677. *The Infrared Spectra and Structures of Some Silver–Ethylenediamine Complexes.*

By G. Newman and D. B. Powell.

The infrared spectra of a number of silver(I)–ethylenediamine complexes have been determined in the region 4000—400 cm.$^{-1}$. Possible structures for these compounds are discussed.

In a recent paper some long-chain polymeric complexes of zinc, cadmium, and mercury(II) with ethylenediamine, were examined.[1] Since silver ion tends to favour linear co-ordination it also might be expected to form similar complexes. However, an investigation of the silver–ethylenediamine system proved more difficult, particularly because of the instability of the complexes in the presence of water.

Few references to silver–ethylenediamine compounds are in the literature. Schwarzenbach *et al.*[2] showed the existence in solution of the complexes AgH en^{2+}, Ag en^{+}, Ag$_2$ en^{2+}, Ag en^{2+}, and, surprisingly, Ag$_2$ en$_2$$^{2+}$. Harris [3] earlier prepared (AgCl)$_2$en, and Schwarzenbach prepared Ag$_2$ en$_2$$^{2+}$ as the sulphate and used cryoscopic measurements to prove that his product was the dimer and not [Ag en]$_2$SO$_4$.

A series of silver complexes has been prepared in the course of the present investigation and their infrared spectra have been obtained (see Table). The results are discussed separately for the individual complexes.

Infrared frequencies (cm.$^{-1}$).

	Hg enCl$_2$	(AgCl)$_2$ en	[Ag en]$_2$PtCl$_4$	[Ag$_2$ en$_2$]Cl$_2$
		3266vs	3380vs	3260s
	3191vs	3238vs	3250vs	3169s
	3125vs	3042s	3151s	2930m
	2949m	2946ms	2946m	2923m
	2892m	2883ms	2888m	2863m
δNH$_2$ scissors	1610ms	1582ms	1590m	1593s
δCH$_2$ scissors	1490m	1469m	1468m	1448s
			1458w	
δCH$_2$ wag	1374?w	1373s	1387w	1388m
				1374m
			1367w	1352m
δNH$_2$ wag	1351m	1319ms	1321m	1319m
				1214w
				1204w
δCH$_2$ twist	1278vw	1278vw	1285vw	1188m
		1154vw	1153vw	
δNH$_2$ twist	1180vs	1084ms	1083vs	1093m
			1055w	1037vs
$\nu_{\text{asym.}}$ C–N	1007vs	1011ms	1014vs	1003vs
			986sh	
			969w	965vs
δCH$_2$ rock	820vw			851m
				840w
				835w
				617w
δNH$_2$ rock	683m	614s	627s	589m
				522m
				475?w
				460?w
	503wm	447m		
		419w		

Complex A, (AgCl)$_2$en.—It might be expected from the formula that this complex contains ethylenediamine as a bridging group between two silver(I) ions and the infrared

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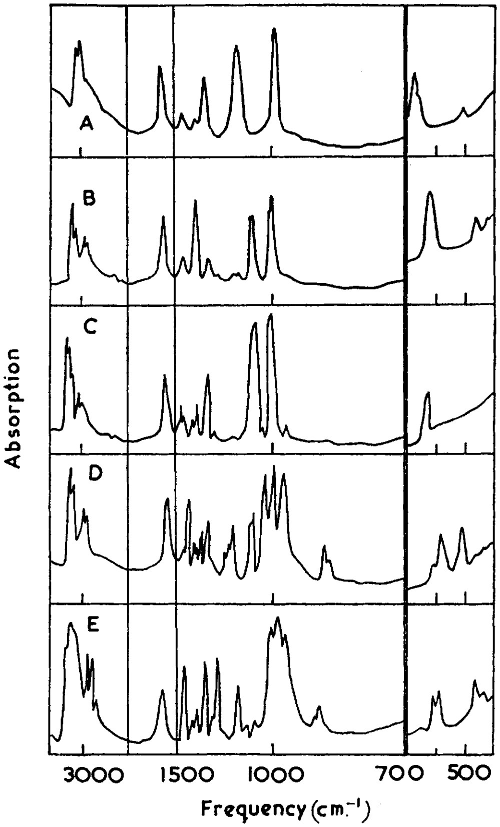
[1] Newman and Powell, *J.*, 1961, 477.

