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# Electronic, Infrared and Far-infrared Study on Pseudotetrahedral Cobalt(II) Zwitterion Complexes

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*Some complexes of the type* $CoX_3(L_N^+)$ *(X = Cl, Br, I) and* $CoX_2Y(L_N^+)$ *(X = Cl, Br; Y = Br, I; X ≠ Y;* $L_N^+$ *= monoprotonated 1-methyl and 2-methylpiperazine) were prepared and investigated by means of magnetic and spectroscopic measurements. All the magnetic and spectroscopic results indicate that* $CoX_3(L_N^+)$ *complexes possess a pseudotetrahedral* $C_{3v}$ *symmetry and the* $CoX_2Y(L_N^+)$ *complexes a* $C_s$ *symmetry. On the basis of these symmetries the bands of their electronic spectra are assigned. Particular attention is paid in this work to the far-infrared spectra and the Co–X, Co–Y and Co–N vibrations of all the complexes are assigned with a reasonable certainty. Tentative assignments of the bending modes of the* $CoX_3(L_N^+)$ *complexes are also made. The influence of a positive charge of the ligand on the donor properties of a nitrogen atom is also investigated.*

## Introduction

Compared with the extensive number of investigations of transition metal complexes with neutral and anionic ligands, relatively few studies with positively charged ligands have been reported. The only planned efforts have been made by Quagliano and coworkers [1–3], who studied the complexes of positively charged amines with transition metal ions, while few examples of complexes, in which a "soft" donor positive-ion ligand is coordinated with metal ions, have been reported [3–6].

In the framework of our systematic studies on the chemical behaviour of piperazine, piperidine and morpholine with metal halides [7, 8] and of their hydrohalide salts with transition metal halides [9–11], we have also investigated the coordination ability of the monoprotonated piperazinium cation [12].

In this paper we report the results obtained upon reaction of the monoprotonated 1-methyl-piperazinium ($1L_N^+$) and 2-methyl-piperazinium ($2L_N^+$) cations with cobalt(II) halides in order to study the influence of the positive charge and of the substituent on the ligand coordination ability and the nature of the distortions of the prepared complexes. These ligands were chosen as having very similar structural and inductive effect; they enable us to observe the effect of the positively charged group on the nitrogen donor.

## Experimental

### *Preparation of the Cation-ligand*

The preparation of the dihydrohalide salts, which are the starting materials, has been previously described [11]. The monoprotonated salts were obtained by adding a stoichiometric amount of an ethanolic amine solution to a dihydrohalide salt solution, by heating until a limpid solution was obtained and by adding diethyl ether.

### *Preparation of the Complexes*

The $CoX_3(L_N^+)$ (X = Cl, Br, I) complexes were prepared by adding an ethanolic solution of the cobalt(II) halides to a boiling ethanolic solution of the corresponding monohydrohalide salt. The $CoX_2Y(L_N^+)$ (X = Cl, Br; Y = Br, I; X ≠ Y) complexes were obtained by mixing an ethanolic solution of monohydro-bromide or iodide salt with an ethanolic solution of cobalt(II) chloride or an ethanolic solution of monohydroiodide salt with an ethanolic solution of cobalt(II) bromide.

### *Physical Measurements*

The room-temperature 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 KCl or KBr pellets and hexachlorobutadiene mulls (4000–500 $cm^{-1}$) or nujol mulls (600–250 $cm^{-1}$) were recorded with a Perkin Elmer 521 spectrophotometer and the far-infrared spectra of nujol mulls (400–60 $cm^{-1}$) with a Perkin Elmer FIS3 spectrophotometer.

