999. *The Sulphur and Selenium Co-ordinate Link: Five-co-ordination in Complexes of Bivalent Palladium and Platinum*

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The molar conductivities of the complexes $(chel)_2Pd(NO_3)_2$ and $(chel)_2Pt(NO_3)_2$, where chel = $PhS{\cdot}C_3H_6{\cdot}SPh$ or $PhSe{\cdot}C_3H_6{\cdot}SePh$, were examined in non-aqueous solvents. The compounds exhibited ion-association, thus implying a co-ordination number of at least five, which was most pronounced in nitromethane solution. The relative behaviour of the two metals when bonded to sulphur and selenium, respectively, is discussed in terms of π-bonding contributions of the metal to the chelate donor atoms. Far-infrared spectra supported the conclusion that platinum forms a weaker π-bond with selenium than with sulphur, while the reverse is true for palladium.

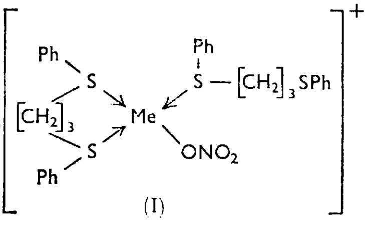
BIVALENT palladium and platinum may exhibit a co-ordination number of five in non-aqueous media, provided that certain types of ligand are present.[1-5] In particular, 2,2′-bipyridyl[4] and tertiary arsines or phosphines are effective in promoting a co-ordination number of five in compounds such as $[(Dias)_2PdCl]NO_3$. The varying extent of five-co-ordination amongst different compounds was explained as being due to variations in π-contribution to the metal–ligand bonds.[5] To justify this opinion further, the present Paper describes an investigation of compounds in which the ligand was either $PhS{\cdot}C_3H_6{\cdot}SPh$ or $PhSe{\cdot}C_3H_6{\cdot}Se{\cdot}Ph$, referred to as " disulphide " and " diselenide," respectively.

It was initially intended to prepare compounds L_2PtX_2 (where X = Cl, Br, or I), but it was found impossible because of the ease with which halide ions replaced one of the ligand molecules. However, it was possible to prepare nitrates and the nitrate ion showed sufficient association with the metal atoms to provide some interesting comparisons with the complexes containing Group V donor atoms.

Ion association was studied by carrying out conductivity measurements over a range of concentrations in nitromethane, *NN*-dimethylformamide, and methanol. In certain cases, a dissociation of the following kind takes place,

$$L_2M^{2+} = 2NO_3^- \rightleftharpoons LM(NO_3)_2 + L$$

In the conductivity measurements, varying excesses of ligand were added, in order to establish whether such an equilibrium obtained, and to permit measurement of the conductivity of the undecomposed compound by driving the equilibrium almost totally to the left-hand side. The conductometric titration of $[Pt(Ph_2S_2C_3H_6)_2]$ with tetramethyl ammonium nitrate in nitromethane verified that one mole of nitrate reacts with one mole of complex (Figure 1). The appearance of an end-point at the appropriate point in the above titration may simply indicate the formation of (I). However, the ligands concerned are



(I)

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[1] C. M. Harris and R. S. Nyholm, *J.*, 1956, 4375.
[2] C. M. Harris, R. S. Nyholm, and D. J. Phillips, *J.*, 1960, 4379.
[3] J. A. Brewster, C. A. Savage, and L. M. Venanzi, *J.*, 1961, 3699.
[4] S. E. Livingstone and B. Wheelahan, *Austral. J. Chem.*, 1964, **17**, 219.
[5] A. D. Westland, *J.*, 1965, 3060.

held so weakly that chelation is probably necessary for their retention. Furthermore, there was no relationship between complex stability and the tendency for a nitrate ion to be associated with the cation.

Conductivity measurements on methanol solutions of dithioether complexes similar to ours were carried out by Chugaeff and Kobljansky,[6] but with a view to examining the dependence of chelate stability upon ring size. Apparently, five-co-ordination was not recognised, although these authors noted that their complexes behaved as weak electrolytes. Livingstone has examined palladium[7] and platinum[8] complexes of the ligand dimethyl-*o*-methylthiophenylarsine and has found that these exist as five-co-ordinate complexes in nitrobenzene. He concluded that the ligand does not promote five-co-ordination to as great an extent as does *o*-phenylenebisdimethylarsine, but this conclusion was apparently based upon the fact that the complexes $(chel)_2PdX_2$ show a strong tendency to decompose to $(chel)PdX_2$ + chel rather than upon a comparison of the equilibria

