

Silver Complexes with Nitrogen Donor Ligands—Co-ordination Number 2 and 3

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Linear two-coordinated silver (I) complexes having the formula $[AgL_2]ClO_4$, where L is 3-chloro, 3-bromo and 3-ethyl pyridine, 3,5-lutidine, 2- and 8-methyl quinoline are characterised. They are 1:1 electrolytes and contain ionic perchlorate group. Also, compounds having the formula $[AgL_2.NO_3]$, where L is 3-chloro and 4-cyano pyridine and 3,5-lutidine have been isolated. These are non-electrolytes and infra-red spectra indicate the presence of co-ordinated nitrate groups and thus exhibit a co-ordination number 3.

Univalent silver forms complexes where the co-ordination numbers exhibited are two¹, three^{2,3,4} and four^{4,5,6}. In case of complexes containing nitrate⁴, cyanide, cyanate and thiocyanate⁷ anions, it has been found that the anions also co-ordinate with metal ion increasing the co-ordination number of the metal, whereas perchlorate remains usually ionic⁴. It was therefore thought worthwhile to study the reactions of silver nitrate and silver perchlorate with several nitrogen donor ligands. In this communication, we report some two and three co-ordinated complexes of silver(I) with several substituted pyridines and quinolines.

EXPERIMENTAL

All chemicals used were of A.R. grade. The purity of the isolated compounds was established by estimating silver which is quite diagnostic to establish the correct composition. The conductance measurements were carried out using a Toshniwal conductivity bridge and a dip type cell. The infra-red absorption spectra were recorded on Nujol mulls using a Unicam SP-200 double beam spectrophotometer. The method of preparation and isolation of these compounds was similar to that reported by Patel and Rao⁸. All the compounds were insoluble in water but fairly soluble in alcohol and acetone. The analytical, conductance and relevant infra-red spectral data are recorded in Table 1.

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TABLE I

Analysis, melting point, conductance and infra-red spectral data of silver (I) complexes with nitrogen donor ligands

Compounds	% Silver		% Halogen		% Nitrogen		Melting point (°C)	Λ_M in acetone (mhos)	Nitrate/Perchlorate absorption bands (cm ⁻¹)
	Found	Reqd.	Found	Reqd.	Found	Reqd.			
[Ag(3-ClPy) ₂]NO ₃	26.87	27.30	16.78	17.02			112	18	1030w, 1036s, 1122m, 1298m
[Ag(3,5-lut) ₂]NO ₃	28.05	28.08			10.70	10.43	143	35	720m, 758vs, 829s, 1042m
[Ag(4-CNPy) ₂]NO ₃	28.78	28.53			18.67	18.50	201	28	1070s, 1205s, 1330s, 13355w
[Ag(3-ClPy) ₂]ClO ₄	24.23	24.82	15.45	15.62			152	143	1076br,
[Ag(3-BrPy) ₂]ClO ₄	20.12	20.62	30.80	30.56			176	148	1096br
[Ag(3-EtPy) ₂]ClO ₄	25.13	25.60					145	166	1081-1107br
[Ag(3,5-lut) ₂]ClO ₄	25.28	25.60			7.20	6.66	195	185	1076-1117br
[Ag(2-MeQ) ₂]ClO ₄	21.15	21.85					200	186	1076br.
[Ag(8-MeQ) ₂]ClO ₄	21.83	21.85					200	168	1095br.

s—sharp, vs—very sharp, m—medium, br—broad. w—weak.

RESULTS AND DISCUSSION

Univalent silver ion has a symmetrical, completely filled 4d¹⁰ non-bonding shell and causes least perturbation to any preferred stereochemistry of the complex. It makes use of sp, sp² and sp³ hybrid bonding orbitals to exhibit co-ordination numbers two, three and four respectively.

Nitrato Complexes: The nitrato complexes reported now have the composition [AgL₂.NO₃] where L is the ligand. They are highly soluble in organic solvents and insoluble in water. The molar conductance, Λ_M , values are low (18–35 mhos) indicating the non-electrolytic nature of the complexes. Hence it is evident that the nitrate group is not ionic but co-ordinated to the metal ion thus making it a three- or four- co-ordinated complex depending upon the unidentate or bidentate behaviour of the nitrate group. It is not always possible to precisely distinguish between mono- and bidentate coordinated nitrate groups on the basis of number or positions of the observed bands. The situation can be envisaged as follows :

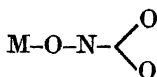


Fig. 1.

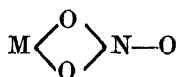


Fig. 2.

It has been pointed out⁹ that the bands in the region 1531–1481, 1290–1253, 1034–970 and 800–781 cm⁻¹ are indicative of unidentate nitrate group. Addison and Simpson reported¹⁰

10. C. C. Addison and W. B. Simpson, *J. Chem. Soc.*, 1965, 598.

the vibrational modes of uni- and bidentate nitrate groups and opined that in the case of a bidentate behaviour, the terminal N—O bond (Fig. 2) approaches a double bond and the N = O stretching frequency lies in the range 1600–1700 cm^{-1} . Whilst it may not be possible to distinguish from other absorption bands, the presence of this N = O stretching band above 1600 cm^{-1} is a definite indication for a bidentate behaviour. In the present investigation, no band above 1600 cm^{-1} is noticed and the absorption bands reported are near about the ranges for a unidentate nitrate group. In the case of $\text{Ag}(4\text{-CNPy})_2\text{NO}_3$ complex, the bands appear to fall much out of the frequency ranges indicated but Nyholm *et al*¹¹ concluded under similar situation the presence of co-ordinated nitrate groups. Hence the co-ordination number of metal ion is presumably three in these complexes. Kimball¹² suggested the trigonal plane, un-symmetrical plane and trigonal pyramid as the possible structures for a complex with co-ordination number three. The exact preferred arrangement can be ascertained only after detailed X-ray crystal structure determination.

Perchlorate Complexes : All the perchlorate complexes were found to be 1 : 1 electrolytes in acetone medium having the molar conductance values in the region 150–180 mhos. Hence an ionic formula may be written as $[\text{AgL}_2] \text{ClO}_4$, where L is the ligand. It is expected that ligands with lower polarisability and greater π -acceptor property favour the perchlorate co-ordination instead of leaving it in the usual ionic state. Even though the halopyridines have lower basicity than pyridines (pK_a values, for pyridine, 3-chloro- and 3-bromo-pyridines are 5.20, 2.80 and 2.84¹³ respectively) the complexes isolated contained only ionic perchlorates as indicated by the conductance measurements. Ionic perchlorate absorb in the region 1050–1170 cm^{-1} and a similar absorption band was observed near about 1100 cm^{-1} (Table I) in confirmation with the conductance results.

2-methyl quinoline and 8-methyl quinoline form complexes with silver perchlorate and it appears that the steric hindrance caused by the methyl groups in 2- and 8- positions is of less significance since the perchlorate complexes are linear molecules. Since co-ordination number 3 is favoured for nitrate complexes, this steric influence of the substituents assumes considerable importance and hence no compound could be isolated with silver nitrate.

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