TABLE I. Analytical Results

| | | Co% | | C% | | H% | | N% | | X% | | M.P. (°C) | $\lambda_m$[a] (S cm$^2$ mol$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | found | calcd | found | calcd | found | calcd | found | calcd | found | calcd | | |
| $CoCl_3(1L_N^+)$ | Blue | 22.22 | 22.11 | 23.01 | 22.52 | 4.93 | 4.92 | 10.69 | 10.52 | 40.08 | 39.93 | 304–6 | 43 |
| $CoBr_3(1L_N^+)$ | Blue | 14.76 | 14.74 | 15.21 | 15.01 | 3.33 | 3.28 | 7.32 | 7.01 | 60.06 | 59.97 | 318–20 | 66 |
| $CoI_3(1L_N^+)$ | Green | 10.70 | 10.89 | 11.38 | 11.10 | 2.65 | 2.42 | 5.08 | 5.18 | 70.76 | 70.41 | 296–8 dec. | dec. |
| $CoCl_2Br(1L_N^+)$ | Blue | 18.22 | 18.95 | 19.62 | 19.30 | 4.41 | 4.22 | 9.19 | 9.01 | | | 296–8 | 51 |
| $CoClBr_2(1L_N^+)$ | Blue | 16.45 | 16.58 | 17.36 | 16.89 | 3.96 | 3.69 | 8.14 | 7.89 | | | >350 | 60 |
| $CoCl_2I(1L_N^+)$ | Blue | 16.99 | 16.46 | 17.66 | 16.77 | 4.42 | 3.66 | 8.23 | 7.83 | | | 275–7 | 67 |
| $CoBr_2I(1L_N^+)$ | Blue | 13.19 | 13.19 | 13.60 | 13.43 | 3.10 | 2.93 | 6.36 | 6.27 | | | >350 | 87 |
| $CoCl_3(2L_N^+)\cdot EtOH$ | Blue | 17.98 | 18.85 | 26.09 | 26.88 | 6.20 | 6.13 | 9.70 | 8.97 | 35.48 | 34.04 | 300–2 | 30 |
| $CoBr_3(2L_N^+)\cdot EtOH$ | Blue | 13.28 | 13.21 | 18.52 | 18.84 | 4.09 | 4.30 | 6.23 | 6.28 | 53.93 | 53.78 | 336–9 | 59 |
| $CoI_3(2L_N^+)\cdot EtOH$ | Green | 10.36 | 10.03 | 13.92 | 14.31 | 3.72 | 3.26 | 4.75 | 4.77 | 65.12 | 64.88 | 290–2dec. | dec. |
| $CoCl_2Br(2L_N^+)$ | Blue | 18.70 | 18.95 | 18.74 | 19.30 | 4.27 | 4.22 | 8.60 | 9.01 | | | 327–9 | 38 |
| $CoCl_2I(2L_N^+)$ | Blue | 17.15 | 16.46 | 16.12 | 16.77 | 4.16 | 3.66 | 7.23 | 7.83 | | | 292–4 | 57 |
| $CoBr_2I(2L_N^+)$ | Blue | 13.07 | 13.19 | 13.30 | 13.43 | 3.14 | 2.93 | 6.12 | 6.27 | | | 295–7 | 75 |

[a] $10^{-3}$ molar in dimethylformamide solution.

TABLE II. Spectral Data (cm$^{-1}$) of the Solid Complexes[a].

