. The co-ordination number acquired by silver(I) seems to depend on the particular ligand combination, the complexes providing a further illustration that silver(I) does not show a great desire to take up one particular co-ordination geometry.

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