[2] Schwarzenbach, Ackerman, Maissen, and Anderegg, *Helv. Chim. Acta*, 1952, **35**, 2337.

[3] Harris, *J. Proc. Roy. Soc. New South Wales*, 1952, **85**, 142.

spectrum confirms this. The spectrum is extremely simple (see Figure) and similar to that of dichloroethylenediaminemercury(II), when account is taken of the expected frequency shifts. The *trans*-bridging polymeric structure of dichloroethylenediaminemercury(II) has been proved by the *X*-ray crystallographic measurements of Brodersen,[4] and confirmed by infrared spectroscopy.[4] If the bridging group were in the *cis*-form, more absorption peaks would have been expected in the spectrum. By comparison with the mercury complex it is suggested that the two strongest bands are $\nu_{\text{asym.}}$ (C–N) 1011 and δ (NH_2) 1084 cm.$^{-1}$.



Infrared spectra of (A) Hg enCl_2, (B) $(AgCl)_2$-en, (C) [Ag en]$_2$$PtCl_4$, (D) [$Ag_2$ en$_2$]Cl_2, and (E) [Zn en$_2$]Cl_2.

Complex B, [Ag en]$_2$$PtCl_4$.—This complex is obtained (*a*) when the solution formed from an excess of the diamine and alcoholic silver nitrate is treated with aqueous potassium tetrachloroplatinate, (*b*) when silver sulphate and the diamine give the salt [Ag_2 en$_2$]SO_4 and this is treated with aqueous potassium tetrachloroplatinate, or (*c*) by treating an excess of the diamine with silver chloride, thus obtaining a salt [Ag_2 en$_2$]Cl_2 which with water gives an insoluble blue product, the filtrate from which with potassium tetrachloroplatinate solution affords the complex as above.

This complex, as the tetrachloroplatinate(II), is surprisingly stable. Its infrared spectrum (see Figure) is simple and similar to that obtained for $(AgCl)_2$en and dichloroethylenediaminemercury(II) except for a few additional weak peaks. The two very strong peaks appear at 1083 and 1014 cm.$^{-1}$ and can be assigned to δ(NH_2) and ν(C–N), respectively. This fact, together with the simplicity in the potassium bromide region, where only one absorption peak is found, indicates that the ligand is in the *trans*(or only slightly perturbed *trans*)-configuration.

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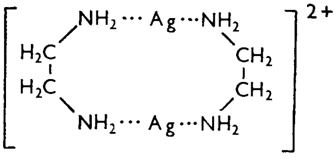
[4] Brodersen, *Z. anorg. Chem.*, 1959, **298**, 142.

If the molecular formula of the compound is the same as its empirical formula, then the complex could be $[Ag\,en]_2PtCl_4$ or the dimeric species $[Ag_2\,en_2]PtCl_4$. Molecular-weight determinations could not be carried out because of the insolubility of the compound. Schwarzenbach postulated that the sulphate $[Ag_2\,en_2]SO_4$ had the structure (I),



(I)

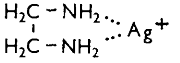
which requires the ligand to have a gauche configuration, even if the simple double-bridge structure is proposed. However, the more silver(I) atoms that are introduced into the ring, the closer the ethylenediamine molecule could approach to a *trans*-configuration. A more probable structure for the compound would seem to be a long-chain polymer with the *trans*-bridging ethylenediamine group, as found in dichloroethylenediaminemercury(II), $Ag^+{-}[NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2{\cdot}Ag^+]_n{-}$.

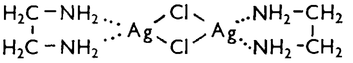
Complex C, $[Ag_2en_2]Cl_2$.—When an excess of ethylenediamine is added to silver chloride a product having empirical formula Ag enCl can be isolated. No other product could be isolated when further ligand was added to the solution or to Ag en Cl (after isolation). Thus no evidence was found of the four-co-ordinate ion $Ag\,en_2^+$. The molecular weight of compound *C* could not be determined because of its instability in water and insolubility in other solvents.

