367. *The Infrared Spectra and Structures of Some Complexes of 1,4-Diselenan*

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A range of inorganic co-ordination complexes of 1,4-diselenan have been prepared. Their infrared spectra have been studied over the frequency range 1750—200 cm.$^{-1}$. Conclusions regarding their structures have been drawn from the infrared and other evidence.

The infrared spectra and structures of a range of complexes containing heterocyclic ligands of the type YC_4H_8X, where $X = Y$ and $O = S$, and $X = Y = O$, S, NH, and NMe, have been discussed previously.[1] Four types of structure are generally found in these compounds: (*a*) long chains of metal ions linked by ligand molecules in the chair configuration, *e.g.*, the 1,4 dioxan complex of mercuric chloride, $HgCl_2(C_4H_8O_2)$; (*b*) complexes containing these ligands again in the chair form, but monoco-ordinated to a metal halide, *e.g.*, $AlCl_3(C_4H_8O_2)$; (*c*) "bridging" complexes, an example of which is $HgCl_2,C_4H_8(NMe)_2,HgCl_2$, in which the di-*N*-methyl piperazine molecule is again in the chair form; and (*d*) chelate structures containing the ligand in the boat form, *e.g.*, $PdCl_2,C_4H_8(NMe)_2$.[2]

Two complexes of 1,4-diselenan (in which $X = Y =$ Se in the formula above) have been previously reported by Gould and Burlant[3] as having the formulæ $PdCl_2(C_4H_8Se_2)$ and $(CdCl_2)_2C_4H_8Se_2$. Owing to the apparent similarity of these compounds and those discussed in the first reference, it was considered that these compounds might be of interest, particularly as 1,4-dithian and 1,4-dioxan gives no complexes of general formula $(MX_2)_2L$ (where $X =$ halogen, $L =$ligand molecule).

A number of complexes of 1,4-diselenan, many of which have not been previously reported, were prepared. They fall into two groups. Two compounds have the general formula $(Mhal_2)_2C_4H_8Se_2$, where $Mhal_2$ represents $HgCl_2$ and $CdCl_2$, whilst the remainder have the formula $Mhal_n(C_4H_8Se_2)$, where $Mhal_n$ represents $PdCl_2$, $PdBr_2$, $PtCl_2$, $AuCl_3$, $AuBr_3$, $CuCl_2$, $CuBr_2$, and CuCl. A complex containing silver nitrate has been prepared,

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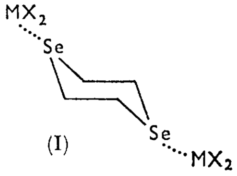
[1] Hendra and Powell, *J.*, 1960, 5105.

[2] Hassel and Pedersen, *Proc. Chem. Soc.*, 1959, 394.

[3] Gould and Burlant, *J. Amer. Chem. Soc.*, 1956, **78**, 5825.

and is of the second type. The infrared spectra of the ligand and co-ordination compounds were recorded over the range 1750—200 cm.$^{-1}$; the frequencies (in cm.$^{-1}$) are listed in the Table.



(I)

The spectra of the ligand and of the complexes of the first type [$(\mathrm{Mhal}_2)_2\mathrm{C}_4\mathrm{H}_8\mathrm{Se}_2$] are very similar at frequencies above 350 cm.$^{-1}$. The ligand has been shown to have the centrosymmetric chair configuration both in the free state[4] and when co-ordinated to iodine.[5] Thus, by analogy with complexes of dioxan,[1,6] it would appear that these complexes contain diselenan molecules in the same configuration. We therefore suggest a bridging structure (I) for these compounds.

The complex of cuprous chloride and also that of silver nitrate (apart from bands due to the nitrate ion) again give spectra closely resembling that of the free ligand. Thus, in an analogous manner to the highly insoluble complexes of 1,4-dithian, whose infrared spectra were similar to that of the ligand, we suggest that polymeric chains of alternate 1,4-diselenan molecules, in the chair configuration, and metal ions are found in these

Infrared spectra of 1,4-diselenan and some of its complexes

$C_4H_8Se_2$	$(HgCl_2)_2C_4H_8Se_2$	$(HgBr_2)_2C_4H_8Se_2$	$(CdCl_2)_2C_4H_8Se_2$	$CuCl(C_4H_8Se_2)$	$AgNO_3(C_4H_8Se_2)$
1408s	1408vs	1395vs	1410w	1416wsh	1406vs
1400wsh				1404vs	
				1390ssh	
1260ssh	1258vs	1258wsh	1264vs	1278wsh	1195wsh
1258s	1248wsh	1245vs	1258wsh	1258vs	1175s
1250ssh					
1135vw	1106w	1126w	1120vs	1118w	1064s
1108s		1095w	1028vw	1112w	1044vw
996vw	1000vw	998w	—	1005vw	—
858vs	865vs	845ssh	860vwsh	860vs	864s
850ssh	844wsh	834vs	838vs	850vs	850s
				840ssh	
574s	564w	565w	562w	566w	575w
400vw	—	—	—	405vw	410vw
	310s	—	—	—	—
	230w, b	250vw	250ssh	—	—
			236s, b		

