986. *The Infrared Spectra and Structures of Metal Complexes of* 1,4-*Dioxan,* 1,4-*Dithian,* 1,4-*Thioxan, Piperazine, and* 1,4-*Dimethylpiperazine.*

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Infrared absorption spectra have been determined for a number of complexes of certain metal chlorides with ligands mentioned in the title, and deductions have been drawn as to their structures.

A NUMBER of co-ordination complexes containing ligands of the type $C_4H_8X_2$ (X = O, S, NH, and NMe) have been prepared previously,[1,2] but there has been comparatively little investigation of their structures. In these complexes the ligand could have either the boat or the chair configuration of the six-membered ring; however, if the ligand is chelated, it must have the boat configuration, whereas if it is attached to different metal atoms it could have other structures. In non-chelate complexes the chair form seems more probable, as it is this form which predominates, for dioxan and dithian, in the free ligand.[3] Hassel and Pedersen [4] have shown from *X*-ray-diffraction evidence that in the complex, $PdCl_2(C_6H_{14}N_2)$, of 1,4-dimethylpiperazine the organic molecule has the boat configuration with its nitrogen atoms attached to the same palladium atom, as suggested previously from infrared evidence.[2]

The infrared spectrum of the 1,4-dioxan compound, $HgCl_2(C_4H_8O_2)$, has been examined in some detail by Tarte and Laurent,[5] who suggest that this compound consists of chains of high molecular weight in which different mercury atoms are linked by dioxan molecules in the chair form. This conclusion has been confirmed by *X*-ray diffraction studies.[6]

If the ligands have the boat rather than the chair structure it would be expected that the spectra would contain more absorption peaks, owing to the increased number of infrared active fundamental vibrations. Ramsey [7] points out that for 1,4-dioxan, in the region 1500—750 cm.$^{-1}$, 17 infrared-active fundamentals are permitted for the boat structure whilst only 11 are permitted for the chair form.

In the present work a number of complexes of this general type, containing the ligands 1,4-dioxan, 1,4-dithian, 1,4-thioxan, piperazine, and 1,4-dimethylpiperazine have been prepared, including some not previously reported. The infrared spectra of these have been examined in order to obtain evidence of the structure of the ligands. No attempt has been made here to make a detailed analysis of the spectra, but a comparison of the spectra of the free ligands with those of the various complexes gives useful information about their structures, and the results obtained are discussed here for each of these ligands.

1,4-*Dioxan and* 1,4-*Dithian Complexes.*—The infrared spectra of metal complexes of the type $M(C_4H_8O_2)$ (M = $HgCl_2$, $CdCl_2$, $CuCl_2$, and $NiCl_2$) and $M(C_4H_8S_2)$ (M = $AuCl_3$, $CuCl_2$, $HgCl_2$, $CdCl_2$, and $PtCl_2$) were obtained. The spectra of the various groups of complexes resemble each other and those of their respective free ligands very closely (Figs. 1 and 2). Apart from some intensity changes the only noticeable differences are the slightly lower frequencies of some absorption bands for the complexes than for the free ligand, the greatest frequency differences being less than 30 cm.$^{-1}$. In addition, a strong absorption peak at about 850 cm.$^{-1}$ appears in the dioxan complexes, probably

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[1] Husemann, *Annalen*, 1862, **126**, 281; Juhasz and Yntema, *J. Amer. Chem. Soc.*, 1940, **62**, 3522; Rheinboldt, Luyken, and Schmittmann, *J. prakt. Chem.*, 1937, **149**, 30; Bouknight and Smith, *J. Amer. Chem. Soc.*, 1939, **61**, 28.

[2] Mann and Watson, *J.*, 1958, 2772.

[3] Hassel and Viervoll, *Acta Chem. Scand.*, 1947, **1**, 149; Malherbe and Bernstein, *J. Amer. Chem. Soc.*, 1952, **74**, 4408; Marsh, *Acta Cryst.*, 1955, **8**, 91.

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

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

[6] Hassel and Hvoslef, *Acta Chem. Scand.*, 1954, **8**, 1953.

[7] Ramsey, *Proc. Roy. Soc.*, 1947, **190**, *A*, 562.

due to splitting of the band at 871 cm.$^{-1}$ for the pure ligand. Solid-phase spectra of both ligands show splitting of this absorption band (cf. Malherbe *et al.*[3]).

