238. *Metal–Pyrazine Complexes. Part I. Compounds with Cobalt(II) Halides.*

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The complexes formed by cobalt(II) halides with pyrazine, methylpyrazine, and 2,5- and 2,6-dimethylpyrazine (2,6-Dmp) are described and their structures discussed. Only one monomer was isolated, the tetrahedral complex $(2,6\text{-Dmp})_2CoI_2$. Several dimers were obtained, of general formula $[LigandCo(Hal)_2]_2$, bridging being through the halogen atoms. The magnetic and spectral data indicate that in these complexes the cobalt is tetrahedrally co-ordinated. Many polymeric complexes $[LigandCo(Hal)_2]_n$ or $[2LigandCo(Hal)_2]_n$ have been prepared; in these the metal atom is usually octahedrally co-ordinated. Bridging, in the former case, is considered to take place by lone-pair donation from both nitrogen atoms of the pyrazine groups. The spectra of these compounds in various solvents have been studied and it is shown that other species such as $[2LigandCo(Acetone)I]^+$ and $[LigandCoI_3]^-$ are formed in solution. The equilibria between octahedral and tetrahedral forms have been investigated and the temperature-dependence of these is discussed.

WE recently reported briefly [1] some studies of the metal complexes formed by various pyrazines. The present paper deals in detail with the chemistry of bivalent cobalt with this type of ligand. The reaction between a cobalt halide and a pyrazine is usually carried out in a solvent, but sometimes by direct mixing. Two main series of complexes are obtained, having the empirical formula $LCoX_2$ and L_2CoX_2, where $L =$ pyrazine or a methylpyrazine, and $X =$ Cl, Br, or I. These series may be further divided according to whether the cobalt atom is octahedral or tetrahedral (Table 1). Spectra [2] and magnetism [3-5] have been used to effect this classification. Octahedral cobalt derivatives are expected to have twin absorption bands in the region 450—630 mμ (ϵ 5—25) and magnetic moments of 4·9—5·3 B.M. Tetrahedral cobalt derivatives should have multiple absorption bands in the region 600—750 mμ (ϵ 10^2—10^3) and magnetic moments of 4·2—5·0 B.M. Square-planar derivatives should have moments of 1·9—2·9 B.M.

TABLE 1.

Cobalt halide–pyrazine complexes.

Ligand	Octahedral	Tetrahedral
Methylpyrazine	MpCoCl$_2$	MpCoBr$_2$
		MpCoI$_2$
2,5-Dimethylpyrazine (Dmp)	2,5-DmpCoCl$_2$	2,5-DmpCoBr$_2$
		2,5-DmpCoI$_2$
Pyrazine (Pyz)	Pyz$_2$CoCl$_2$	
	Pyz$_2$CoBr$_2$	
	Pyz$_2$CoI$_2$	
2,6-Dimethylpyrazine (Dmp)	(2,6-Dmp)$_2$CoCl$_2$	(2,6-Dmp)$_2$CoI$_2$
	(2,6-Dmp)$_2$CoBr$_2$	

The tetrahedral complexes may be monomeric, dimeric, or polymeric, but all the octahedral complexes are polymeric, with ligand bridges. A study of the infrared spectra of the pyrazine ligands bonded to cobalt and other metals leads us to believe that it is possible to distinguish between a pyrazine bonded at one end only to a metal atom, and a pyrazine bonded at each end to a different metal atom. In general, complexes with a metal at one end only, *e.g.*, $(2,5\text{-DmpCoBr}_2)_2$ (below) have one more infrared absorption

[1] Lever, Lewis, and Nyholm, *Nature*, 1961, **189**, 58.
[2] Lewis and Wilkins, " Modern Coordination Chemistry," Interscience Publ. Inc., London, 1960.
[3] Figgis and Nyholm, *J.*, 1959, 338.
[4] Figgis and Nyholm, *J.*, 1954, 12.
[5] Lever, Lewis, and Nyholm, unpublished work.

maximum than corresponding complexes with a metal at both ends, *e.g.*, 2,5-DmpCu$_2$Br$_2$.[1,2] The position of the extra maximum depends on the pyrazine concerned, but occurs in the region 8—11 μ. Neither metal–nitrogen nor metal–halogen single-bond frequencies are expected below 15 μ. Any consistent changes in the spectra for different complexes involving the same ligand may therefore arise through changes in the stereochemical environment, *i.e.*, symmetry, of the ligand itself. The simpler spectra (see p. 1244) of ligands bonded at both ends to metal atoms presumably result from the higher symmetry of such a system than of a singly linked pyrazine. This study implies that for all polymeric octahedral complexes of the LCoX$_2$ class bridge-formation is through the pyrazine ligand, whilst for those of the L$_2$CoX$_2$ class it is through the halogen only.

Complexes [LigandCO(Hal)$_2$]$_n$.—The following abbreviations are used in this paper: Pyz = pyrazine; Mp = methylpyrazine; Dmp = dimethylpyrazine.
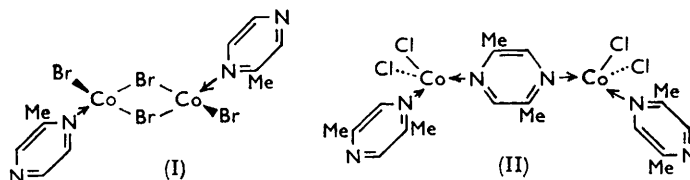
TABLE 2.