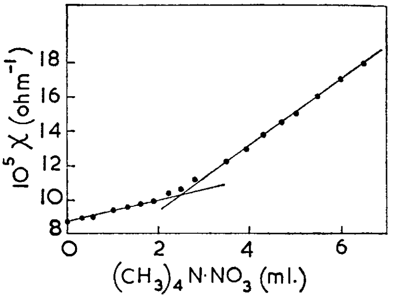

FIGURE 1. Conductometric titration of $(Ph_2S_2C_3H_6)_2Pt(ClO_4)_2$ (5×10^{-4}M; 25 c.c.) with $[(CH_3)_4N]NO_3$ (5×10^{-3}M) in nitromethane

$$(dias)_2Pd^{2+} + X^- \rightleftharpoons (dias)_2PdX^+$$

and

$$(C_6H_4AsSMe_3)_2Pd^{2+} + X^- \rightleftharpoons (C_6H_4AsSMe_3)_2PdX^+$$

We expected that the greater electronegativity of sulphur compared to that of phosphorus would enhance ion association in sulphur complexes by increasing the positive charge on the central atom. However, it seemed less certain how the association would be affected by the replacement of sulphur by selenium or tellurium. It was found[5] that the heavier Group V atoms had a greater tendency to promote ion association, possibly because of greater back-donation from the central atom. There appears to be no information in the literature about the relative π-acceptor ability of the chalcogens.

We hoped to include an organic ditelluride amongst the ligands used, but an attempt to prepare $PhTe{\cdot}C_3H_6{\cdot}TePh$ by reaction of NaTePh with 1,3-dibromopropane was unsuccessful.

The nitrate salts were prepared in two stages. One chelating ligand was added to an alkali chloro-salt of bivalent palladium or platinum and a Magnus type of salt was obtained. When these salts were heated, the complexes $LPdCl_2$ and $LPtCl_2$ were obtained which, when treated with a second mole of ligand in the presence of two moles of silver nitrate, gave solutions of the desired nitrate salts. The perchlorates were prepared by adding a little perchloric acid to solutions of the appropriate nitrates.

RESULTS AND DISCUSSION

The molar conductivities of the nitrate and perchlorate salts at $c = 5 \times 10^{-4}$M in dimethylformamide, methanol, and nitromethane are listed in Table 1. The figures in the columns headed " moles excess of ligand " indicate the number of moles of excess of ligand

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[6] L. A. Chugaeff and A. G. Kobljansky, *Z. anorg. Chem.*, 1913, **83**, 8, 159.
[7] S. E. Livingstone, *J.*, 1958, 4222.
[8] B. Chiswell and S. E. Livingstone, *J.*, 1960, 1071.

added per mole of complex in order to provide a limiting maximum conductance by shifting equilibria such as

$$(chel)_2Pd^{2+} + 2NO_3^- \rightleftharpoons (chel)Pd(NO_3)_2 + chel$$

In one case, that of $(PhS{\cdot}C_3H_6{\cdot}SPh)_2Pd(NO_3)_2$ in nitrobenzene, the equilibrium lay so far to the right that a limiting conductance value could not be obtained. The occurrence of such equilibria was established by (*a*) noting the dependence of conductivity upon concentration of excess of ligand (Figure 2 shows such a case), and (*b*) observing a levelling or even a decrease in conductance upon dilution to sufficiently low concentrations. In the absence of such an equilibrium, the expected behaviour upon dilution of an electrolyte exhibiting marked ion-association is as shown in Figure 3 for $(PhS{\cdot}C_3H_6{\cdot}SPh)_2Pt(NO_3)_2$. The pronounced curvature of the plots is independent evidence of five-co-ordination at higher concentrations to give systems which behave essentially as strong 1 : 1 electrolytes.

