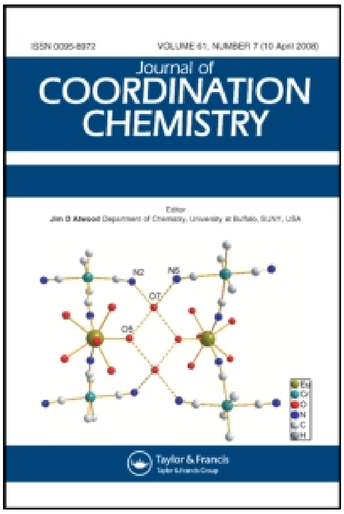

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STUDY ON THE PSEUDOTETRAHEDRAL AND TETRAHEDRAL COBALT(II) COMPLEXES

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STUDY ON THE PSEUDOTETRAHEDRAL AND TETRAHEDRAL COBALT(II) COMPLEXES

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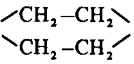
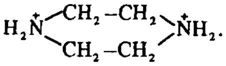
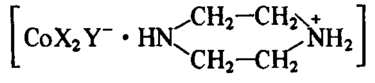
Pseudotetrahedral zwitterionic complexes of stoichiometry $CoX_3(L_N^+)$(X = Cl, Br and I) and $CoX_2Y(L_N^+)$ (X = Cl and Y = Br and I; X = Br and Y = I), where L_N^+ represents the cationic ligand  were prepared and tetrahedral complexes of stoichiometry $CoX_4(L^{2+})$, where X = Cl, Br and I and L^{2+} represents the cationic ligand . In the pseudotetrahedral zwitterionic complexes, the electronic spectra may be assigned assuming an effective C_{3v} symmetry and the low symmetry ligand field is proposed to be less important than the spin-orbit coupling effects, vibronic coupling and Jahn–Teller distortions. The i.r. spectra of the zwitterionic complexes suggest a lack of influence of the cationic site on the ligand properties of the donor atom. The magnetic properties and electronic spectra of the $CoX_4(L^{2+})$ complexes were correlated and the ligand field strength (10Dq), the Racah parameters (B′) and the spin-orbit coupling constants (λ′) were calculated. From B′ and λ′ we obtained evidence that appreciable overlap of metal and ligand orbitals occurs in these complexes. In addition the far i.r. spectra and tentative assignments of Co–X and Co–N absorption are also discussed.

INTRODUCTION

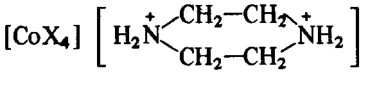
The chemical behaviour of the hydrohalide salts of piperazine, piperidine and morpholine was recently investigated by studying their tetrahalo- and mixed-tetrahalo-cuprates.[1, 2] These complexes showed two types of geometries: the planar and the tetrahedral, depending on NH . . . X hydrogen bonding interactions. In particular with the piperazinium dictation some complexes, having thermocromic behavior were found to present both geometries. In the present paper we wish to report the results obtained upon reaction of the piperazinium monocation (L_N^+) and piperazinium dictation (L^{2+}) with cobalt halides i.e., the formation of the zwitterionic complexes



$$\left[CoX_2Y^- \cdot HN\begin{matrix}CH_2-CH_2\\CH_2-CH_2\end{matrix}\overset{+}{N}H_2\right]$$

(X = Y = Cl, Br, I; X = Cl and Y = Br, I; X = Br and Y = I)

and the tetrahalo-cobaltate complexes



$$[CoX_4]\left[H_2\overset{+}{N}\begin{matrix}CH_2-CH_2\\CH_2-CH_2\end{matrix}\overset{+}{N}H_2\right]$$

(X=Cl, Br, I)

The nature of the distortion of these complexes and the possible influence of a positive charge transmitted via a saturated organic bridge to a donor atom are investigated.

EXPERIMENTAL

The piperazinium dihydro- and monohydrohalides were prepared as previously described.[2]

Preparation of the Complexes

$CoCl_3(L_N^+)$ and $CoCl_2Br(L_N^+)$ complexes were obtained by adding a methanolic solution of $CoCl_2 \cdot 6H_2O$ to a boiling solution of the piperazinium monohydrochloride or monohydrobromide, respectively, in methanol. In these preparations the metal to ligand molar ratio was 1:2.