The similarity of spectra of the complexes and the free ligand has been previously observed for $HgCl_2(C_4H_8O_2)$ and interpreted as indicating that the organic molecules exist in the same configurations in the complexes and in the free ligand. Since there is good evidence that both dioxan and dithian consist of molecules in the chair configuration in both the liquid and the solid state, it is probable that the structures of the ligands in these complexes are also of the chair type. These complexes all give an analysis $M(C_4H_8O_2)$ or $M(C_4H_8S_2)$ and, if the metal atoms have their usual co-ordination numbers, the complexes could either have a monomeric structure in which a chelate ligand occupies *cis*-positions about the metal nucleus, or a polymeric structure with chains of metal atoms linked by dioxan or dithian molecules. Since dioxan and dithian appear to have the chair configuration in these complexes, the latter type of structure is more probable.

FIG. 1. *Infrared spectra of*: (1) 1,4-*dioxan and its complexes,* (2) $L,HgCl_2$, (3) L,Al_2Br_6, *and* (4) $L,TiBr_4$.

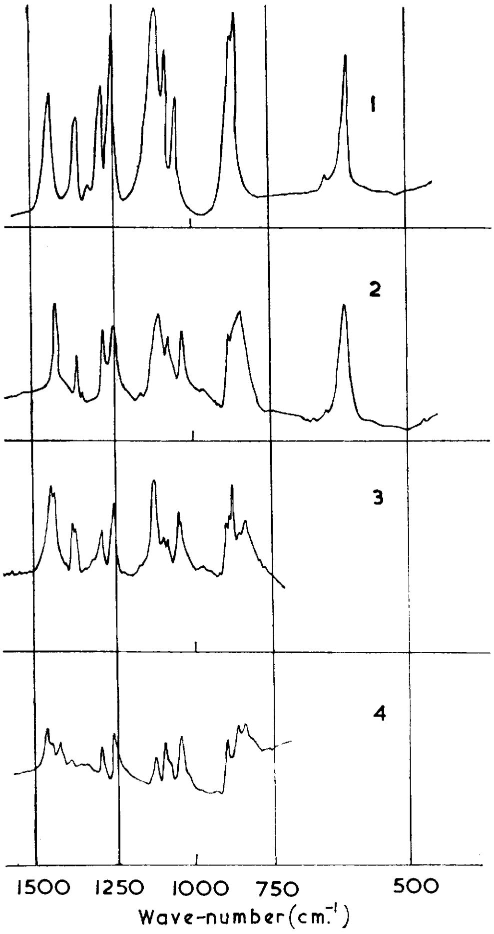
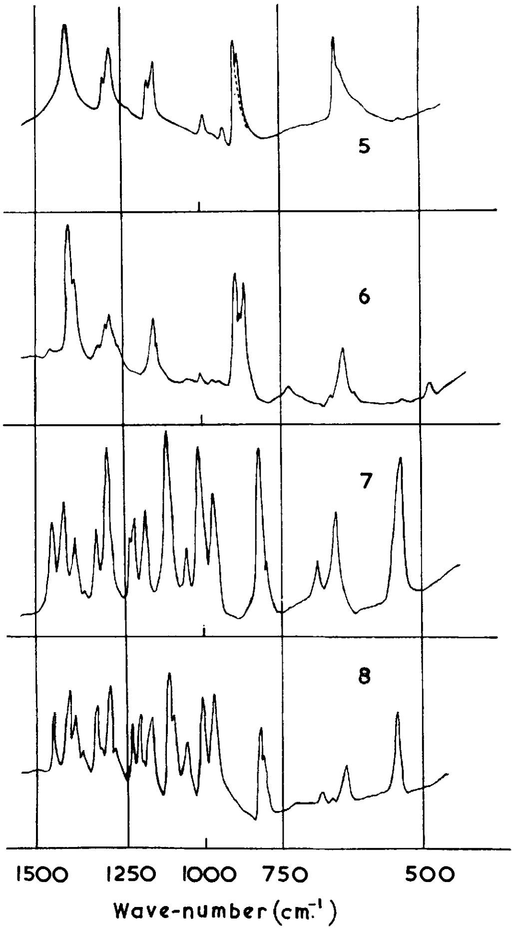


FIG. 2. *Infrared spectra of*: (5) 1,4-*dithian and* (6) *its complex,* $L,HgCl_2$; (7) 1,4-*thioxan and* (8) *its complex,* $L_2,HgCl_2$. *The broken line in* (5) *is the spectrum of* 1,4-*dithian in* CCl_4.