Complex	Stereo-chem.*	Colour	κ †	Magn. moment ‡	λ$_{max.}$ (mμ) (ε) (for solvents, etc., see footnotes)
[PyzCoCl$_2$]$_n$	Octa	Pink	—	4·92	—
[PyzCoBr$_2$]$_n$	,,	,,	—	5·04	See Fig. 1
[PyzCoI$_2$]$_n$	,,	Orange	—	5·26	—
[MpCoCl$_2$]$_n$	,,	Violet	—	5·36	
(Mp)$_4$CoCl$_2$	,,	Pink	—	5·28	See Fig. 10
[MpCoBr$_2$]$_2$	Tetra	Blue	24	4·68	(1) 672 (377), 635s (309), 595s (165)
[MpCoI$_2$]$_2$	,,	Green	74	4·59	See Fig. 4
[2,5-DmpCoCl$_2$]$_n$ ...	Octa	Violet	19	5·4	See Fig. 1
[2,5-DmpCoBr$_2$]$_2$ ...	Tetra	Blue	35	4·65	(2) 658 (452), 642s (425), 600 (260)
[2,5-DmpCoI$_2$]$_2$	,,	Green	37	4·54	(3) 738s (377), 700 (490), 685 (460), 625s (256)
(2,5-Dmp)$_3$Co$_2$Cl$_4$ ...	,,	Blue	— -	4·76	(4) 670s (268), 645 (310), 635s (305), 613 (316), 582s (233)
[(2,6-Dmp)$_2$CoCl$_2$]$_n$...	Octa	Violet	12 (12)	5·46	(5) 670s (308), 640 (415), 610 (525), 574 (394)
					(6) 670 (264), 645s (226), 617s (219), 575 (180)
					(7) 670 (360), 650 (297), 610 (254), 575 (297)
[(2,6-Dmp)$_2$CoBr$_2$]$_n$	,,	,,	(14)	5·34	(8) 650 (746), 640 (740), 594 (431)
					(9) 650 (652), 635 (690), 595 (430)
(2,6-Dmp)$_2$CoI$_2$	Tetra	Green	93 (11)	4·73	(10) 740s (235), 686 (1000), 658s (815), 626 (490)
Anhyd. CoI$_2$	,,	Black	32	—	(11) 690 (406), 675s (400), 657s (372), 622s (224)
(Ph$_3$MeAs)$_2$CoI$_4$	,,	Brown	—	—	(12) 742 (1240), 692s (660), 672s (530)

* Octa = octahedral; Tetra = tetrahedral. † Conductivity (ohm⁻¹ mole⁻¹ cm.⁻²) of 0·0005M-solutions in COMe$_2$. Values in parentheses refer to solutions in MeNO$_2$. Ref. compounds: [Ph$_3$MeAs]I in MeNO$_2$, 85; LiI in COMe$_2$, 135. ‡ B.M. at 25°.

Solvents, etc.: (1) COMe$_2$, 0·0027M; (2) 2,5-Dmp, 0·005M; (3) COMe$_2$, 0·00125M; (4) 2,5-Dmp, 0·002M; (5) MeNO$_2$, 0·002M; (6) COMe$_2$, 0·0009M; (7) COMe$_2$, 0·011M; (8) MeNO$_2$, 0·0013M; (9) COMe$_2$, 0·0028M, plus 2,6-Dmp (10 mol.); (10) MeNO$_2$, 0·0007M; (11, 12) COMe$_2$, 0·0006M.

Methylpyrazine complexes. Dichloro(methylpyrazine)cobalt(II) is violet-pink and has a diffuse reflectance spectrum (Fig. 1) and a magnetic moment (Table 2) clearly classifying it as an octahedral complex. It is insoluble in most solvents but dissolves slightly in

acetone. However, dibromo- and di-iodo(methylpyrazine)cobalt(II), which are blue and green, respectively, are soluble in most solvents and have spectra (Table 2, Fig. 2) and magnetic moments characteristic of tetrahedral cobalt. The iodide is dimeric in camphor,

but the bromide is insufficiently soluble for a molecular-weight determination. The most likely formulation of these two complexes is that of halogen-bridged dimers (I), involving tetrahedral cobalt. No tetrahedral, halogen-bridged cobalt dimers have been reported previously. Alternatively their formulation as tetrahedral polymers which on dissolution form dimers (*e.g.*, $2,5\text{-DmpCoI}_2$; see below) cannot be entirely ruled out. Methylpyrazine derivatives bonded at one nitrogen atom only, *e.g.*, $(\text{Mp})_4\text{CoCl}_2$ (see below)

FIG. 1.   Octahedral diffuse reflectance
spectra.

A, $2,5\text{-DmpCoI}_2$.   D, PyzCoBr_2.
B, MpCoCl_2.   E, $(2,6\text{-Dmp})_2\text{CoCl}_2$.
C, PyzCoCl_2.   F, $(2,6\text{-Dmp})_2\text{CoBr}_2$.
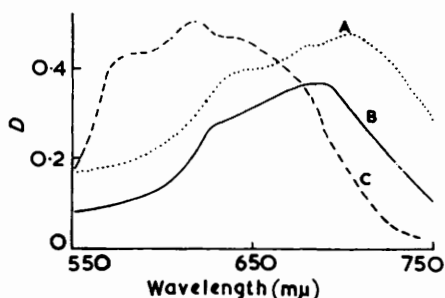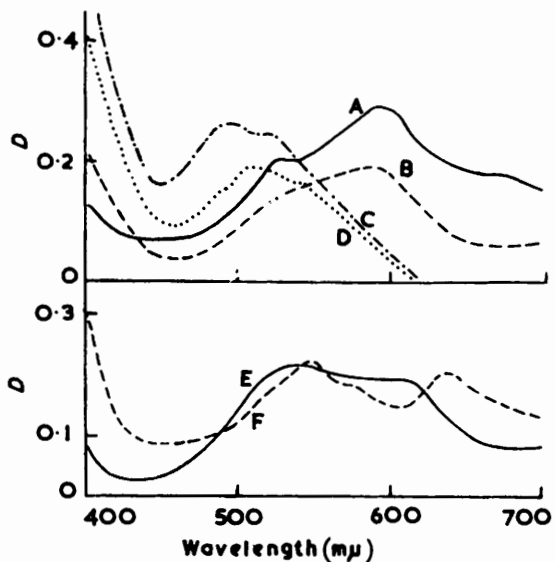
FIG. 2.   Tetrahedral diffuse reflectance
spectra.