$CoBr_3(L_N^+)$, $CoBr_2I(L_N^+)$, $CoCl_2I(L_N^+)$ and $CoI_3(L_N^+)$ complexes were obtained as mentioned above, by starting from ethanolic solution of the metal salt ($CoBr_2 \cdot 2H_2O$ in the former two complexes, $CoCl_2 \cdot 6H_2O$ and $CoI_2 \cdot 4H_2O$, respectively, in the

others) and from an ethanolic solution of the piperazinium monohydrobromide in the first complex and piperazinium monohydroiodide in the others.

$CoCl_4(L^{2+})$ complex was prepared by mixing a warm solution of $CoCl_2 \cdot 6H_2O$ (1 mM) salt with a boiling ethanolic–methanolic (1:1) solution of piperazinium dihydrochloride (4 mM).

$CoBr_4(L^{2+})$ complex was prepared by mixing a boiling ethanolic solution of $CoBr_2 \cdot 2H_2O$ salt (1 mM) in methylcellosolve and the piperazinium dihydrobromide (1 mM) in the same solvent. On cooling at 4–5°C a blue compound precipitated.

$CoI_4(L^{2+})$ complex was prepared by mixing a boiling ethanolic solution of $CoI_2 \cdot 4H_2O$ salt to a piperazine excess and adding hydrogen iodide until complete reaction was obtained. A green compound precipitated instantaneously.

Physical Measurements and Analyses

The electronic spectra of the solid compounds were recorded with a Shimadzu MPS 50L spectrophotometer. Samples were prepared by grinding the complexes on a filter paper as support. The infrared spectra of KBr pellets were recorded with a Perkin–Elmer 521 (4000–250 cm^{-1}) and the far-infrared spectra of nujol mulls with a Perkin–Elmer FIS3 (400–30 cm^{-1}) spectrophotometer.

The room-temperature magnetic moments were measured by the Gouy method by using $HgCo(NCS)_4$ or $Ni(en)_3S_2O_3$ as calibrants and correcting for diamagnetism with the appropriate Pascal constants.[3,4] The $CoX_4(L^{2+})$ magnetisms were also corrected for the temperature independent paramagnetism (TIP).[5]

Analyses

Nitrogen, carbon and hydrogen were analysed using a Perkin–Elmer 240 Elemental Analyser by Mr. G. Pistoni. The halogens were directly analysed on the aqueous solution of the complexes with the Volhard method.

RESULTS AND DISCUSSION

The compounds we studied are listed in Table I, which gives their colors, melting points and analytical data. All the complexes are sufficiently stable in the solid state to be handled in air, except the highly hygroscopic $CoI_4(L^{2+})$ complex.

TABLE I
Analytical data

		Co %		C %		H %		N %		X %		M.P. °C
		calcd.	found	calcd.	found	calcd.	found	calcd.	found	calcd.	found	
$CoCl_4(L^{2+})$	blue	20.40	20.34	16.62	16.88	4.19	4.20	9.70	9.71	49.10	49.06	350
$CoBr_4(L^{2+})$	blue	12.63	12.65	10.28	10.73	2.59	2.63	6.00	6.16	68.49	68.30	341–4d
$CoI_4(L^{2+})$	green	9.00	8.69	7.39	7.66	1.85	2.18	4.28	4.13	77.54	77.91	270–3d
$CoCl_3(L_N^+)$	blue	23.26	22.91	18.94	19.08	4.77	4.86	11.05	11.29	41.97	41.60	330–3d
$CoBr_3(L_N^+)$	blue	15.24	14.96	12.41	12.40	3.13	3.29	7.24	7.36	61.98	61.55	331–3d
$CoI_3(L_N^+)$	green	11.17	11.26	9.09	9.21	2.29	2.26	5.31	5.51	72.14	72.35	308–11d
$CoCl_2Br(L_N^+)$	blue	19.79	19.75	16.11	16.33	4.06	4.08	9.40	9.20			323–7d
$CoCl_2I(L_N^+)$	blue	17.09	16.98	13.92	14.00	3.51	3.52	8.12	8.21			319–22d
$CoBr_2I(L_N^+)$	blue-green	13.59	13.27	11.06	11.08	2.78	2.81	6.45	6.30			326–9d

The room-temperature magnetic susceptibilities of the complexes (Tables IV and V) from 4.34–4.83 B.M. fall in the range acceptable for d^7 Co(II) in a tetrahedral (T_d) or pseudotetrahedral (C_{3v} or C_s) ligand field. The increase in the moments in the series Cl < Br < I reflects the increased contribution to the moment due to spin-orbit coupling.