TABLE 1

Conductivities of complex metal nitrates and perchlorates (ohm^{-1} mole^{-1}) at $c = 5 \times 10^{-4}$M

	Dimethylformamide		Methanol		Nitromethane	
Compound	μ	Moles excess of ligand	μ	Moles excess of ligand	μ	Moles excess of ligand
$(PhSC_3H_6SPh)_2Pd(NO_3)_2$ (I)	135	18	173	0	65	125
$(PhSC_3H_6SPh)_2Pd(ClO_4)_2$ (II)	148	0	Insol.	—	169	41
$(PhSeC_3H_6SePh)_2Pd(NO_3)_2$ (III)	130	12	136	0	109	28
$(PhSeC_3H_6SePh)_2Pd(ClO_4)_2$ (IV)	135	0	Insol.	—	163	0
$(PhSC_3H_6SPh)_2Pt(NO_3)_2$ (V)	125	5	130	0	73	0
$(PhSC_3H_6SPh)_2Pt(ClO_4)_2$ (VI)	144	0	Insol.	—	166	81
$(PhSeC_3H_6SePh)_2Pt(NO_3)_2$ (VII) ...	138	0	169	44	108	70
$(PhSeC_3H_6SePh)_2Pt(ClO_4)_2$ (VIII) ...	144	0	Insol.	—	181	22

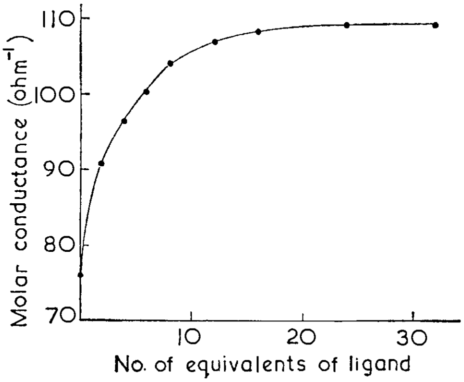

FIGURE 2. Molar conductance of $(Ph_2Se_2C_3H_6)Pd(NO_3)_2$ (5×10^{-4}M) as a function of concentration of excess of $Ph_2Se_2C_3H_6$ in nitromethane

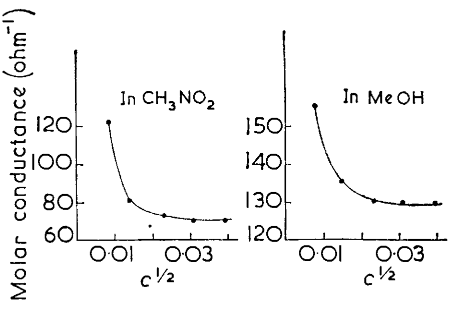

FIGURE 3. Molar conductance of $(Ph_2S_2C_3H_6)Pt(NO_3)_2$ as a function of (concentration)$^{1/2}$

The equilibria involving loss of one of the chelating ligands are of interest in themselves. The figures given in the columns headed " Moles excess of ligand " provide semi-quantitative measures of the stabilities of the complexes, zero representing a complex which is undecomposed. Platinum–sulphur complexes are more stable than palladium–sulphur complexes, while the reverse is true for the selenium analogues in methanol and nitromethane. The stabilities of the selenium complexes in the nitrate form are reversed in dimethylformamide.

The complexes are generally least stable in nitromethane; an exception is

$(PhS{\cdot}C_3H_6{\cdot}SPh)_2Pt(NO_3)_2$. The lower stability of the perchlorate salt must be attributed to a very low solvation energy of the perchlorate ion. Because of this, and of the relatively low stability of all the complexes, the perchlorate ion is able to expel a chelate ligand and co-ordinate to the metal atoms; this situation is practically unknown in solution.[9] Perchlorate co-ordination does not occur with our compounds in dimethylformamide.

The molar conductivities indicate an increase in ion-association when sulphur is replaced by selenium in the palladium complexes. This corresponds to the increase previously observed [5] when phosphorus was replaced by arsenic. Platinum compounds show the reverse effect, even though the organo-phosphine and -arsine complexes of both metals behaved alike. We conclude that either the platinum–sulphur or the platinum–selenium bond is anomalous. It appears that the anomaly is due to an abnormally weak π-bond from platinum to selenium. This conclusion is based on two observations. The first is the order of stability, *viz.*, $R_2S > R_2Te > R_2Se$, for complexes of the general types $(R_2M)_2PtCl_2$ and $[R_2MPtCl_2]_2$.[10] The general behaviour of the complexes seems to suggest that the platinum–selenium bond is unusually weak.

The metal–ligand stretching frequencies listed in Table 2 for the compounds *cis*-$(R_2M)_2PtCl_2$, provide the second reason. The donor ligand–metal grouping gives rise to two stretching modes. There is a much larger decrease in those frequencies when sulphur is replaced by selenium in the platinum complexes than there is in the corresponding palladium compounds. Further, in passing from platinum to mercury complexes there is a decrease in sulphur frequencies but an increase in selenium frequencies.