Sheka and Karlysheva[8] report the existence of some complexes of aluminium halides

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[8] Sheka and Karlysheva, *Zhur. obshchei Khim.*, 1951, **21**, 833.

in which dipole-moment evidence has shown that the dioxan molecule is joined to aluminium by only one oxygen atom. It was considered that, because of the lower symmetry of the ligand molecules, the infrared spectra of these compounds might show interesting differences from those discussed above. The compounds $Al_2Br_6(C_4H_8O_2)$ and $AlCl_3(C_4H_8O_2)$ which are stated to be of this type, were prepared and their infrared spectra obtained, but it was found that the spectra of these two complexes were again similar to that of the free ligand; however, there is an additional band at about 850 cm.$^{-1}$, as in the other series of complexes examined, and some of the absorption bands are split into doublets. There are also some marked changes in the strengths of the bands (Fig. 1). It is clearly difficult to distinguish between these complexes and others containing dioxan in the chair form and doubly co-ordinated.

Rolsten and Sisler[9] report a compound $TiBr_4(C_4H_8O_2)$ and suggest, on the basis of its infrared spectrum and preliminary *X*-ray investigations, that it contains chelated dioxan molecules. This compound was prepared, and its infrared spectrum obtained. The absorption-band frequencies agreed closely with those published and, apart from some intensity variations, the spectrum of this compound resembles that of $Al_2Br_6(C_4H_8O_2)$. It therefore probably has the same structure, *i.e.*, the chair configuration of the six-membered ring with one oxygen atom attached to a metal ion. This conclusion is supported by Daasch's recent work.[10]

1,4-*Thioxan Complexes*.—Three co-ordination complexes of thioxan have been prepared having empirical formulæ $HgCl_2(C_4H_8OS)_2$, $CuCl_2(C_4H_8OS)_2$, and $PtCl_2(C_4H_8OS)_2$, and their spectra, together with that of the free ligand in the liquid phase, have been obtained. Again the spectra of the complexes and ligand are very similar, suggesting that the structures of the six-membered ring are the same in all cases. The formulæ of the complexes indicate that, if the metal ions have their usual co-ordination numbers, the complexes are monomeric and contain thioxan in the chair form, either sulphur or oxygen being joined to the metal atom.

No cases have been found where a metal ion forms bonds with both oxygen and sulphur so as to give a polymer. This was expected since oxygen and sulphur show marked differences in their tendencies to form bonds with metal ions.

Piperazine Complexes.—The structure of piperazine, unlike those of dioxan and dithian, has received little attention, apart from an investigation of 1,4-dichloropiperazine reported by Andersen and Hassel.[11] The infrared spectrum of piperazine in CCl_4 in many respects resembles those of 1,4-dithian and -dioxan, so it seems probable that it has the same structure. Two additional absorption peaks found in the region of 1100 cm.$^{-1}$ are probably associated with the NH group vibrations. This structure was confirmed by the preparation of a complex in which piperazine "bridges" two metal atoms. The reaction of aqueous piperazine and Zeise's salt ($K[C_2H_4PtCl_3],H_2O$) gives a compound $(PtCl_2,C_2H_4)_2(C_4H_{10}N_2)$ (I). The *trans*-directive property of the ethylene group causes the piperazine molecule to occupy a bridging position between two platinum atoms, the nitrogen atoms being linked *trans* to the ethylene groups. The piperazine molecule in this case would, for steric reasons, probably have the chair configuration. This formation of a "bridge complex" is similar to the behaviour of ethylenediamine which, in spite of its normal strong tendency to form chelate complexes, gives a "bridge complex" containing ethylenediamine in the *trans*-configuration.[12] The spectrum of compound (I) was found to be very similar to that of piperazine in CCl_4, when allowance had been made for the absorption bands due to the ethylene groups.

The spectrum of crystalline anhydrous piperazine was very complex, and the absorption peaks tended to be broad and rounded, these effects probably being due to hydrogen

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[9] Rolsten and Sisler, *J. Amer. Chem. Soc.*, 1957, **79**, 1819.