Electronic Spectra

The d–d electronic spectral data of the solid compounds, reported in Table II, provides the most important information about the nature of these complexes. Most of the complexes show absorption in the 4000 cm^{-1} region due to vibrational overtones, which were identified by comparison with the spectra of the hydrohalide salts. These bands are generally weak compared with those due to the electronic transitions.

In crystal fields of symmetry lower than T_d the orbital triplet levels are split as shown in Table III.

In discussing the electronic spectra of the compounds, the following notation will be used: $^4A_2 \rightarrow {}^4T_2 = \nu_1$, $^4A_2 \rightarrow {}^4T_1(F) = \nu_2$, $^4A_2 \rightarrow {}^4T_1(P) = \nu_3$.

Complexes of C_{3v} and C_s symmetry. In this section we consider the $CoX_3(L_N^+)$ (X = Cl, Br and I) and $CoX_2Y(L_N^+)$ (X = Cl and Y = Br and I; X = Br and Y = I) complexes. If we assign to these complexes a C_{3v} and C_s symmetry, respectively, the number of the bands, as expected from orbital calculation due to the trigonal splitting of the quartet states of the d^7 configuration in pseudotetrahedral symmetry is reported in Table III. In our complexes the number of experimental band components of ν_2 and ν_3 (Table II and Figures 1 and 2) is larger than expected for $CoX_3(L_N^+)$ and for $CoX_2Y(L_N^+)$ complexes.

TABLE III
Symmetry correlations for T_d, C_{3v} and C_s symmetries

T_d	C_{3v}	C_s
A_2	A_2	A″
T_1	$A_2 + E$	A′ + 2A″
T_2	$A_1 + E$	2A′ + A″

The low energy bands in the $CoX_3(L_N^+)$ complexes, which arise from the trigonally split $T_1(F)$ state, are well separated; therefore we may assign the bands in the 4000–5100 cm^{-1} region to the $^4A_2(F) \rightarrow {}^4A_2(T_1,F)$ and the bands in the 6000–8000 cm^{-1} region to the $^4A_2(F) \rightarrow {}^4E(T_1,F)$.

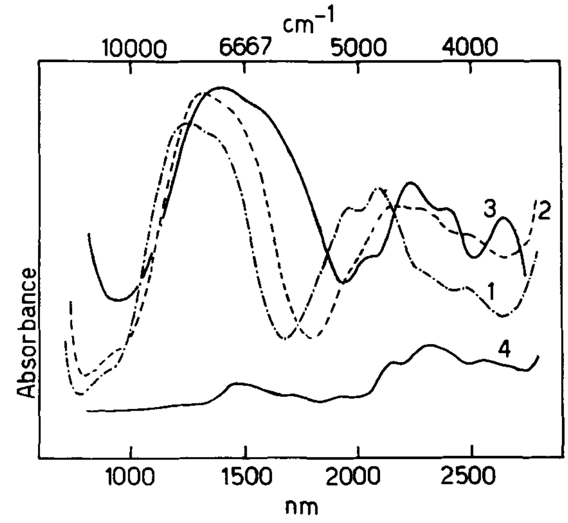


FIGURE 1 Electronic spectra of the solid psudotetrahedral $CoCl_3(L_N^+)$ (–·–), $CoBr_3(L_N^+)$ (– – –) and $CoI_3(L_N^+)$ (——) complexes.