A, $[\text{MpCoI}^2]_2$.   B, $(2,6\text{-Dmp})_2\text{CoI}_2$.
C, $(2,5\text{-Dmp})_3\text{Co}_2\text{Cl}_4$.
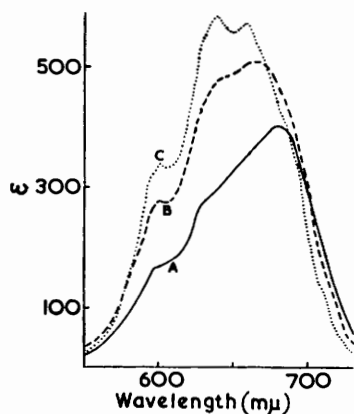
FIG. 3.   Spectrum of $(2,6\text{-Dmp})_2\text{CoBr}_2$ in
acetone.

A, 0·00016M.   B, 0·0032M.   C, 0·032M.

and a considerable number of nickel derivatives to be discussed shortly,[5] have an infrared absorption band of medium intensity near 1248 cm.[-1]. This band is not present in spectra of derivatives in which there is bonding at both nitrogen atoms. For the bromide and iodide under discussion this band is very weak.

To achieve six co-ordination, the chloride complex must either have chloride ions bridging three cobalt atoms, or chloride bridges to two cobalt atoms plus a methyl-pyrazine bridge. The former case would involve methylpyrazine bonded at one nitrogen atom only so that the complex should exhibit an infrared absorption band at 1248 cm.[-1],

are generally regarded as arising from tetrahedral cobalt. Alternative explanations are that the compounds are mixtures of octahedral and tetrahedral isomers, that they are comparatively short-chain octahedral polymers (say, $n = 40$—70), which terminate in tetrahedral cobalt atoms. Since the absorption bands of tetrahedral cobalt are very much more intense these atoms would give rise to detectable absorption even if the solute has a concentration as low as 1%. Since all the known tetrahedral cobalt pyrazine complexes are fairly soluble, whilst some of these violet-pink polymers are very insoluble, the former explanation seems unlikely, and we conclude that the violet polymers are indeed terminated by tetrahedral cobalt atoms. There is probably, however, a further, contributory, factor: the position of the octahedral maximum, ~590 mμ, indicates a low value for Dq, the mean crystal-field splitting energy, and the band might well be expected to tail into the " tetra-hedral " region. That this is only contributory is shown by the fact that in the case of the dibromide $(2,5\text{-Dmp})_2\text{CoBr}_2$ it is possible, by varying the mode of crystallisation, to obtain deep blue isomers which must evidently contain fairly short chains. The magnetic moments of these blue isomers are still, however, above 5 B.M., though not as high as those of the violet-pink forms.

Solution Absorption Spectra.—The complexes, $(2,5\text{-DmpCoBr}_2)_2$ *and* $(\text{MpCoBr}_2)_2$. The dimethylpyrazine complex is dimeric in 2,5-dimethylpyrazine solution, and its visible absorption spectrum in this solvent (Table 2) may be tentatively considered characteristic of the general species $(\text{LCoBr}_2)_2$ where L = a pyrazine ligand.

A solution of the complex $(\text{MpCoBr}_2)_2$ in acetone is a non-conductor, and the spectrum, which is unaffected by the addition of an excess of methylpyrazine, closely resembles that obtained by dissolving $(2,5\text{-DmpCoBr}_2)_2$ in acetone (Table 3). The latter spectrum is

TABLE 3.

Solution spectra in acetone: $\lambda_{max.}$ (mμ); ε in parentheses.

L	L_2CoI_2			LCoI_3^-		
Mp	735s (374)	690 (920)	630s (420)	735 (1270)	700 (672)	665s (364)
2,5-Dmp	735s (420)	695 (635)	625s (282)	745 (1200)	702s (635)	672s (420)
2,6-Dmp	735s (220)	690 (1155)	625s (518)	735 (1165)	700 (635)	665s (365)
	$(\text{Ph}_3\text{MeAs})_2\text{CoI}_4$ in COMe_2			742 (1240)	692s (660)	672s (530)

	$(\text{LCoBr}_2)_2$		
Mp	672 (377)	635s (309)	595s (169)
2,5-Dmp	672 (430)	635s (333)	595s (180)
2,6-Dmp	677 (404)	625s (270)	595s (164)

sufficiently similar to the spectrum in 2,5-dimethylpyrazine to make it clear that both compounds dissolve in acetone as dimers. This provides further indirect evidence for the dimeric nature of dibromo(methylpyrazine)cobalt(II). These complexes have very similar diffuse reflectance spectra which are almost identical with their solution spectra, and the solution spectra obey Beer's law (c 0·0001—0·001M).

2,6-Dimethylpyrazinecobalt halides. As already mentioned, the 2,6-dimethylpyrazine octahedral polymers are soluble in acetone in which they yield deep blue solutions evidently containing tetrahedral cobalt. This is suggested both by their absorption spectra and by magnetic determinations. Dibromobis-(2,6-dimethylpyrazine)cobalt(II) has a magnetic moment of 5·37 B.M. in the solid state, but of only 4·1 B.M. ($\pm$10%) in a 2% acetone solution.