[10] Daasch, *Spectrochim. Acta*, 1959, 726.

[11] Andersen and Hassel, *Acta Chem. Scand.*, 1949, **3**, 1181.

[12] Powell and Sheppard, *J.*, 1959, 3089.

bonding in the solid state. Two complexes of the type $M(C_4H_{10}N_2)$ ($M = CdCl_2$ and $HgCl_2$) were prepared. Their absorption spectra in general closely resembled those of the " bridge complex " (I) and of piperazine in solution, but in some regions were rather more complex (Fig. 3). The additional absorption bands cannot be due to N–H vibrations; as in the complex $CdCl_2(C_4H_{10}N_2)$ conversion of NH groups into ND causes the shifting of only two peaks to lower frequency values. It is possible that the slightly more complex nature of the spectra of these two compounds is due to the formation of isomers involving axial and equatorial positions of the hydrogen atoms and metal ions about the nitrogen atoms.

FIG. 3. *Infrared spectra of: piperazine* (9) *in* CCl_4 *and* (12) *in the solid state; and of its complexes,* (10) $L,(PtCl_2C_2H_4)_2$, (11) $L,CdCl_2$, *and* (13) $L_2,PdCl_2$.

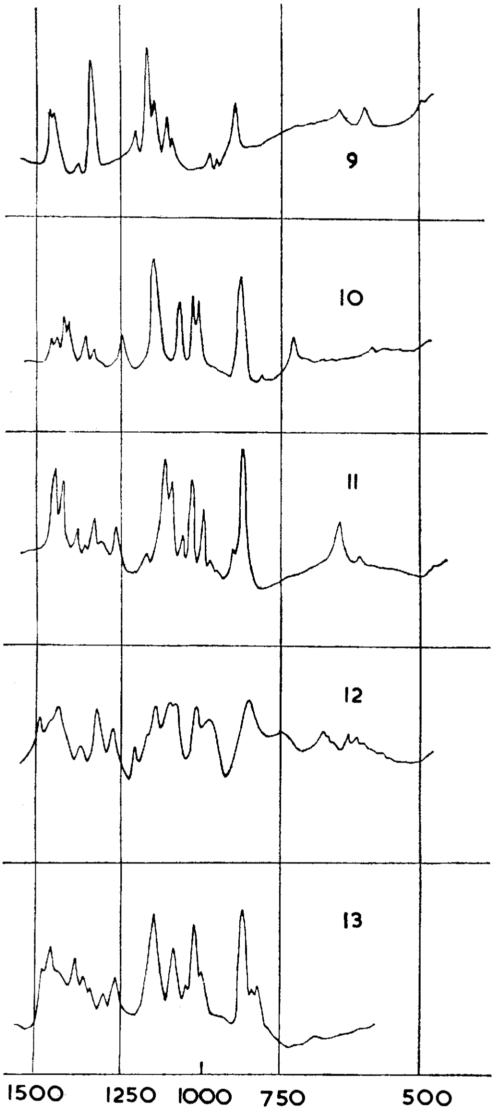
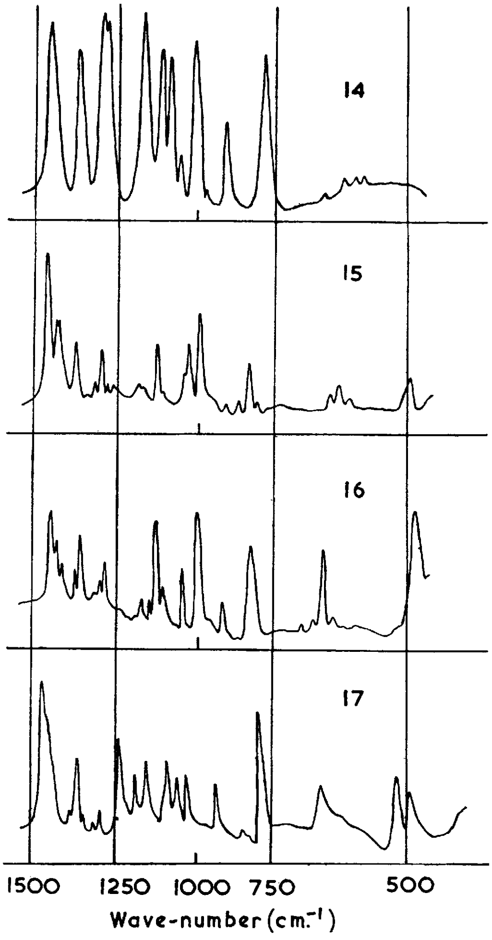


FIG. 4. *Infrared spectra of:* (14) *liquid* 1,4-*dimethylpiperazine and its complexes,* (15) $L,(PtCl_2C_2H_4)_2$, (16) $L,(HgCl_2)_2$, *and* (17) PdL_2Cl_2.