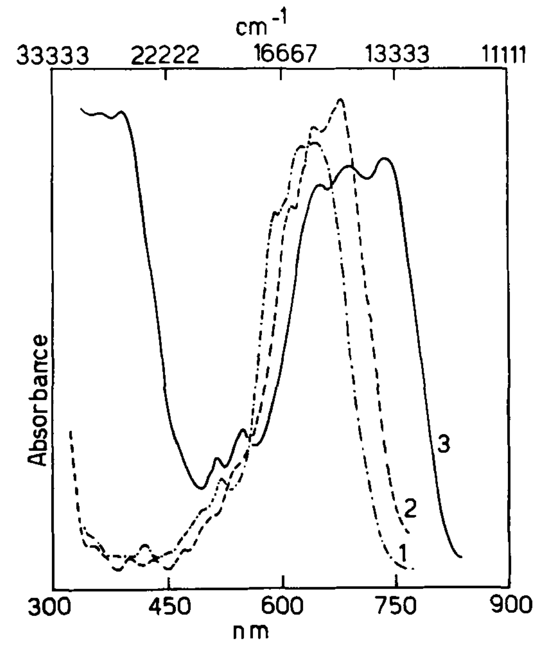


FIGURE 2 Electronic spectra of the solid pseudotetrahedral $CoCl_3(L_N^+)$ (–·–), $CoBr_3(L_N^+)$ (– – –) and $CoI_3(L_N^+)$ (——) complexes.

The ν_3 is a multicomponent absorption and, as an accurate band assignment in the reduced symmetry is not possible, the crystal field parameters Dσ, which is the only contributor to the $T_1(P)$ state and is derivable directly from the spectra,[6] may not be measured.

TABLE II
Spectral data (cm^{-1}) of the solid complexes[a]

	ν_2			ν_3		
$CoCl_4(L^{2+})$	4720(43) 4980(46) 5490(50) 6210(51)			14750(101) 16390(88	15380sh(98) 16580sh(74)	17700sh(13) 18480sh(11) 19120(18) 20280sh(9) 22620(6) 24810(2) 26810(3)
$CoBr_4(L^{2+})$	4690sh(47) 5130(49) 6060(48)			14180(92) 15290(83)	14710sh(85) 15870sh(68)	16950(19) 17610(18) 18080(18) 19010sh(17) 20410sh(5) 22320sh(4) 23260(17) 25190(4) 22030sh(50) 27780(1)
$CoI_4(L^{2+})$	4610(53) 5050(53)			12820(89) 14600(73	13700sh(79)	16000sh(17) 17240sh(8) 18280(8) 19230(11) 20210(19) 20660sh(16) 21320(29) 22030sh(50) 25970(99)
$CoCl_3(L_N^+)$	4760(34) 5100(33)	7090sh(39) 7940(41)	10200sh(4)	15550(79) 16920(67)	16000(78) 18590sh(11)	19340(10) 20040sh(7) 20530sh(5) 22470(3) 23920(4) 25970(1) 28170sh(5)
$CoBr_3(L_N^+)$	4650(38) 5100sh(25)	6760sh(53) 7520(54)	12200sh(7)	14750(85) 15590sh(74)	15630(80) 16390sh(68)	18520sh(18) 19490(12) 20200sh(9) 21230(6) 22990(5) 24880(5) 26740sh(5) 28250(7)
$CoI_3(L_N^+)$	4180sh(26) 4510(30) 4940sh(18)	6170sh(50) 7140(58)		13610(74) 15460(68)	14490(72)	16670sh(40) 18180(30) 19460(25) 21460sh(25) 22620(60) 25580(84) 28170(85)
$CoCl_2Br(L_N^+)$	4740(46) 5050(43)	6450sh(53) 7630(54)		15040(85) 16670sh(73)	16030sh(80)	19050sh(25) 20330sh(16) 23310(10) 25250(11) 28250(10)
$CoCl_2I(L_N^+)$	1720(40) 5050sh(38)	6670sh(59) 7520(64)		14810(100) 16420(94)	15650sh(97)	18690sh(35) 19610(23) 21460(19) 22940(22) 24630sh(50) 29410(116)
$CoBr_2I(L_N^+)$	4330(41) 4610(39) 5130sh(21)	6540sh(55) 7250(59)		14330(87) 15870sh(74)	15150sh(83)	19230sh(22) 20410(18) 26320sh(89)

[a] In parenthesis are reported the relative absorbance in arbitrary scale.