(*a*) The chloride is monomeric and a non-electrolyte in acetone (Table 2), indicating dissolution as the simple tetrahedral monomeric polymer unit L_2CoCl_2. [This behaviour is similar to that of the violet (polymeric) (pyridine)$_2$CoCl$_2$ which [7] forms the blue monomer in solution.] The spectrum in acetone does not obey Beer's law (Table 2), the extinction coefficients increasing with increasing concentration. However, the band positions remain

[7] Gill and Nyholm, *J. Inorg. Nuclear Chem.*, 1961, **18**, 88.

essentially unaltered, showing that the tetrahedral species is still L_2CoCl_2. Evidently a tetrahedral–octahedral equilibrium with the solvent is present, the octahedral form not absorbing in the region 600—700 mμ:

$$(2,6\text{-Dmp})_2CoCl_2 + 2S \rightleftharpoons S_2(2,6\text{-Dmp})_2CoCl_2 \quad (S = \text{solvent, acetone})$$
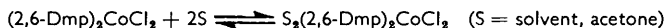
The dilute solution shows a very slight dependence on added 2,6-dimethylpyrazine, leading to an overall slight increase in intensity. It appears, therefore, that there is a further equilibrium of the type

$$S_2(2,6\text{-Dmp})_2CoCl_2 + S \longrightarrow S_3(2,6\text{-Dmp})CoCl_2 + 2,6Dmp$$

which lies predominantly to the left.

The spectrum in nitromethane is almost identical in band position with that in acetone, so that the same tetrahedral species must be present there. The nitromethane solution obeys Beer's law and the absorption is independent of added 2,6-dimethylpyrazine. This suggests that there is no octahedral form present, a view supported by the fact that the extinction coefficients in nitromethane are greater than those in acetone.

(*b*) The bromide, in nitromethane, has a spectrum whose bands, though remaining essentially in the same position, increase in intensity with increasing concentration. Addition of 10 mol. of 2,6-dimethylpyrazine results in a small (about 20%) increase in intensity but no change in band position, suggesting that nitromethane is a sufficiently strong donor to enter into a tetrahedral–octahedral equilibrium:

$$(2,6\text{-Dmp})_2CoBr_2 + 2MeNO_2 \rightleftharpoons (MeNO_2)_2(2,6\text{-Dmp})_2CoBr_2$$

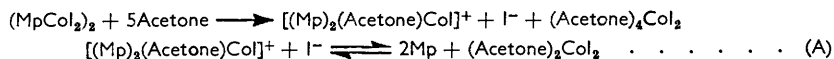The slight ligand-dependence suggests some small dissociation of the octahedral complex.

In acetone there is a change in shape of the curve as well as in intensity, with change of concentration (Fig. 3). In very dilute solutions the spectrum is virtually identical with that of the $(LCoBr_2)_2$ dimers, suggesting the presence of $(2,6\text{-DmpCoBr}_2)_2$. In concentrated solutions, or on the addition of an excess of 2,6-dimethylpyrazine to the dilute solution, the spectrum is almost identical with that in nitromethane given by $(2,6\text{-Dmp})_2CoBr_2$. The following equilibrium is suggested:

$$2(2,6\text{-Dmp})_2CoBr_2 \rightleftharpoons [(2,6\text{-Dmp})CoBr_2]_2 + 2(2,6\text{-Dmp})$$
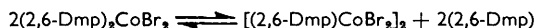
A molecular-weight determination in acetone gave, as expected, a value less than the formula weight.

Iodocobalt Complexes.—Despite difference in the stoicheiometry of the solids, acetone solutions of iodo-(methylpyrazine)-, -(2,5-dimethylpyrazine)-, and -(2,6-dimethylpyrazine)-cobalt complexes are very similar under analogous conditions. The solution spectra are dependent on concentration, added pyrazine ligand, added iodide ion, and temperature. The spectrum of di-iodo(methylpyrazine)cobalt(II) over a range of concentrations in acetone shows isosbestic points (Fig. 4), demonstrating the presence of two tetrahedral species in equilibrium, the total amount remaining independent of dilution. On extreme dilution the spectrum approximates to that obtained by dissolving anhydrous cobalt iodide in acetone (Table 2). Since this solution is virtually a non-electrolyte, the species is considered to be $(\text{acetone})_2CoI_2$, the most likely alternative tetrahedral species, namely, $[(\text{Acetone})CoI_3]^-$ and $[CoI_4]^{2-}$ being excluded by the spectra (Table 2, Fig. 8) and conductivity. Iodo(methylpyrazine)cobalt in solution is an electrolyte, and hence the other tetrahedral component, which must obviously contain methylpyrazine, must be an electrolyte. In order for there to be a dependence on dilution, there must be an unequal number of components on each side of the equilibrium. The only reasonable tetrahedral species which fits these requirements is $[(Mp)_2(\text{Acetone})CoI]^+I^-$. As the intensity of the tetrahedral absorption is very much increased by addition of ligand, a third (octahedral) species which reacts with the added ligand must almost certainly be present in solution. Indeed, in this case, such a component is necessary to balance the equation. Since the

total tetrahedral content is constant, so must be the total octahedral content. The following reaction and equilibrium in acetone is proposed:

$$(MpCoI_2)_2 + 5Acetone \longrightarrow [(Mp)_2(Acetone)CoI]^+ + I^- + (Acetone)_4CoI_2$$

$$[(Mp)_2(Acetone)CoI]^+ + I^- \rightleftharpoons 2Mp + (Acetone)_2CoI_2 \quad \cdots \cdots \quad (A)$$

The complex $(2,5\text{-}DmpCoI_2)_2$ in acetone also shows a well-defined isosbestic point and similar tetrahedral species (Fig. 5). A third concentration (c 0·00125M) (Table 2) was
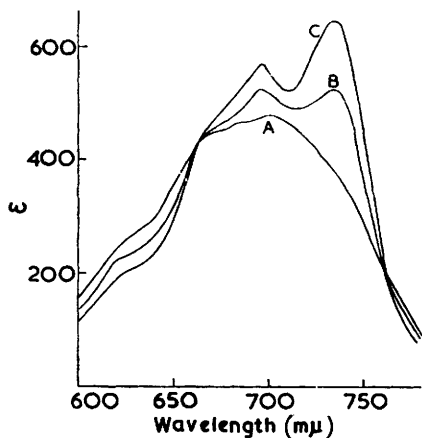

FIG. 4. Spectrum of $(MpCoI_2)_2$ in acetone.