$CuCl_2(C_4H_8Se_2)$	$CuBr_2(C_4H_8Se_2)$	$PtCl_2(C_4H_8Se_2)$	$PdCl_2(C_4H_8Se_2)$	$PdBr_2(C_4H_8Se_2)$	$AuCl_3(C_4H_8Se_2)$
1424vw	1420w	1408s	1404s	1404s	1408s
1404vw	1412vw				
1390vw	1400vw				
1252s	1255s	1244w	1245w	1240w	1266s
1245wsh	1240s	1222vw			
1124w	1135vw	1165w	1138s	1160w	1112s
1090vw	1124w	1098w	1125s	1120s	1090w
	1035vw		1088w	1086w	882vw
997vw	995				
854s	848w				857vs
840s	828w				840vs
764vw	760w	753s	750w	750w	775w
750vw		736s			736w
		657w	655vw	655wsh	575vs
				645w	
564s	580sh	533vw	526vw	525vw	540w
	564w				
	530w				
330vs		324vs	318s	268s	348s
		314vs	303s	253s, b	330vs
280s, b		234vw	244vw	244wsh	306s

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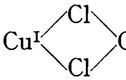
[4] Marsh and McCollough, *J. Amer. Chem. Soc.*, 1951, **73**, 1106.

[5] McCollough, Chao, and Zuccaro, *Acta Cryst.*, 1959, **12**, 815.

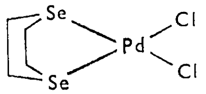
[6] Tarte and Laurent, *Bull. Soc. chim. France*, 1957, 403.

compounds. The absence of bands below 300 cm.$^{-1}$ in the cuprous chloride complex may be due to: (*a*) the possibility of formation of  $Cu^I\langle{}^{Cl}_{Cl}\rangle Cu^I$ bridges alternating with bridging pairs of 1,4-diselenan molecules. The halogen group may well absorb at frequencies below 220 cm.$^{-1}$, since ν_{Cu-Cl} (terminal) will occur at higher frequencies than $\nu_{Cu-Cl-Cu}$; or (*b*) an ionic structure in which the copper atoms are linked by 1,4-diselenan molecules.

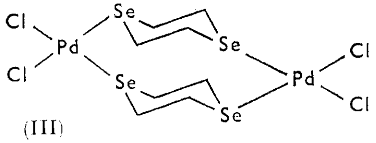
Above 350 cm.$^{-1}$, the spectra of the two cupric halide complexes show very similar characteristics to those of the complexes discussed above, thus suggesting that these compounds have similar structures to those of the copper(I) and silver(I) complexes. Below 350 cm.$^{-1}$, the spectrum of the cupric chloride complex closely resembles that given by Adams *et al.*[7] for crystalline anhydrous cupric chloride. The analogous bromide complex did not show any definite bands, even when the compound was examined in the spectral range 250—150 cm.$^{-1}$; thus, it is difficult to decide on the structure of this compound. It is suggested, therefore, that the cupric chloride–diselenan complex consists of infinite chains of $CuCl_2$ and diselenan molecule in the " chair " configuration. Different possible structures containing these features can be devised, but, unfortunately, it is impossible to distinguish between them by use of infrared spectroscopy.

The infrared spectra of the complexes of palladium(II) and platinum(II) are similar, but differ markedly from those reported above. The differences are particularly noticeable in the region 800—600 cm.$^{-1}$, where the skeletal modes of vibration in the ligand molecule are expected to be of primary importance. It would therefore appear that the ligand exists in some form other than the centrosymmetric chair.

Thus, a polymeric structure similar to that suggested for the silver nitrate complex, or one inolving mono-co-ordinated diselenan molecules, seems unlikely. The palladium(II) complex, $PdCl_2(C_4H_8Se_2)$, was found to be very slightly soluble in warm water, giving a pale yellow solution. Treatment of this solution with silver nitrate did not give an immediate precipitate of silver chloride. The complex was recrystallised from hot water, and analysed as $PdCl_2(C_4H_8Se_2)$. Unfortunately, the solubility of the complex is too low to permit a molecular-weight determination. It therefore seems reasonable to suggest two alternative structures, (II) and (III), for these complexes.



(II)



(III)

Structure (II) might well show the chemical properties given above, but the presence of the cyclic ligand in the boat configuration is unlikely, since the very large size of the hetero-atoms would cause a large degree of steric strain. Structure (III) would have similar chemical properties to (II), and would be expected to exhibit a considerably perturbed infrared spectrum of the ligand (in the chair form), owing to the close proximity of the two rings. The infrared spectum of a ligand molecule in the boat configuration would be considerably more complex than that in the chair form, owing to loss of symmetry. The appearance of doublets in the metal–halogen " stretching " region for these compounds, with a peak-to-peak separation of approximately 15 cm.$^{-1}$, suggests the presence of *cis*-dihalogen groups. This property has been previously observed by Coates and Parkin,[8] and also by Adams *et al.*,[9] for complexes of the type PtX_2Y_2, where X is a halogen and Y a ligand containing phosphorus, sulphur, or selenium. For a structure involving a bridging

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[7] Adams, Goldstein, and Mooney, *Trans. Faraday Soc.*, 1963, **59**, 2228.
[8] Coates and Parkin, *J.*, 1963, 421.
[9] Adams, Chatt, Geratt, and Westland, *J.*, 1964, 734.

and a terminal chlorine atom, a separation between the two bands of about 50 cm.$^{-1}$ is expected.