TABLE IV
Magnetic moments and band splittings (cm^{-1}) in some pseudotetrahedral cobalt(II) complexes

		$^4T_1(F)$			
	μ_{eff}	A_2	E	Δ^a	$D\tau$ (approx.)
$CoCl_3(L_N^+)$	4.31	4930	7630	2700	270
$CoBr_3(L_N^+)$	4.47	4590	7300	2710	270
$CoI_3(L_N^+)$	4.66	4390	6940	2550	255
$CoCl_2Br(L_N^+)$	4.41	4820	7410	2590	260
$CoCl_2I(L_N^+)$	4.46	4810	7250	2440	244
$CoBr_2I(L_N^+)$	4.41	4390	6990	2600	260

$^a\Delta = {}^4E(T_1, F) - {}^4A_2(T_1, F)$.

From the splitting of the band arising from transitions to components of the $^4T_1(F)$ level, we may calculate an approximate value of the crystal field parameter $D\tau$, which gives a measure of the trigonal distortion.

The selected A_2 and E bands, obtained from the weighted center of the multicomponent ν_2 bands, and the $D\tau$ parameter are reported in Table IV together with the room-temperature magnetic moments.

For a series of trigonally distorted pseudotetrahedral $[MX_3L]$ complexes of the same ion, the magnitude of the crystal field parameter $D\tau$ will be related to the difference in field strength between the unique ligand L and the three ligands X.[6] While in our complexes the absorption maxima shift toward lower energies as X changes from Cl to I, as expected on the basis of the relative positions of the halides in the spectrochemical series, on the contrary practically identical values of $D\tau$ are observed, although they contain ligands of appreciable spectrochemical difference such as Cl, Br and I.

This may suggest that the lower symmetry effects on the orbital energy levels are only in part responsible for the presence of the components of the T bands of trigonal (CoX_3L) complexes. Although the high $D\tau$ values may indicate the contrary, their similarity suggests a negligible effect of a low symmetry component of the crystal field.

If the lower symmetry effects on the orbital energy levels were the principal factor responsible for the splitting of the T bands, the electronic spectra of the $CoX_2Y(L_N^+)$ complexes should be quite different from those of the trigonal $CoX_3(L_N^+)$ complexes. On the other hand the spectra are identical with one another, and the electronic spectra of the $CoX_2Y(L_N^+)$ complexes (Table II) may also be explained on the basis of a C_{3v} symmetry, instead of an expected C_s symmetry. The $D\tau$ parameters of these complexes are also reported in Table IV and no substantial difference of distortion is found between the $CoX_3(L_N^+)$ and $CoX_2Y(L_N^+)$ complexes.

The similarity of the electronic spectra of the $CoX_3(L_N^+)$ and $CoX_2Y(L_N^+)$ complexes may be explained considering that the substitution occurs among the halides, which, being σ only ligands, have similar effect. The change in the M—X bond lengths causes the slight red shift of the d—d bands, as it was experimentally observed in the distorted tetrahedral $CuX_mY_n^{2-}$ $(m + n = 4)$ complexes.[1,2] This hypothesis also explains the difference between the spectra of the pseudotetrahedral $CoX_3(L_N^+)$ and $CoX_2Y(L_N^+)$ complexes and the tetrahedral CoX_4^{2-} complexes, which may be due to a reasonable π component of bonding in the metal–nitrogen bond, when a halide around the cobalt(II) ion in the CoX_4^{2-} complexes is replaced by a nitrogen atom.

Vibronic coupling effects, spin-orbit-coupling effects and Jahn–Teller distortions could account for most basic features of the structures of d—d bands in our pseudotetrahedral cobalt (II) complexes in a greater part than the geometry effects. We suppose that the spin-orbit coupling effects and the Jahn–Teller distortions contribute in the same amount. In fact the width of the d—d bands (300–700 cm^{-1}) in the near-infrared spectra of these complexes is too large to be only attributable to the spin-orbit coupling effects, considering that the magnitude of the spin-orbit coupling constant for the Co^{2+} ion is 178 cm^{-1}, but too narrow to be only attributable to the Jahn–Teller distortions.[7]

TABLE V
Spectral and magnetic data and derived electronic structure parameters for the tetrahalo–cobalt(II) complexes

	ν_2 cm^{-1}	ν_3 cm^{-1}	Dq cm^{-1}	B′ cm^{-1}	$\beta(B'/B^a)$	TIP c.g.s. units × 10^{+6}	μ B.M.	λ'^b cm^{-1}
$CoCl_4(L^{2+})$	5500	14750	315	719	0.744	663	4.71	166
$CoBr_4(L^{2+})$	5050	14190	289	705	0.729	723	4.78	165
$CoI_4(L^{2+})$	4760	12740	273	621	0.642	766	4.83	165

^{a}B (free ion) = 967 cm^{-1}.
$^b\lambda'$ These parameters were calculated omitting the θ values, λ (free ion) = 178 cm^{-1}.