A, 0·00019M.   B, 0·00153M.   C, 0·00614M.
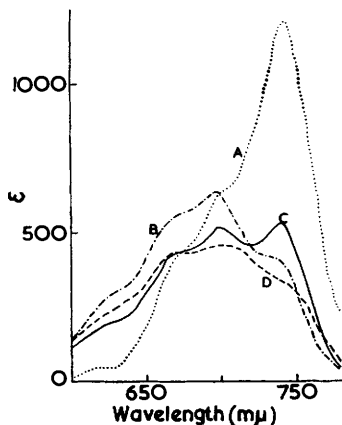
FIG. 5. Spectrum of $(2,5\text{-}DmpCoI_2)_2$ in acetone.

A, 0·0125M plus NaI (10 mol.).
B, 0·0125M plus 2,5-Dmp (10 mol.).
C, 0·0125M.   D, 0·0005M.
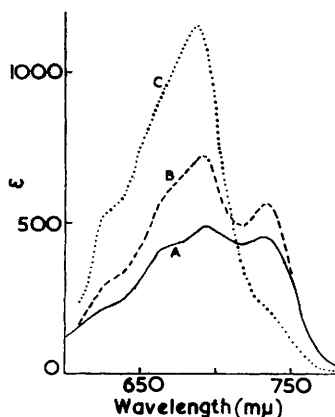
FIG. 6. Spectrum of $(2,6\text{-}Dmp)_2CoI_2$ in acetone.

A, 0·00035M.   B, 0·0074M.
C, 0·0074M + 2,6-Dmp (10 mol.).
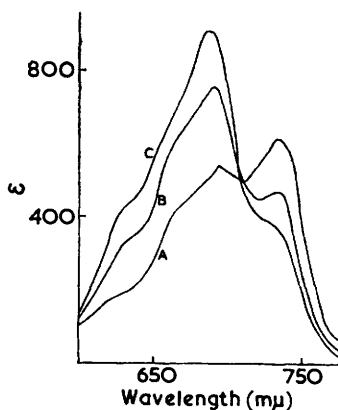
FIG. 7. Spectrum of $(MpCoI_2)_2$ in acetone: dependence on added methylpyrazine.

A, 0 mol.   B, 5 mol.   C, 20 mol.

omitted from the graph for clarity, but its curve passes through the same point. The 2,6-dimethyl complex behaves analogously. A similar reaction must therefore occur with these two complexes. In the latter case, the extra pyrazine molecule will displace the equilibrium (A) more to the left, so that a higher conductivity than in the other cases would be expected, and is observed (Table 2). This result is also suggested by the spectra of the 2,6-dimethylpyrazine derivative (Fig. 3). No octahedral component to balance the equation is necessary in this case, but nevertheless it must be present to

explain the changes in intensity. Since (Acetone)$_2$CoI$_2$ is definitely in equilibrium with an octahedral species in acetone, it will provide a mechanism for some of the cobalt ion to be converted into an octahedral form. The pyrazine cobalt cation is also probably in equilibrium with this octahedral component.

Addition of an excess of the corresponding pyrazine to these iodides has an identical effect on the spectra. Clearly the same type of species is involved (Figs. 5—7). With the monomeric di-iodobis-(2,6-dimethylpyrazine)cobalt(II), this same spectrum is obtained merely by dissolution in nitromethane. Since the nitromethane solution is a non-electrolyte, and the spectrum is independent of added 2,6-dimethylpyrazine, it must contain the simple (2,6-Dmp)$_2$CoI$_2$ species. By analogy, therefore, addition of an excess of the corresponding pyrazine to the acetone solutions must produce a complex L$_2$CoI$_2$.
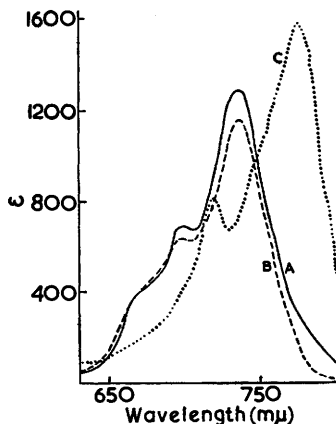

FIG. 8. Spectral dependence on added sodium iodide (10 mol.).

A, (MpCoI$_2$)$_2$.　　B, (2,6-Dmp)$_2$CoI$_2$.
C, (Ph$_3$MeAs)$_2$CoI$_4$.
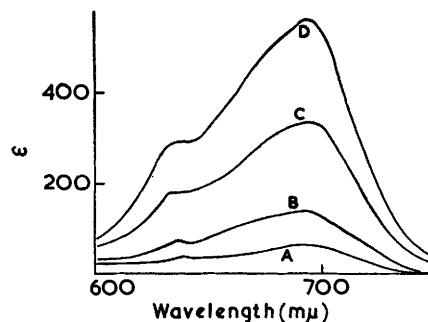
FIG. 9. Spectrum of (MpCoI$_2$)$_2$ in methyl-pyrazine : dependence on temperature.

A, 22·5°.　B, 34·5°.　C, 52·5°.　D, 68°.

Addition of iodide ions leads to the same spectrum in each case (Figs. 5 and 8). It is significant that almost the same spectrum is obtained by dissolving (Ph$_3$MeAs)$_2$(CoI$_4$) in acetone (Table 2). In the presence of added iodide ions, this spectrum alters (Fig. 8). It is believed [8] that a solution of the complex ion [CoI$_4$]$^{2-}$ in acetone forms the [LCoI$_3$]$^-$ ion (L = acetone), and that this re-forms the [CoI$_4$]$^{2-}$ ion on addition of an excess of iodide. The close similarity between the [(Acetone)CoI$_3$]$^-$ spectrum and the observed pyrazine spectra must indicate the presence of the [LCoI$_3$]$^-$ ion, where L = methylpyrazine or 2,5- or 2,6-dimethylpyrazine. Apparently in this case the pyrazine ligand is not replaced by iodide when an excess of iodide ions is added. If the pyrazine ligand is added to a solution containing an excess of iodide ions, a further slight increase in intensity occurs, proving that the species present contains pyrazine ligand.