TABLE 2

Infrared spectra of complexes MX_2(chel) over the range 375—250 cm.$^{-1}$

Compound	M–chel stretching	M–X stretching	Other bands
$[(PhSC_2H_4SPh)PdCl_2]$	331vs 312vs	277vs	350sh
$[(PhSC_3H_6SPh)PdCl_2]$	323vs 308vs	278s 262s	347 sh 343w
$[(PhSC_3H_6SPh)PdBr_2]$	316s		349w 332sh 278w
$[(PhSeC_3H_6SePh)PdCl_2]$	314vs 296m	286s 274·5s	350w
$[(PhSeC_3H_6SePh)PdBr_2]$	314·5w 297s	255s	273w
$[(PhSC_3H_6SPh)PtCl_2]$	350s 329vs	317vs 312·5vs	
$[(PhSC_3H_6SPh)PtBr_2]$	349sh 324w	266·5m	
$[(PhSeC_3H_6SePh)PtCl_2]$	294vs 285s	320vs 314vs	
$[(PhSeC_3H_6SePh)PtBr_2]$	296s 283w	269w	350w 270w
$(PhSC_3H_6SPh),xHgCl_2$	323w 314vs	346vs	278w
$HgBr_2,x(PhSC_3H_6SPh)$	327·5w 314w	306w	283w
$HgCl_2,x(PhSeC_3H_6SePh)$	334sh 305vs	368m 350m	278w

It was argued [5] that, in the complexes L_4PdCl_2 and L_4PtCl_2, where L refers to a monodentate ligand or half of a bidentate ligand, the tendency towards ion-association is dependent upon the effective nuclear charge of the central atom, this increasing with increasing π-bonding ability in the series of donor atoms, P, As, Sb. If we apply the same reasoning to the complexes of palladium, we conclude that selenium forms a stronger π-bond than sulphur. With platinum the reverse is the case, again suggesting that the π-contribution to the platinum–selenium bond is abnormally slight.

Our view of relative π-bonding tendency is supported further by Jensen's values [11] of dipole moments for platinum complexes of type *cis*-$[L_2PtCl_2]$ where $L = Et_2S$, Et_2Se, Et_2Te. Assuming a contribution of 2D from each Pt–Cl bond [12] and platinum–ligand bond angles of 90°, we obtain the following group moments for Pt–L: Pt–SEt_2, 4·7D; Pt–$SeEt_2$, 4·4D; Pt–$TeEt_2$, 2·2D. A contrary trend would be expected on the basis of decrease in

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[9] J. Pluščec and A. D. Westland, *Chem. Comm.*, 1965, 69.

[10] J. Chatt and L. M. Venanzi, *J.*, 1955, 2787.

[11] K. A. Jensen, *Z. anorg. Chem.*, 1935, **225**, 97; 1937, **231**, 365.

[12] J. Chatt, J. D. Garforth, N. P. Johnson, and G. A. Rowe, Proc. 8th Internat. Conf. Co-ordination Chemistry, 1964, 204.

electronegativity of the donor atoms. Also, the increasing bond-length from left to right in the series should enhance the moment. A marked increase in back-bonding in going from sulphur to tellurium accounts for the group moments and, moreover, the relatively small difference between sulphur and selenium is in accord with the above reasoning. We have given evidence [13] for a parallel trend in π-bonding: $Cl < Br < I$, in the complexes py_2PtX_2. Thus, groups (V), (VI), and (VII) seem to behave alike in respect of π-bonding to palladium and platinum.

EXPERIMENTAL

Conductivity Measurements.—These were carried out at 25°C with an Industrial Instruments model RC16B2 a.c. bridge. Correction was made for solvent conductivity. Solvents were carefully dried.

Infrared Spectra.—Far infrared spectra were obtained with a Perkin-Elmer model 13G spectrometer fitted with a 30 micron grating and set for double-beam operation. Samples were mulled with Nujol and examined between cæsium iodide plates.

Preparation of Complexes.—All 1 : 1 addition complexes were prepared by a procedure of which the following is typical.