Furthermore there is one important feature worth pointing out concerning the electronic spectra of these complexes. A blue shift of the ν_3 band is found on going from CoX_4^{2-} to $CoX_3(L_N^+)$ in agreement with that predicted for similar complexes.[7]

As in the $CoX_4(L^{2+})$ complexes, described below, the series of weak intensity bands at higher energies than the ν_3 bands is probably due to spin-forbidden transitions. In the $CoI_3(L_N^+)$, $CoCl_2I(L_N^+)$ and $CoBr_2I(L_N^+)$ complexes the high-intensity bands at 28170, 29410 and 26320 cm^{-1}, respectively, may be due to charge-transfer transitions.

Complexes of T_d symmetry. The spectra of the $CoX_4(L^{2+})$ derivatives (shown in Figures 3 and 4 and reported in Table II) show the characteristic long visible wave length absorption (ν_3) which usually is found for tetrahedral Co(II) compounds. They also exhibit the multicomponent absorption in the 10000 to 5000 cm^{-1} range (ν_2) found for Co(II) in tetrahedral surroundings.

The complex splitting patterns of the ligand field bands in the spectra of tetrahedral cobalt(II) complexes can be due to different effects such as spin-orbit coupling, vibronic coupling, Jahn–Teller distortions of the excited states, mixing of ${}^2G$ states with the ${}^4P$ quartets and orbital splitting due to low symmetry of the ligand field. None of these factors alone can account satisfactorily for the experimental number and type of band components. Each of the above mentioned factors has received, more or less in isolation, attention in the literature. For tetrahedral Co(II) complexes the most detailed data is that on the $CoCl_4^{2-}$ ion (8), where it was found that the splitting of orbitally degenerate excited electronic states is dominated by low symmetry components (C_s) of the crystal field, rather than by spin-orbit coupling. Orbital splittings in pseudotetrahedral Co(II) complexes of lower symmetry were reported and discussed by some authors.[6–14]

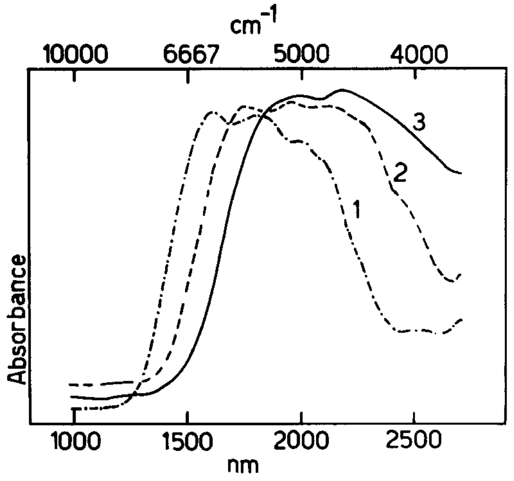


FIGURE 3 Electronic spectra of the solid tetrahedral $CoCl_4(L^{2+})$ (–··–), $CoBr_4(L^{2+})$ (– – –), $CoI_4(L^{2+})$ (——) complexes.