| | | $^4A_2(F) \rightarrow {}^4A_2(T_1, F)$ | $\rightarrow {}^4E(T_1, F)$ | $\rightarrow {}^4A_2(T_1, P), \rightarrow {}^4E(T_1, P)$ | |
|---|---|---|---|---|---|
| $CoCl_3(1L_N^+)$ | solid | 4740(24) | 7250sh (~42) 7870(45) | 15000(94) 16950sh (~80) | 18620sh (~38) 19420(42) 20000sh (~25)<br>20410(20) 21460sh (~16) 22220(14)<br>23810(16) 26040(17) 28010(18) |
| $CoCl_2Br(1L_N^+)$ | solid | 4650(29) 5850(5) | 700sh (~40) 7630(43) | 15310(76) 16130sh (~73) 16810sh (~63) | 19420sh (~25) 20830sh (~14) 23810(10)<br>25320(11) 27780sh (~12) |
| $CoClBr_2(1L_N^+)$ | solid | 4580(20) | 7410(49) | 15040(72) 15630sh (~68) 16660sh (~40) | 19610sh (~19) 20410sh (~10) 21510sh (~8)<br>23530(8) 25320(8) 27780(9) |
| $CoCl_2I(1L_N^+)$ | solid | 4610(18) 5840(4) | 7040sh (~40) 7580(44) | 15390(75) 16670sh (~65) | 19610(10) |
| $CoBr_3(1L_N^+)$ | solid | 4400(24) | 6250sh (~40) 7320(47) | 14930(85) 15630(81) 16530sh (~75) | 18420sh (~32) 19610(18) 21190(12)<br>23260(11) 24690(12) |
| $CoBr_2I(1L_N^+)$ | solid | 4310(28) | 6540sh (~45) 7190(52) | 14710(85) 16130sh (~74) | 19610sh (~18) 20410sh (~12) 28170sh (~92) |
| $CoI_3(1L_N^+)$ | solid | 4000(18) | 6170sh (~40) 6800(45) | 13510(58) 14540(56) 15270sh(50) | 18180(23) 19420(16) 20410sh (~15) 25970(86) |
| $CoCl_3(2L_N^+)$ | solid | 5150(22) | 7250(51) 8030(55) | 15270sh (~80) 16130(84) 17150(70) | 19460sh (~23) |
| $CoCl_2Br(2L_N^+)$ | solid | 5080(22) | 6990sh (~51) 7810(55) | 15390(120) 16810(105) | 19230sh (~30) 20410sh (~10) 22220(10)<br>23810(13) 25640sh (~15) |
| $CoCl_2I(2L_N^+)$ | solid | 4760(20) 5790(16) | 6890sh (~39) 7750(42) | 15080(96) 15750(87) 16670sh (~60) | 17240sh (40) 18870sh (~22) 19610(20)<br>21600 (16) 23100sh (21) 25130sh (45) |

| | | | | | |
|---|---|---|---|---|---|
| $CoBr_3(2L_N^+)$ | solid | 4720(21) | 6820sh (~53) 7410(58) | 14930(90) 15530sh (86) 16390(67) | 18520sh (~35) 19610sh (~24) 21600(20)<br>23260(22) 25000(24) 27030sh (~25) |
| $CoBr_2I(2L_N^+)$ | solid | 4650(21) 5880(15) | 6490sh (~34) 7460(41) | 14490(89) 15150(83) 16390sh (~70) | 19420sh (~21) 20620(13) 22730sh (~15) |
| $CoI_3(2L_N^+)$ | solid | 4310(19) | 6170sh (~42) 6890(51) | 13640(87) 14600(85) 15270sh (78) | 18020(37) 19610(32) 25000 sh<br>(~105) 25970(108) |

[a] The parenthesis contains the relative absorbance in arbitrary scale of the solid complexes.

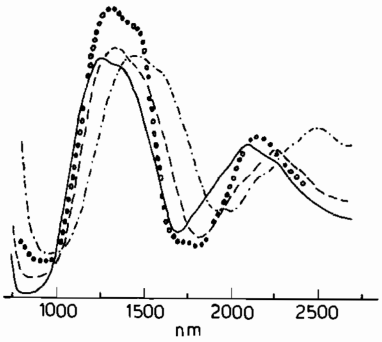

Figure 1. Electronic spectra of the solid pseudotetrahedral $CoCl_3(1L_N^+)$ (——), $CoBr_3(1L_N^+)$(-----), $CoI_3(1L_N^+)$ (-·-·-), $CoCl_2Br(1L_N^+)$ (·····) complexes.

The room-temperature magnetic susceptibilities were measured with 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. The conductivities of the complexes in dimethylformamide (DMF) solution were measured with a WTW (Wissenschaftlich-Technische Werkstatten) D 812 conductivity meter, LBR, at 25 °C.

### *Analyses*

Nitrogen, carbon and hydrogen were analysed using a Perkin Elmer 240 Elemental Analyser by Mr. Giuseppe Pistoni. Halogens were directly titrated in the aqueous solution of the complexes with the Volhard method.

## Results and Discussion

The physical characteristics of the compounds synthesized are given in Table I. All the compounds are crystalline, stable in air, virtually insoluble in non-polar organic solvents and decompose in water. The striking inorganic character of these complexes is also demonstrated by their thermal stability.

### *Electronic Spectra and Magnetic Moments (Tables II and III)*

A pseudotetrahedral stereochemistry may be assigned to all the complexes reported in this paper on the basis of their electronic spectra, which closely resemble those of other $CoX_3L$ complexes for which this type of structure has been well recognized [1–6]. (Figs. 1 and 2).