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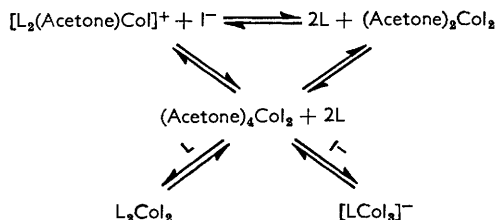
[8] T. M. Dunn, personal communication.

The behaviour in acetone is therefore represented by the annexed scheme, where L is a pyrazine ligand.   The central octahedral species is not well defined and is probably in equilibrium with a small proportion of a further ionic octahedral complex, since an acetone solution of cobalt iodide does conduct electricity.   The comparatively low intensity of the $(2,5\text{-Dmp})_2\text{CoI}_2$ species in the presence of a given amount of free ligand (Table 3), presumably means that in this case the equilibrium lies appreciably on the octahedral side.

The spectrum of $L_2\text{CoI}_2$ and $[\text{LCoI}_3]^-$ is almost independent of L (for the pyrazine class of ligand at least) (Table 3).   This is not too surprising since we are altering methyl substituents on the pyrazine nucleus only.   Apparently these changes have very little effect on the crystal-field strength of the pyrazine ligand.   The same conclusion may be reached from consideration of the diffuse reflectance spectra of octahedral cobalt, though there is some evidence that pyrazine itself may have a higher field strength than its methyl-substituted derivatives.   This point will be discussed in more detail in a later paper.   All three ligands are very weak bases [9] although the pK_a values vary widely (methylpyrazine and 2,6-dimethylpyrazine have pK_a 1·5 and 2·5, respectively).
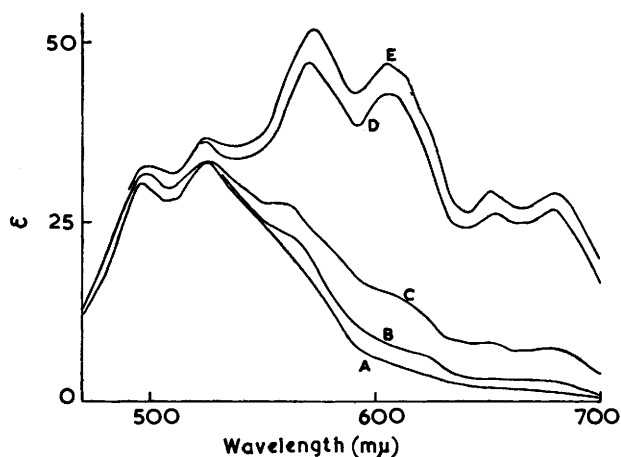

FIG. 10.   Spectrum of $(\text{Mp})_4\text{CoCl}_2$ in methylpyrazine: dependence on temperature.

A, 25°.   B, 38°.   C, 50°.   D, 69°.
E, 72°.

ε

Wavelength (mμ)

A solution of the complex $(\text{MpCoI}_2)_2$ in methylpyrazine is yellow but on warming becomes intensely green; on cooling, the colour change is reversed.   This was followed spectrophotometrically (Fig. 9).   It is fairly evident that there is a tetrahedral–octahedral equilibrium dependent on temperature.   The position of the absorption bands in the hot solution clearly indicates the presence of $(\text{Mp})_2\text{CoI}_2$.   A similar spectral behaviour is noted with solutions of MpCoCl_2 (Fig. 10) and $(\text{MpCoBr}_2)_2$.   Presumably complexes $(\text{Mp})_2\text{CoCl}_2$ and $(\text{Mp})_2\text{CoBr}_2$ are formed in the hot solutions.

The spectrum of the iodide $(\text{MpCoI}_2)_2$ in acetone is also temperature-dependent, the equilibrium (A) moving to the right with increasing temperature.   It should be noted that the reflectance spectrum of this compound (Fig. 2) differs from those of all the acetone species, in agreement with its formulation as a dimer in the solid state.

The temperature-dependence of magnetic susceptibility for a number of these complexes has been measured; these results will be discussed later.

It is surprising, at first sight, that the position of the methyl group in the ligand leads to a change in the type of complex formed.   The changes observed may be rationalised in terms of (a) ligand polarisability, and (b) steric interaction by the methyl group.   In general, the more readily the σ-pair of electrons on the ligand is polarisable, the fewer molecules of ligand are required by the metal ion to effect electroneutrality (Pauling electroneutrality principle).   For complexes formed with a given pyrazine and various

[9] Keyworth, *J. Org. Chem.*, 1959, **24**, 1355.

halides, the change from octahedral to tetrahedral stereochemisty occurs in going from the chloride to the iodide. This is in agreement with the effects due to polarisation of the halogen ligand. The changes that occur with variation in the pyrazine are probably associated with a combination of both polarisation and steric phenomena.
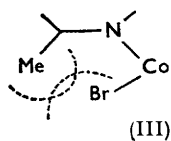
It is of interest that for molecules where there is a methyl group *ortho* to the nitrogen atom, there would be, in octahedral complexes involving bonding at that nitrogen atom, steric interaction between a bromide or iodide ion and the methyl group (cf. III). Whereas the chloride may be octahedral for all the pyrazines studied, the bromide and iodide of 2,5-dimethylpyrazine, where this effect must operate, are tetrahedral. On this basis it appears that the methylpyrazine ligand is bonding through the N^1 atom in the case of the tetrahedral bromide and iodide, whereas the 2,6-dimethylpyrazine, in the octahedral bromide, appears to be bonding through the N^4 atom.