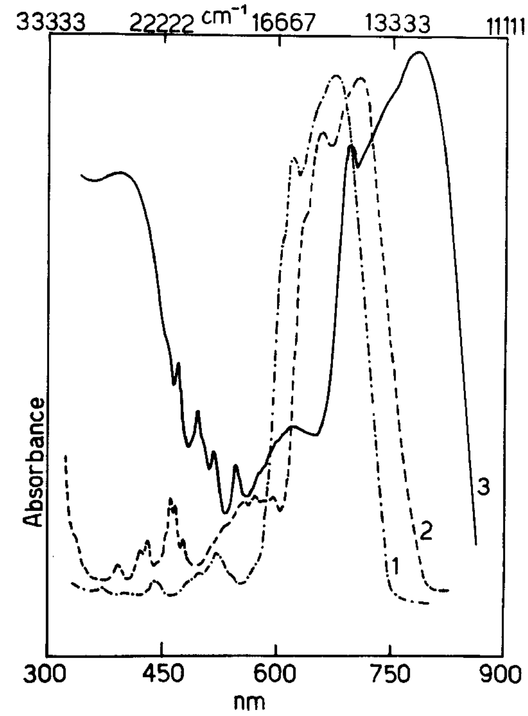


FIGURE 4 Electronic spectra of the solid tetrahedral $CoCl_4(L^{2+})$ (–··–), $CoBr_4(L^{2+})$ (– – –), $CoI_4(L^{2+})$ (——) complexes.

In our complexes the modulus of the ligand field strength 10Dq and the effective value of the Racah interelectronic repulsion integral B′ were calculated from the weighted center of the ν_2 and ν_3 bands by using the Tanabe and Sugano matrices as previously described.[12] From the magnetic susceptibility values corrected for the diamagnetism using Pascal's constants[15] and for temperature independent paramagnetism (TIP) (the TIP in tetrahedral cobalt(II) is given by $8N\beta^2/\Delta = 2.09/\Delta$[16]) and the 10Dq values, the approximate values of the spin-orbit coupling constants λ' of the complexes are calculated from the equation $\mu = 3.89 - 15.56\lambda'/\Delta$.[16]

All the parameters are summarized in Table V and clearly indicate crystal field strengths of the order $I^- < Br^- < Cl^-$ and closely agree with the values reported for other CoX_4^{2-}.[12,17,18] The B′ values which are of the order of 65 to 75% of the free ion value and the λ′ values (165–166 cm^{-1}) compared to the free ion 178 cm^{-1} for all the complexes, suggest that there is appreciable orbital overlap.

The series of weak bands between 17700–26810 16950–27780 and 16000–25970 cm^{-1} in the chloride, bromide and iodide complexes, respectively, is probably due to transitions to various components of such states as ^2G, ^2H and ^2D. No attempts were made to identify these bands any further, since distortion would preclude any accurate assignment. The last band in the $CoI_4(L^{2+})$ complex at 25970 cm^{-1} is most probably due to a charge–transfer process, as its high intensity suggests.[12,19,20]

Infrared Spectra

In the infrared spectra (4000–400 cm^{-1} region) we have previously found[2] stronger hydrogen-bonding in the $CuX_4(L^+ \cdot HX)_2$ complexes having square planar geometry than in the $CuX_4(L^{2+})$ having tetrahedral geometry by the shift of the N–H bending modes appearing at 914–930 and 560–570 cm^{-1} in the dihydrohalide salts. The $CoX_4(L^{2+})$ complexes have infrared spectra very similar to those of the tetrahedral $CuX_4(L^{2+})$ complexes. NH . . . X hydrogen bonding of strength similar to that found in the dihydrohalide salts is sufficient to stabilize the tetrahedral geometry in these complexes.

In the piperazinium monohydrohalide salt spectra a considerable number of i.r. bands are present. In these salts in the 4000–2000 cm^{-1} region the NH and $\overset{+}{N}H_2$ bands are well separated, the former appearing at 3200–3000 cm^{-1} and the latter at 2750–2300 cm^{-1}, as supported by shift of these bands at 2450–2150 and 2000–1700 cm^{-1}, respectively, in the deuteriated salts. The NH stretching frequencies are greatly reduced in frequency, with respect to free piperazine (ν(NH) 3350 cm^{-1})[21] indicating strong interactions of this group with others in the free ligands. The further lowering of these bands of 15–60 cm^{-1} in the cobalt complexes indicates that this group is involved in the cobalt coordination.

In the 1600–1540, 1110–1000, 900–800 and 500–400 cm^{-1} regions in the monohydrohalide salts some multiple bands appear, shifting to lower energies on deuteration and assignable to the bending of the indistinguished NH or $\overset{+}{N}H_2$ groups.

In the complexes only one sharp band appears in the above cited regions. These absorption maxima shift slowly (10–15 cm^{-1}) toward lower energies as X changes from Cl to I. This is probably indicative of an apparent lack of influence of the positive site on the ligand properties of the donor atom. This observation has been pointed out in other zwitterionic complexes[5] and appears to be quite general for all such systems in which the donor atom, L, and the cationic charge, L$^+$, are separated by a saturated organic skeleton.