The symmetry of the metal–ligand environment in our complexes is approximately $C_{3v}$ and even lower in those cases where two different halides are coordinated. The reduction of symmetry from $T_d$ to $C_{3v}$ and $C_s$ should result in significant changes in the energy levels of the d electrons. Consequently, one would expect the orbital contribution to the magnetic moments to be smaller than for $T_d$, and the "d–d"

TABLE III. Magnetic Moments and Band Splittings (cm$^{-1}$) in Some Pseudotetrahedral Cobalt(II) Complexes.

| | $\mu_{eff}$ | $^4T_1(F)^a$ | | $\Delta^b$ | $D\tau$ (approx) |
|---|---|---|---|---|---|
| | | $A_2$ | E | | |
| $CoCl_3(1L_N^+)$ | 4.40 | 4720 | 7690 | 2970 | 300 |
| $CoCl_2Br(1L_N^+)$ | 4.48 | 4650 | 7520 | 2870 | 290 |
| $CoClBr_2(1L_N^+)$ | 4.50 | 4580 | 7410 | 2830 | 280 |
| $CoCl_2I(1L_N^+)$ | 4.55 | 4610 | 7460 | 2850 | 285 |
| $CoBr_3(1L_N^+)$ | 4.55 | 4400 | 7200 | 2800 | 280 |
| $CoBr_2I(1L_N^+)$ | 4.58 | 4310 | 7140 | 2830 | 280 |
| $CoI_3(1L'_N)$ | 4.62 | 4000 | 6730 | 2730 | 270 |
| $CoCl_3(2L_N^+)$ | 4.52 | 5150 | 7810 | 2660 | 265 |
| $CoCl_2Br(2L_N^+)$ | 4.57 | 5050 | 7550 | 2500 | 250 |
| $CoCl_2I(2L_N^+)$ | 4.66 | 4760 | 7410 | 2650 | 265 |
| $CoBr_3(2L_N^+)$ | 4.60 | 4720 | 7190 | 2470 | 250 |
| $CoBr_2I(2L_N^+)$ | 4.58 | 4650 | 7140 | 2490 | 250 |
| $CoI_3(2L_N^+)$ | 4.72 | 4310 | 6710 | 2400 | 240 |

$^a$The selected $A_2$ and E bands are obtained from the weighted center of the low-energy bands. $^b\Delta = {}^4E(T_1, F) - {}^4A_2(T_1, F)$.

electronic transitions to T states to be split into two and three components for $C_{3v}$ and $C_s$ symmetries, respectively. In fact the observed room-temperature magnetic moments of the complexes (Table III) are lower than those found for $T_d$ $CoX_4$(n-methylpiperazinium) complexes [11] and fall in the upper part of the range characteristic of cobalt(II) in a weak tetrahedral field [13]. The trend of the magnetic moment values, increasing in the sequence Cl < Br < I, is consistent with an increasing contribution to the "spin-only" value as the halide ligand field strength decreases [14, 15].

In the electronic spectra the low energy bands, which arise from the trigonally split $T_1(F)$ state, are well separated and may be assigned as reported in Table II. The d–d band appearing in the visible region (13500–17500 cm$^{-1}$) is a multicomponent absorption probably arising as a result of both spin–orbit coupling and the trigonal potential.

The crystal field parameter $D\tau$ which gives a measure of the trigonal distortion is obtained from the splitting from the $A_2$ and E bands [16, 17] (Table III) and, being a direct measure of the difference in Dq values between the halide X and the ligand L, suggests that the ligand field strength of the 1-methyl-piperazinium cation-ligand is greater than that of the 2-methyl-piperazinium cation-ligand. By comparing the $D\tau$ parameters with those of other substituted piperazinium cation-ligands we obtain this spectrochemical series: 1,1,4-trimethylpiperazine [18] ≅ 1,4-dimethylpiperazine [1] < piperazine [11] < 2-methylpiperazine < 1-methylpiperazine, consistent with a greater coordination ability of secondary nitrogen atom than the tertiary nitrogen atom.