The insoluble picrate of the complex ion $[Pd(C_4H_{10}N_2)_2]^{2+}$ has been isolated from an aqueous solution of the chloride by Mann and Watson [2] and, on the basis of its analysis and chemical properties, shown to contain the chelated ligand. Attempts to isolate the compound $Pd(C_4H_{10}N_2)_2Cl_2$ (II) from this aqueous solution for infrared examination gave products containing an excess of piperazine; however, a new method of preparation has been devised giving a pure product. The spectrum obtained from compound (II) shows marked differences from those of the other piperazine complexes examined and provides additional evidence that these previously considered compounds have the chair structure.

The evidence indicates that the mercury and cadmium chloride piperazine complexes have similar structures to those of dioxan and dithian, but with the additional complication that axial and equatorial co-ordination positions cause rather more absorption bands in the spectra.

1,4-*Dimethylpiperazine Complexes.*—The preparations of 1,4-dimethylpiperazine and the complex $PdCl_2(C_6H_{14}N_2)$ have been reported by Mann and Watson,[2] who give evidence from its chemical properties and molecular weight that the complex is monomeric and therefore contains chelated 1,4-dimethylpiperazine. This has been confirmed by *X*-ray analysis by Hassel and Pedersen.[4] We have prepared a very stable, water-insoluble complex $(HgCl_2)_2(C_6H_{14}N_2)$, and also a "bridge complex" $(PtCl_2,C_2H_4)_2(C_6H_{14}N_2)$ (III) analogous to compound (I) for piperazine. The spectra of the "bridge complex" (III) and of the mercury-containing compound are very similar (Fig. 4), suggesting that $(HgCl_2)_2(C_6H_{14}N_2)$ has a structure in which the mercury atoms are linked by a dimethylpiperazine molecule, as in (III). The palladium complex, $PdCl_2(C_6H_{14}N_2)$, which is known to contain the chelate dimethylpiperazine ligand, has a very different and more complex spectrum, as would be expected, since many more fundamental vibrations are infrared-active in the boat form of the ligand, this structure being present in a chelate complex.

TABLE 1. *Infrared spectra of dioxan and some of its complexes.*

Dioxan (liq.)	$HgCl_2$ $(C_4H_8O_2)$	$CdCl_2$ $(C_4H_8O_2)$	$CuCl_2$ $(C_4H_8O_2)$	$NiCl_2$ $(C_4H_8O_2)$	Al_2Br_6 $(C_4H_8O_2)$	$AlCl_3$ $(C_4H_8O_2)$	$TiBr_4$ $(C_4H_8O_2)$
2955s	2961m	2994w	2983m	3005w		3025m	
2902ms	2919ms	2954wm	2927ms	2925wm	N.I.*		N.I.*
2849s	2862m	2850vw	2860wm	2865m		2969m	
2744w	2857m	2771vw		2750w			
2860w							
						1525w	
1452m	1441s	1430m	1441s	1456s	1450s	1455m	1458ms
1368wm	1374m	1373wm	1374mw	1440ms	1440sm	1449m	1430m †
1323vw				1372w	1385m 1374m	1388m 1379w	1382ms
1289m	1287s	1284wm	1289ms	1299ms 1267m	1295m	1264ms	1298ms
1256vs	1256s	1254s	1256s	1256ms	1256s	1224m	1256ms
1121vvs	1109s	1112ms 1105s	1109s	1110vs	1126vs 1098wm	1170w 1157w	1121m
1081ms	1079m	1079s	1073sm	1080s	1084wm	1101s	1070s
1048m	1034ms	1031ms	1031sm	1050ms	1051s 1045sh	1059s 1051s	1039s
888sh	888m	889s	885m	913m 888s	899wm 885wm	902s	888m
871vs	843vs	872ms 845vs	851vs	871vs	876vs 831s	857s	829m 804m †
	669w		667vw	682ms			
614vs	615vs	620s	612s	629s 615s	N.I.	N.I.	N.I.
	469vw			523m			
462vw	456vw		452vw				

* N.I. = not investigated.