Far i.r. Spectra

The far i.r. spectra for the complexes and the appropriate starting amine hydrohalide salts are listed and assigned in Table VI.

Since several sets of compounds of the same stereochemistry were available in which the halogen varied from Cl to Br to I, it was possible to assign the metal–halogen stretching vibrations (Table VI) with reasonable certainty. For the tetrahedral complexes the ratios: ν(M–Br)/ν(M–Cl) and ν(M–I)/ν(M–Cl), were about 0.75 and 0.65[22].

The far i.r. spectra of the $CoX_4(L^{2+})$ complexes are in excellent agreement with values quoted for tetrahedral tetrahalo cobalt(II).[23–26] Observed splittings of the fundamental i.r. active ν(Co–X) vibration may be attributed to crystal effects.[25]

For molecules of the type $CoX_3(L_N^+)$ (C_{3v} symmetry), two ν(M–X) and one ν(M–L) vibrations are expected to be infrared active[22] and for molecules of the type $CoX_2Y(L_N^+)$ (C_s symmetry) two ν(M–X), one ν(M–Y) and one ν(M–L) vibrations are expected to be i.r. active. In both the complexes the ν(M–Hal) vibrations are tentatively assigned and the number of experimental bands found to be equal to the theoretical bands support the assignment.

We had greater difficulty in assigning the ν(Co–N) vibration. By comparison of the far i.r. spectra of these complexes with those of the $CoX_4(L^{2+})$ complexes, we observe two absorption regions at 316–275 and 230–220 cm^{-1} in which bands appear, assignable to ν(Co–N) vibration. In the 230–220 cm^{-1} region only one band, absent in the $CoX_4(L^{2+})$ complexes, appears. On the assumption that, for a series of compounds of the same stereochemistry, the ν(M–L) vibrations will occur at approximately the same frequencies in the chloro, bromo and iodo analogs of a given metal, in the absence of significant coupling with ν(M–X) vibrations, we tentatively assign this band to the theoretically expected ν(Co–N) stretching band. This assignment is also supported as in this region the Co–N vibrations of other pseudotetrahedral complexes of the cobalt(II) with pyrazine[27] (ν(Co–N) 250–230 cm^{-1}), thiazole and 4-methylthiazole (ν(Co–N) 250 cm^{-1})[28] and pyridines (ν(Co–N) 252–246 cm^{-1})[22] appear.

TABLE VI
Far-infrared spectra (400–60 cm^{-1}) of the cationic ligands and the complexes^a

	ν(Co–Cl)		ν(Co–Br)		ν(Co–I)		ν(Co–N)	Other far i.r. bands
L · (HI)$_2$								371ms 271s 260sh 155mb 120vs
L · HCl								283m 210vs 175sb 107m 72m
L · HBr								330s 275s 185s 143m 113vs 64m
L · HI								318m 283w 250w 213sh 187vs 116vs 105sh 75m
CoCl$_4$(L^{2+})	312vs	292vs						260ms 167vs 150sh 99m 68w
CoBr$_4$(L^{2+})			240sh	224vs				260ms 137vs 105w 93w 70w
CoI$_4$(L^{2+})					197	186vs		250vs 120s 86w 72w
CoCl$_3$(L$\overset{+}{\text{N}}$)	329vs	313vs					222m	303sh 283m 172w 118w
CoBr$_3$(L$\overset{+}{\text{N}}$)			254sh	245s			226m	315w 302w 276wb 178w 154w 120w
CoI$_3$(L$\overset{+}{\text{N}}$)					220s	208vs	232sh	306m 280w 138m 112m 72m
CoCl$_2$Br(L$\overset{+}{\text{N}}$)	311vs	300s	250mb				230m	330sh 283sh 208w 166m 114s
CoCl$_2$I(L$\overset{+}{\text{N}}$)	321vs	298vs			195m		226m	280sh 260m 155sb 115s 86w 72w
CoBr$_2$I(L$\overset{+}{\text{N}}$)			245ms	225s	209m		(225s)	316w 300vw 280w 175w 150ms 114ms 92s

^{a}The spectra of the L(HX)$_2$ (X=Cl and Br) are reported in ref. 2.

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