Dichloro-1,3-*di(phenylthio)propanepalladium*(II), $[\{C_3H_6(SPh)_2\}PdCl_2]$. Potassium chloropalladite (1·5 g.) was dissolved in 1 : 1 ethanol–water (150 c.c.) containing a few drops of 6N-hydrochloric acid and 1,3-di(phenylthio)propane (1·2 g., 1 mol.) added. The resultant mixture was shaken for 2 hr. The yellow precipitate, when collected and recrystallised from dimethylformamide, yielded a brownish-orange *compound* (1·8 g., 87%), m. p. 257—260° (Found: C, 41·15; H, 3·7; S, 14·95. $C_{15}H_{16}Cl_2PdS_2$ requires C, 41·15; H, 3·7; S, 14·65%). Other halogeno-compounds so prepared were as follows (the percentage yields are given in brackets following the formulæ).

Dibromo-1,3-*di(phenylthio)propanepalladium*(II), $[\{C_3H_6(SPh)_2\}PdBr_2]$ (82%) orange crystals, m. p. 242—243·5° (decomp.) (Found: C, 34·25; H, 3·2; S, 12·45. $C_{15}H_{16}Br_2PdS_2$ requires C, 34·21; H, 3·06; S, 12·18%).

Dichloro-1,3-*di(phenylseleno)propanepalladium*(II), $[\{C_3H_6(SePh)_2\}PdCl_2]$ (88%) orange-yellow crystals, m. p. 221° (darkened) melted 234° (Found: C, 33·6; H, 3·2. $C_{15}H_{16}Cl_2PdSe_2$ requires C, 33·9; H, 3·05%).

Dibromo-1,3-*di(phenylseleno)propanepalladium*(II), $[\{C_3H_6(SePh)_2\}PdBr_2]$ (84%) red crystals, m. p. 241·5—243° (decomp.) (Found: C, 29·1; H, 2·95. $C_{15}H_{16}Br_2PdSe_2$ requires C, 29·05; H, 2·6%).

Dichloro-1,3-*di(phenylthio)propaneplatinum*(II), $[\{C_3H_6(SPh)_2\}PtCl_2]$ (68%) yellow, microcrystalline, m. p. 282·5—285·5° (Found: C, 34·8; H, 3·05; S, 12·45. $C_{15}H_{16}Cl_2PtS_2$ requires C, 34·2; H, 3·05; S, 12·2%).

Dibromo-1,3-*di(phenylthio)propaneplatinum*(II), $[\{C_3H_6(SPh)_2\}PtBr_2]$ (58%) yellow, microcrystalline, m. p. 270—282° (Found: C, 29·5; H, 2·75; S, 10·6. $C_{15}H_{16}Br_2PtS_2$ requires C, 29·3; H, 2·6; S, 10·4%).

Dichloro-1,3-*di(phenylseleno)propaneplatinum*(II), $[\{C_3H_6(SePh)_2\}PtCl_2]$ (33%) yellow crystals, m. p. 231·5—235° (Found: C, 29·0; H, 2·9. $C_{15}H_{16}Cl_2PtSe_2$ requires C, 29·05; H, 2·6%).

Dibromo-1,3-*di(phenylseleno)propaneplatinum*(II), $[\{C_3H_6(SePh)_2\}PtBr_2]$ (32%) yellow-orange, microcrystalline, m. p. 245—248° (Found: C, 25·5; H, 2·3. $C_{15}H_{16}Br_2PtSe_2$ requires C, 25·4; H, 2·25%).

Bis-1,3-*di(phenylthio)propanepalladium*(II) *nitrate* (I). Dichloro-1,3-di(phenylthio)propanepalladium (1·0 g.) was suspended in methylene dichloride (150 c.c.) and additional disulphide (0·6 g., 1 mol.) and silver nitrate (0·775 g., 2 mol.) added. The mixture was shaken for 8 hr. and the resulting precipitate of silver chloride was removed. The filtrate was evaporated to dryness and taken up in dimethylformamide, from which the greenish-yellow *product* (0·9 g.), m. p. 167—168·5°, was crystallised by evaporation under reduced pressure, washed with acetone and dried *in vacuo* at 110° (Found: C, 48·0; H, 4·55; S, 16·9. $C_{30}H_{32}N_2O_6PdS_4$ requires C, 48·0; H, 4·3; S, 17·1%).

Bis-1,3-*di(phenylthio)propanepalladium*(II) *perchlorate* (II). Compound (I) (0·35 g.) was

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[13] A. D. Westland and L. Westland, *Canad. J. Chem.*, 1961, **39**, 324.

dissolved in water (15 c.c.) and 70% perchloric acid (0·1 c.c.) added. A yellow-green *perchlorate* (0·32 g.) formed immediately; it exploded when heated to 259° (Found: C, 43·35; H, 4·0; S, 15·4. $C_{30}H_{32}Cl_2O_8PdS_4$ requires C, 43·65; H, 3·9; S, 15·55%).