The infrared spectrum is shown in the Figure. It is quite complex, containing many more peaks than are in that of $(AgCl)_2en$. Consequently the infrared evidence points to a *cis*- or gauche configuration of the ethylenediamine group. Three strong absorption peaks are found near 1000 cm.$^{-1}$, as compared with two peaks found in the spectrum of dichloroethylenediaminemercury(II). The spectrum is characteristic of that expected from a complex having the ligand in the gauche configuration. In particular, the doublet found near 840 cm.$^{-1}$ is typical of many of the chelated ethylenediamine complexes examined by Powell and Sheppard.[5] The spectrum as a whole shows a marked similarity to that of bisethylenediaminezinc chloride (see Figure). Thus in considering possible structures one must envisage a simple chelate or a cyclic complex.

If the molecular formula of the compound is Ag enCl the only possible structure consistent with the spectroscopic evidence is (II). This, however, is unlikely since, as many authors have pointed out, ethylenediamine is unable to form a chelate complex with the silver atom and still retain the linear co-ordination.[6]

(II)





(III)

It seems much more probable that the compound is dimeric, possibly (I) or (III). Both the structures could account for the decomposition in water to form the *trans*-bridging complex $[Ag\,en]_2^{2+}$. Structure (I) retains a co-ordination number of two and is similar to that postulated by Schwarzenbach for $[Ag_2en_2]SO_4$. Structure (III) has four-co-ordinate silver, which is known in chelated complexes, although no indication of the $Ag\,en_2^+$ species has yet been found. Of the two structures the gauche double-bridging structure (I) seems the more probable.

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[5] Powell and Sheppard, *J.*, 1961, 1112.

[6] Schwarzenbach, *Helv. Chim. Acta*, 1953, **36**, 23; Irving, Williams, Ferrett, and Williams, *J.*, 1954, 3500; Bailar, Symposium on Inorganic Polymers, Nottingham, July, 1961.

EXPERIMENTAL

Anhydrous ethylenediamine was dehydrated immediately before use, as described by Putnam and Kobe.[7]

Complex A, $(AgCl)_2en$.—This was prepared by Harris's method. However, an excess of silver chloride was essential to avoid formation of mixtures. Silver chloride was ground for some time in ethylenediamine. Then the clear viscous liquid was filtered from the excess of silver chloride and poured into absolute alcohol, affording a white precipitate. The complex was filtered off, washed with alcohol and ether, and dried *in vacuo* (P_2O_5). It is sensitive to light and decomposes in water (Found: C, 6·8; H, 2·4. Calc. for $C_2H_8Ag_2Cl_2N_2$: C, 6·9; H, 2·3%).

Complex B, $[Ag_2en_2]Cl_2$.—This was prepared in analogous manner to $(AgCl)_2en$, but with an excess of ethylenediamine such that after stirring all the silver chloride dissolved. The white *complex* is light-sensitive and decomposed by water (Found: C, 11·7; H, 4·0. $C_4H_{16}Ag_2Cl_2N_4$ requires C, 11·8; H, 3·9%).

Complex C, $[Ag\ en]_2PtCl_4$.—(*a*) The chloride $[Ag_2en_2]Cl_2$ was dissolved in water. A highly unstable residue remained, which became blue almost immediately. To the filtrate a solution of potassium tetrachloroplatinate(II) was added until precipitation was complete. The pink powder was washed with water, alcohol, and ether and dried *in vacuo* (P_2O_5).

(*b*) The sulphate $[Ag_2en_2]SO_4$[2] was dissolved in water and a solution of potassium tetrachloroplatinate(II) added. The pink precipitate was treated as in (*a*).

(*c*) Ethylenediamine was added to alcoholic silver nitrate. A white precipitate was formed but more ethylenediamine was added until it just redissolved. A solution of potassium tetrachloroplatinate(II) was then added, precipitating the *complex* (Found: C, 7·2; H, 2·5. $C_4H_{16}Ag_2Cl_4N_4Pt$ requires C, 7·1; H, 2·4%). An excess of ethylenediamine must be avoided to prevent mixed products. The *complex* is extremely stable and may be kept in a vacuum-desiccator in daylight for several days.

Spectra.—Frequency measurements were made from spectra obtained with a Hilger H.800 spectrophotometer with rock-salt and potassium bromide optics. However, the Figures are taken from similar spectra obtained with the Perkin–Elmer Infracord instrument in the rock-salt region. The samples were examined as dispersions in liquid paraffin or hexachlorobutadiene.

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[7] Putnam and Kobe, *Inorg. Synth.*, Vol. II, p. 197.