EXPERIMENTAL

The magnetic determinations were carried out by the Gouy method, with a tube calibrated with copper sulphate pentahydrate and mercuric tetrathiocyanatocobaltate(II),[10] the calibrations being consistent. The visible spectra were determined with a Unicam S.P. 500 spectrophotometer, and the infrared spectra with a Grubb–Parsons G.S. 2A spectrometer.

Carbon and hydrogen were determined in this Department by Mr. A. Winter, and nitrogen by the Oxford Microanalytical Laboratory.

Determination of the Cryoscopic Constant (K_f) *of 2,5-Dimethylpyrazine.*—The cryoscopic constant of 2,5-dimethylpyrazine, m. p. 15°, was obtained by determining the freezing point of solutions of azobenzene (" AnalaR " recrystallised from chloroform). A mean value of 5·44° per mole per kg. was obtained (0·13—0·27M). A simple double-walled melting-point apparatus was used with a Beckmann thermometer. Exploratory experiments indicated that K_b, the boiling-point constant, was less than 1° per mole per kg.

Principal infrared absorption bands (5—15 μ) (in cm.$^{-1}$).

(Italicised maxima are held to characterise bonding by one nitrogen atom only.)

(A) All pyrazine cobalt complexes: 1720 ± 5(w); 1405 ± 2(vs); 1298(w); 1150(s); 1113 ± 3(vs); 1052(vs); in addition to those below.

$(Pyz)_2CoCl_2$: *983*s; 819s; 810s
$(Pyz)_2CoBr_2$: *982*s; 820s; 814s
$(Pyz)_2CoI_2$: *983*s; 813s

(B) All methylpyrazine cobalt complexes: 1600 ± 15(w–m); 1505 ± 10(w–m); 1403 ± 7(w); 1300 ± 2(m); 1173 ± 2(s); 1074 ± 10(s); 1041 ± 6(w–m); 734 ± 8(s); 720 ± 1(s); in addition to those below.

$MpCoCl_2$:   — ; 1163s; — ;   — ;   824m; 816s
$MpCoBr_2$:   *1250*vw; 1163s; 1150sh; 1028m; 831m; 815w
$MpCoI_2$:   *1250*vw; 1163s; 1142sh; 1024m; 824s; —
$(Mp)_4CoCl_2$: *1246*s; 1152s; — ;   1024s; 842s; 832s

(C) All 2,5-dimethylpyrazine cobalt complexes: 1492 ± 3(m–s); 1333 ± 5(m); 1265 ± 6(w–m); 1154 ± 5(s); 970 ± 4(m); 887 ± 5(m); 742 ± 7(w–m); 722 ± 3(m); in addition to those below.

2,5-$DmpCoCl_2$:   — ; 1068s; 1040m
2,5-$DmpCoBr_2$:   *1075*s; 1055s; 1031s
2,5-$DmpCoI_2$:   — ; 1073s; 1022s
$(2,5-Dmp)_3Co_2Cl_4$: *1079*s; 1059s; 1038s

(D) All 2,6-dimethylpyrazine cobalt complexes: 1592(m–s); 1530 ± 10(s); 1424 ± 6(sh); 1401 ± 2(w); 1284 ± 1(s); 1254 ± 4(s); 1173 ± 2(vs); 1022 ± 4(s); 946 ± 4(m); 917(w); 868 ± 2(s); 764 ± 5(vw–m); 746 ± 8(m); 733(vs); 719 ± 1(sh); in addition to those below.

$(2,6-Dmp)_2CoCl_2$: *1167*s
$(2,6-Dmp)_2CoBr_2$: *1164*s
$(2,6-Dmp)_2CoI_2$: *1152*s

Dichlorodi(pyrazine)cobalt(II).—Cobalt chloride hexahydrate (2 g., 1 mol.), dissolved in hot water (6 ml.), was added to pyrazine (1·4 g., 2 mol.) dissolved in a similar volume of hot

[10] Figgis and Nyholm, *J.,* 1958, 4190.

water. After $\frac{1}{2}$ hr., the *complex*, obtained as pink crystals, was filtered off, washed with a small volume of cold water, then ethanol and ether, and dried in a vacuum-desiccator (yield 1·65 g., 49%) (Found: C, 33·7; H, 3·5; Cl, 24·5; Co, 20·6; N, 19·2. $C_8H_8Cl_2CoN_4$ requires C, 33·1; H, 2·8; Cl, 24·5; Co, 20·3; N, 19·3%).

Dibromodi(pyrazine)cobalt(II).—Procedure was as above. The *complex* (51%) was obtained as pink crystals (Found: C, 26·1; H, 2·4; Br, 42·2; Co, 15·3; N, 14·85. $C_8H_8Br_2CoN_4$ requires C, 25·4; H, 2·1; Br, 42·2; Co, 15·55; N, 14·8%).

Di-iododi(pyrazine)cobalt(II).—Cobalt bromide hexahydrate (1 g.) in hot water (5 ml.) was added to pyrazine (1·5 g.) and sodium iodide (2 g.) in hot water (10 ml.). The *complex*, obtained as yellowish-red crystals, was filtered off, recrystallised from water containing 2% of sodium iodide, and dried in a vacuum-desiccator (yield, 2·55 g., 57%) (Found: Co, 13·2; N, 12·4; I, 53·9. $C_8H_8CoI_2N_4$ requires Co, 12·5; N, 11·9; I, 53·7%).

Dichlorotetra(methylpyrazine)cobalt(II).—Cobalt chloride hexahydrate was recrystallised three times from methylpyrazine. The hot, intensely blue, solution, became pink on cooling and deposited large pink crystals of the *complex* in high yield. This was washed with a small volume of light petroleum (b. p. 60—80°) and dried over concentrated sulphuric acid (Found: C, 47·6; H, 5·2; Cl, 14·4; Co, 11·6. $C_{20}H_{24}Cl_2CoN_8$ requires C, 47·45; H, 4·7; Cl, 14·0; Co, 11·6%). When warmed to 50°/15 mm. or washed with ethanol the complex yielded the product described in the next paragraph, as indicated by infrared spectra.