Bis-1,3-*di*(*phenylseleno*)*propanepalladium*(II) *nitrate* (III). This was prepared analogously to (I) to give a mustard-coloured *compound* with m. p. 168—172·5° (Found: C, 38·75; H, 3·65. $C_{30}H_{32}N_2O_6PdSe_4$ requires C, 38·4; H, 3·45%).

Bis-1,3-*di*(*phenylseleno*)*propanepalladium*(II) *perchlorate* (IV). Compound (III) (0·3 g.) was dissolved in a mixture of water (50 c.c.) and ethanol (20 c.c.) and concentrated perchloric acid (0·2 c.c.) added. The yellow *perchlorate* (0·19 g.), which exploded at 203°, was precipitated immediately (Found: C, 35·45; H, 3·4. $C_{30}H_{32}Cl_2O_8PdSe_4$ requires C, 35·55; H, 3·2%).

Bis-1,3-*di*(*phenylthio*)*propaneplatinum*(II) *nitrate* (V). Dichloro-1,3-di(phenylthio)propaneplatinum (2·5 g.) was suspended in ethanol (500 c.c.) and disulphide ligand (1·24 g., 1 mol.) added. A solution of silver nitrate (1·62 g., 2 mol.) in ethanol was added and the mixture shaken for 3 hr. The precipitate of silver chloride was separated and left in contact with three portions (100 c.c.) of methanol for 2 hr. The filtrate and methanol extracts, when evaporated, gave a pale yellow microcrystalline *product* (2 g.), which decomposed at 181° (Found: C, 43·5; H, 3·7; S, 14·95. $C_{30}H_{32}N_2O_6PtS_4$ requires C, 42·9; H, 3·85; S, 15·25%).

Bis-1,3-*di*(*phenylthio*)*propaneplatinum*(II) *perchlorate* (VI). The nitrate salt (0·15g.) was dissolved in warm methanol (35 c.c.)and water (5 c.c.) added. Concentrated perchloric acid (0·1 c.c.) gave the pale yellow *perchlorate*, which was collected, washed with water and then with methanol and dried *in vacuo* (0·13 g.). It exploded at 227° (Found: C, 39·05; H, 3·5; S, 13·65. $C_{30}H_{32}Cl_2O_8PtS_4$ requires C, 39·4; H, 3·55; S, 14·0%).

Bis-1,3-*di*-(*phenylseleno*)*propaneplatinum*(II) *nitrate* (VII). The 1 : 1 chloro-complex, $[\{C_3H_6(SePh)_2\}PtCl_2]$, (2 g.) was suspended in ethanol (250 c.c.) and further diselenide ligand (1·14 g., 1 mol.) and silver nitrate (1·09 g., 2 mol.) added. The mixture was shaken for 2 hr. and the precipitate of silver chloride was separated and extracted with methanol in a Soxhlet apparatus. The alcoholic solutions when evaporated yielded a pale yellow *complex*, (1·15 g.) which was recrystallised from methanol, m. p. 174·5—179° (Found: C, 34·75; H, 3·4. $C_{30}H_{32}N_2O_6PtSe_4$ requires C, 35·05; H, 3·15%).

Bis-1,3-*di*(*phenylseleno*)*propaneplatinum*(II) *perchlorate* (VIII). The nitrate (VII) (1 g.) was dissolved in water (70 c.c.) containing methanol (30 c.c.). Addition of concentrated perchloric acid (0·2 c.c.) precipitated the pale yellow *perchlorate* (0·99 g.), m. p. 185·5—206·5° which was washed with water and dried *in vacuo* at 100° (Found: C, 32·5; H, 3·3. $C_{30}H_{32}Cl_2O_8PtSe_4$ requires C, 32·7; H, 3·0%).

Mercury Preparations.—The disulphide and diselenide ligands did not produce well-defined products with mercuric chloride and bromide. Ethanolic solutions of these halides reacted with the ligands at room temperature to produce precipitates in which the ligand : mercuric halide ratio was less than 1 : 1. The selenide apparently did not react with mercuric bromide. The far-infrared spectra of these preparations appeared qualitatively identical to those of the corresponding, but well-defined, platinum complexes.

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