† The spectrum of $TiBr_4(C_4H_8O_2)$ gives frequency values in good general agreement with those published by Rolsten and Sisler,[9] but the two marked peaks have not been previously reported.

EXPERIMENTAL

The infrared spectra were obtained on a Hilger H800 double-beam spectrometer, samples being dispersed in Nujol or hexachlorobutadiene except where stated otherwise. The absorption peak frequency values (cm.$^{-1}$) are listed in the Tables.

TABLE 2. *Infrared spectra of dithian and some of its complexes.*

Dithian	$AuCl_3(C_4H_8S_2)$	$CuCl_2(C_4H_8S_2)$	$HgCl_2(C_4H_8S_2)$	$CdCl_2(C_4H_8S_2)$	$PtCl_2(C_4H_8S_2)$
2933wm					
2891m					2978s
2801wm	N.I.	N.I.	2972wm	2900vvw	2819ms
			2924m		
			1854w		
1408ms	1407ms	1409sm	1407s	1403ms	1416s
		1394sm	1396m, sh		
	1326w				
1298m	1295s	1284sm	1292m, sh, 1281ms	1297m	
1278ms	1278w	1267sm	1256vw	1275ms	1278ms
	1264w				1264w, 1242wm
1183m, 1152s	1155s	1153m	1152m	1161ms	1171wm, 1124wm
	1031w	1136m		1034w	
997wm, 941wm	966w	1000wm	1000w	970w	992w
902vs, 888m *	888s	900ms, 886s	910s, 893m	898ms	907wm
	742w	718vw	885s	790vs	764wm
663vs	669vw	669m	666w	664m	787ms
650vw, sh	650ms	654s	654s	654sm	670w
			508wm		536w
477w	514m	485m	484wm		500w
470mw	474m	465vw	471vw	490w, 482w	
456vw		456vw	456vw		

* Although observed in a dispersion in liquid paraffin, this peak was not found in CCl_4 solution.

TABLE 3. *Infrared spectra of thioxan and some of its complexes.*

Thioxan	$PtCl_2(C_4H_8OS)_2$	$CuCl_2(C_4H_8OS)_2$	$HgCl_2(C_4H_8OS)_2$
2916s			2975w
2885s			2933m
2829s	N.I.	N.I.	2843m
2725w			2893ms
2669w			
1451m	1447s	1447m	1449m
1418ms	1410s	1413s	1403ms
1387m	1379m	1385sm	1385m, 1360w
1319m	1312m	1317w, 1306w	
1289vs	1275s	1278sm, 1258wm	1278s, 1256w
1217m, sh	1211wm	1211w	1211ms
1203ms	1194ms, 1183wm	1185s	1188ms
1172s	1160ms, 1152mw	1160ms	1155ms
1105vs	1098vs	1098vs	1101vs, 1087sh
1045wm	1051s	1045vs	1048ms
1006s	994s	997vvs	1000vs
966s	976s	963vs	963vs
826s	823m	820vvs	820s
806s			809m
690wm			
663ms		655m	647m
553vs	568s	561s	563s

The complexes were usually prepared by the published methods of the authors referred to in the text. The following new *compounds* were prepared as follows:

$HgCl_2(C_4H_8OS)_2$ and $CuCl_2(C_4H_8OS)_2$ by addition of an alcoholic solution of the anhydrous metal halide to an alcoholic solution of 1,4-thioxan prepared by Swistak's method[13] [Found: C, 19·75; H, 3·45. $HgCl_2(C_4H_8OS)_2$ requires C, 20·0; H, 3·4. Found: C, 29·0; H, 4·85.

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[13] Swistak, *Compt. rend.*, 1955, **240**, 1544.