The formula and the similarity between the infrared spectra of the gold(III) complex and the ligand lead to the suggestion, assuming four-co-ordination, of a monomeric structure, in which mono-co-ordinated diselenan molecules in the " chair " configuration are involved. This suggestion is, however, open to considerable suspicion, as the loss of symmetry in the diselenan molecule would probably cause splitting of many of the infrared bands of the ligand. This effect is observed in some 1,4-dioxan complexes.[1]

Thus, in conclusion, it is suggested that the complexes of 1,4-diselenan exhibit a wider range of structures than has been found, to date, for the related ligands 1,4-dioxan and 1,4-dithian.

EXPERIMENTAL

The infrared spectra were obtained with a Hilger H800 spectrometer equipped with rock-salt and cæsium-iodide optics. Some of the complexes were examined over the range 250—150 cm.$^{-1}$ on a vacuum grating far-infrared spectrometer, to be described elsewhere. Samples were examined as dispersions in liquid paraffin and hexachlorobutadiene. Diselenan was investigated in solution and as a mull. Chemical analysis were carried out for carbon and hydrogen.

1,4-*Diselenan*.—This was prepared from aluminium selenide and ethylene dibromide by the method of Gould and Burlant.[3] The complexes were prepared by adding a strong ethanolic solution of the ligand to a solution of the metal halide in a suitable solvent.

Palladium(II) *and Platinum*(II) *Complexes*.—The addition of a hot ethanolic solution of 1,4-diselenan to a warm aqueous solution of the respective tetra-halide gave rise to a crystalline precipitate in a few seconds. This was separated and washed with ethanol. The palladium(II) chloro-compound was bright yellow (Found: C, 13·3; H, 2·3. Calc. for $C_4H_8Cl_2PdSe_2$: C, 12·3; H, 2·2%). The compound was recrystallised from hot water (Found: C, 12·2; H, 2·2%). The *bromo-compound* was orange-yellow (Found: C, 10·2; H, 1·8. $C_4H_8Br_2PdSe_2$ requires C, 10·0; H, 1·7%). The *platinum*(II) *chloro-compound* crystallised as a pale yellow powder (Found: C, 10·1; H, 1·7. $C_4H_8Cl_2PtSe_2$ requires C, 10·0; H, 1·7%).

Cadmium and Mercury Complexes.—By the addition of a warm alcoholic solution of the respective halide to a warm alcoholic solution of 1,4-diselenan, a white micro-crystalline precipitate of the cadmium or *mercury complex* was immediately formed (Found: C, 8·6; H, 1·5. Calc. for $C_4H_8Cd_2Cl_4Se_2$: C, 8·3; H, 1·4%) (Found: C, 6·6; H, 1·0. $C_4H_8Cl_4Hg_2Se_2$ requires C, 6·3; H, 1·0%).

Gold(III) *Complexes of* 1,4-*Diselenan*.—These were prepared by the addition of a warm alcoholic solution of tetrachlorauric(III) acid and potassium tetrabromoaurate(III) to a warm ethanolic solution of 1,4-diselenan. The *chloro-compound* was pale yellow (Found: C, 9·3; H, 1·7. $C_4H_8AuCl_3Se_2$ requires C, 9·3; H, 1·4%). The *bromo-compound* was deep brown (Found: C, 7·4; H, 1·4. $C_4H_8AuBr_3Se_2$ requires C, 7·4; H, 1·4%).

Copper(II) *Chloride and Bromide Complexes*.—These were prepared by mixing a hot ethanolic solution of the respective anhydrous halide with a hot solution of 1,4-diselenan. The *copper*(II) *chloride complex* crystallised as dark violet crystals (Found: C, 13·8; H, 2·3. $C_4H_8Cl_2CuSe_2$ requires C, 13·8; H, 2·3%). The bromo-compound was a brown powder (Found: C, 10·4; H, 1·7. $C_4H_8Br_2CuSe_2$ requires C, 10·9; H, 1·8%).

Copper(I) *Chloride*–1,4-*Diselenan Complex*.—A hot solution of copper(I) chloride in ethanol acidified with a few drops of hydrochloric acid was added to a hot ethanolic solution of 1,4-diselenan. A white microcrystalline *powder* formed within a few seconds (Found: C, 14·8; H, 2·4. $C_4H_8ClCuSe_2$ requires C, 15·3; H, 2·5%).

Silver Nitrate–1,4-*Diselenan Complex*.—A hot solution of silver nitrate in ethanol and water was mixed with a hot ethanolic solution of 1,4-diselenan, a white powdery *precipitate* being formed (Found: C, 8·7; H, 1·6. $C_4H_8AgNO_3Se_2$ requires C, 8·7; H, 1·5%).

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