Dichloro(methylpyrazine)cobalt(II).—Cobalt chloride hexahydrate (1·3 g.) and methylpyrazine (3 ml.) were kept at 100° for $\frac{1}{2}$ hr. The product (2·0 g.), after trituration with ether, was extracted (Soxhlet) with acetone. The *complex*, a pale violet-pink powder, was dried at 50°/15 mm. (Found: C, 27·4; H, 3·4; Cl, 31·1; Co, 25·8. $C_5H_6Cl_2CoN_2$ requires C, 26·8; H, 2·7; Cl, 31·7; Co, 26·3%).

Dibromo(methylpyrazine)cobalt(II).—Cobalt bromide hexahydrate was twice recrystallised from methylpyrazine, and the resultant pink crystals were heated at 80°/15 mm. for 1 hr. The blue product, *dibromo(methylpyrazine)cobalt*(II), was rapidly obtained (Found: Br, 50·7; Co, 18·6; N, 9·4. $C_5H_6Br_2CoN_2$ requires Br, 51·1; Co, 18·8; N, 9·0%).

Di-iodo(methylpyrazine)cobalt(II).—Dibromo(methylpyrazine)cobalt(II) was refluxed in ethanol with a large excess of sodium iodide for $\frac{1}{2}$ hr. The solvent was then removed and the green residue extracted (Soxhlet) with ether (sodium-dried), yielding the pure deep green *complex* (Found: C, 14·7; H, 1·7; Co, 13·9; I, 62·2; N, 7·0. $C_5H_6CoI_2N_2$ requires C, 14·8; H, 1·5; Co, 14·5; I, 62·4; N, 6·9%).

Tetrachlorotris-(2,5-dimethylpyrazine)dicobalt(II).—Cobalt chloride hexahydrate was recrystallised twice from 2,5-dimethylpyrazine. The azure-blue crystals of the *complex* were washed with ether and dried in a desiccator (Found: Cl, 24·2; Co, 19·7; N, 13·8. $C_{18}H_{24}Cl_4Co_2N_6$ requires Cl, 24·3; Co, 20·2; N, 14·3%).

Dichloro-(2,5-dimethylpyrazine)cobalt(II).—Tetrachlorotris-(2,5-dimethylpyrazine)dicobalt(II) was extracted (Soxhlet) with acetone. The *complex*, a violet-pink, hygroscopic powder, was dried at 50°/15 mm. (Found: C, 30·9; H, 3·9; Cl, 29·6; Co, 24·5; N, 11·6. $C_6H_8Cl_2CoN_2$ requires C, 30·3; H, 3·4; Cl, 29·8; Co, 24·75; N, 11·8%).

Dibromo-(2,5-dimethylpyrazine)cobalt(II).—Cobalt bromide hexahydrate was twice recrystallised from 2,5-dimethylpyrazine. The blue crystalline *complex* was washed with ether and dried in a vacuum-desiccator (Found: C, 22·6; H, 2·8; Br, 49·6; Co, 17·8. $C_6H_8Br_2CoN_2$ requires C, 22·1; H, 2·5; Br, 48·9; Co, 18·0%).

Di-iodo-(2,5-dimethylpyrazine)cobalt(II).—This *compound* was prepared in the same way as di-iodo(methylpyrazine)cobalt (Found: C, 17·25; H, 2·3; Co, 13·4; I, 60·0; N, 6·75. $C_6H_8CoI_2N_2$ requires C, 17·1; H, 1·9; Co, 14·0; I, 60·3; N, 6·7%). Some difficulty was experienced in obtaining an accurate cobalt analysis.

Dichlorobis-(2,6-dimethylpyrazine)cobalt(II).—Stoicheiometric proportions of cobalt chloride hexahydrate and 2,6-dimethylpyrazine were heated at 100° for $\frac{1}{4}$ hr. The crude *complex* was purified by twice recrystallising it from hot acetone in which it is sparingly soluble (Found: C, 41·9; H, 5·1; Cl, 20·2; Co, 16·8; N, 16·1. $C_{12}H_{16}Cl_2CoN_4$ requires C, 41·6; H, 4·7; Cl, 20·5; Co, 17·0; N, 16·2%).

Dibromobis-(2,6-dimethylpyrazine)cobalt(II).—This *product* was prepared in the same way as the dichloride (Found: C, 33·1; H, 4·1; Br, 36·8; Co, 12·9; N, 13·0. $C_{12}H_{16}Br_2CoN_4$ requires C, 33·1; H, 3·7; Br, 36·7; Co, 13·5; N, 12·9%).

Di-iodobis-(2,6-dimethylpyrazine)cobalt(II).—This *product* was prepared in the same way as

di-iodo(methylpyrazine)cobalt (Found: C, 27·8; H, 3·4; Co, 11·0; I, 48·2; N, 10·2. $C_{12}H_{16}CoI_2N_4$ requires C, 27·2; H, 3·0; Co, 11·1; I, 48·0; N, 10·6%).

Molecular-weight Determinations.—Results were as tabulated (E = ebullioscopic, C = cryoscopic, R = Rast).

Complex	Solvent	Concn. (M)	Method	M (Found)	M (Reqd.)
$(2,6\text{-Dmp})_2CoCl_2$	$COMe_2$	0·033, 0·06	E	351, 370	346
$(2,6\text{-Dmp})_2CoBr_2$	,,	0·07, 0·065	E	266, 297	435
$(2,6\text{-Dmp})_2CoI_2$	Camphor	0·45	R	475, 490	529
$MpCoI_2$	$COMe_2$	0·05	E	272	407
	Camphor	0·13	R	840, 870	407
$(2,5\text{-Dmp})CoBr_2$...............	2,5-Dmp	0·09	C	672, 675	327
$(2,5\text{-Dmp})CoI_2$	,,	0·1, 0·11	C	860, 930	421

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