TABLE 4. *The infrared spectra of piperazine and some of its complexes.*

Piperazine					
(solid)	(soln.)	$CdCl_2(C_4H_{10}N_2)$	$HgCl_2(C_4H_{10}N_2)$	$(PtCl_2,C_2H_4)_2(C_4H_{10}N_2)$	$Pd(C_4H_{10}N_2)_2Cl^2$
	3328vw	3202s	3123s	3174s	3140s
2941m	2944ms	2932wm	2932w		
2814m		2847wm	2830w	2843w	2969wm
2742m					
2269m					
2250m					
1674 (rounded)			1678vw		
1479sm	1458ms			1463w	1452s
1449s	1444ms, 1382w	1445s, 1428ms	1447m, 1418ms	1452m, 1432ms	1433s (rounded sh)
1323s	1320s	1373w, 1345vw	1377m, 1347w	1421ms, 1368m	1362ms
1271sm		1326wm, 1254m	1314w, 1256w	1346w, 1250ms	1278m, 1250ms
1197w				1157vs	1143ms
1174sh	1177m		1174vw		
1161ms		1165w, 1155w			
1127s	1138vs		1130vw		
1106s	1115ms	1114vs	1110m		
1080s	1076m	1097s	1072vs	1073sm	1079ms
1034vw	1056wm	1047m, 1021s	1040vw	1031s, 1010s	1022s, 1000wm
977m	933w	996ms, 873vw	1017m, 1000m	882vs	882vs
839vs	852m	894w, 850vs	966vw, 890w	812vm	848sh, 827w
742ms			879ms, 858vs		
				710m	710vw
663mw			690wm		
616w	633wm	647ms	673m, 656vw	No peaks in KBr region	615vw, 512vw
603w	570wm	609wm			415vw
463vw	472wm		458vw		
	442w				

TABLE 5. *The infrared spectra of di-*N*-methylpiperazine and some of its complexes.*

Dimethylpiperazine	$PdCl_2(C_6H_{14}N_2)$	$(HgCl_2)_2C_6H_{14}N_2$	$(PtCl_2,C_2H_4)_2C_6H_{14}N_2$
2927s	3042w, 3006m		3022mw
2893wm	2935s, 2891m	N.I.	2983mw
2845m	2839w		2930ms
2800s			
2974ms			
2292wm			
1455s	1483w sh, 1472sh		
	1452vs	1444vs	1455vs
		1427m, 1413ms	1430m, 1421m
1374s	1376vw	1372m	1374m
	1357s	1362s	1306w
	1337vw		
	1306vw	1298wm	1289m, 1264w
1295s, 1284s	1284wm	1284ms	1247w, 1174vw
1171s	1236s	1233w	1157vw
	1188m	1163wm	
1121s	1152ms	1138wm	1109ms
1093s	1084ms	1115vs, 1095m	
1059wm	1053ms	1031sm	
1017s	1025ms	983s	1014ms
919ms	935ms	905wm	980s, 896w
	851w		854w, 820ms
806s	792vvs	815s	795w
	648m		650w
		636s	637m
No absorption peaks in the KBr region	520s		617w
			516m
	497mw		
		469vs	

$CuCl_2(C_4H_8OS)_2$ requires C, 28·0; H, 4·7%]. $PtCl_2(C_4H_8OS)_2$ by addition of 1,4-thioxan to an aqueous solution of K_2PtCl_4 [Found: C, 20·5; H, 3·4. $PtCl_2(C_4H_8OS)_2$ requires C, 20·2; H, 3·4%]. $(HgCl_2)_2C_6H_{14}N_2$ by mixing alcoholic solutions of mercuric chloride and 1,4-dimethylpiperazine [Found: C, 11·0; H, 2·5. $(HgCl_2)_2C_6H_{14}N_2$ requires C, 11·0; H, 2·15%]. $PdCl_2(C_4H_{10}N_2)_2$ by treatment of an acetone solution of bisbenzonitrilepalladium(II) chloride with anhydrous piperazine [Found: C, 27·1; H, 5·65. $PdCl_2(C_4H_{10}N_2)_2$ requires C, 27·4; H, 5·75%].

Microanalyses of *compounds* (I) and (III) are as follows: Found for (I): C, 14·35; H, 2·9. ($Pt_2Cl_4C_8H_{18}N_2$ requires C, 14·2; H, 2·7%). Found for (III): C, 17·3; H, 3·25. ($Pt_2Cl_4C_{10}H_{22}N_2$ requires C, 17·0; H, 3·2%).

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