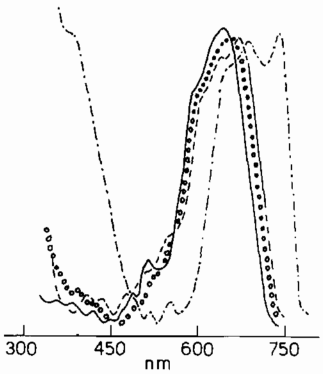

Figure 2. Electronic spectra of the pseudotetrahedral $CoCl_3(1L_N^+)$ (——), $CoBr_3(1L_N^+)$ (-----), $CoI_3(1L_N^+)$ (-·-·-), $CoCl_2Br(1L_N^+)$ (·····) complexes.

It is amply clearly demonstrated [1–6, 12, 19] that the presence of a positive charge on a cation-ligand has very little influence on the ligating character of the donor atom, although it favors the formation of the $CoX_3(L^+)$ complexes and contributes to their stability, as suggested by their high melting point and low solubility in non-polar solvents. However, the difference in the ligand field strength of our cation-ligands, which have the same coordination site, the same flexible structure and differ only in the position of the methyl group, is tentatively attributed to the effect of the positive charge on the cation-ligand exhibited by the presence of the methyl group in a different position: Another significant result of the present work is that the electronic spectra of the $CoX_3(L_N^+)$ and $CoX_2Y(L_N^+)$ complexes are identical with one another. This enables us to assign the spectra of the $CoX_2Y(L_N^+)$ complexes on the basis of a $C_{3v}$ symmetry, instead of an expected $C_s$ symmetry. This suggests that spin–orbit coupling effects are the principal factor responsible for the splitting of the T bands, prevailing on the geometry effects.

Spectra and electrical conductances of the complexes are measured in N,N'-dimethylformamide solution (Table 1). Molar conductances at 25 °C ranged from 30 to over 87 S cm$^2$ mol$^{-1}$ indicating that a significant amount of dissociation occurs. In fact the values increase in the series Cl < Br < I, consistent with the weaker ligand field strength and electronic density of the heavier halides.

The main difference of the electronic spectra in solution is the shift of the low energy bands at lower energies than in the spectra of the solid, indicating the existence of a solvation equilibrium [3, 5].

### *Infrared Spectra*

In the amine monohydrohalides a complex series of absorptions are found at 2900–2400 cm$^{-1}$ region

TABLE IV. Correlation of $T_d$ Symmetry with $C_{3v}$, $C_{2v}$ and $C_s$ Symmetries for the Normal Modes of Vibrations[a].

| $T_d$<br>$MX_4$ | $C_{3v}$<br>$MX_3Z$ | $C_{2v}$<br>$MX_2Z_2$ | $C_s$<br>$MX_2YZ$ |
|---|---|---|---|
| $A_1$ $\nu_s(MX)$ | $A_1$ $\nu(MZ)$ | $A_1$ $\nu_s(MZ)$ | $A'$ $\nu(MZ)$ |
| $T_2$ $\nu_{as}(MX)$ | $A_1$ $\nu_s(MX)$ | $A_1$ $\nu_s(MX)$ | $A'$ $\nu_s(MX)$ |
| | $E$ $\nu_{as}(MX)$ | $B_1$ $\nu_{as}(MX)$ | $A''$ $\nu_{as}(MX)$ |
| | | $B_2$ $\nu_{as}(MZ)$ | $A'$ $\nu(MY)$ |

[a] All the modes are infrared and Raman active except the $A_1$ mode of $T_d$ symmetry which is only Raman active.

in the 1-methylpiperazinium cation-ligand and at 3160, 3050 and 2700–2400 cm$^{-1}$ regions in the 2-methylpiperazinium cation-ligand, which became attenuated on deuteration, indicating that the NH motions are involved [20]. The positions of these bands are in agreement with the other secondary or tertiary amine hydrohalides [20, 21].

The bands at 3160, 3050 and 2700–2400 cm$^{-1}$ in the monoprotonated 2-methylpiperazine ligand, which may be assigned to $\nu$(NH) and $\nu(\overset{+}{N}H_2)$ vibrations, appear almost unchanged in the complexes.

The absence of bands at energy greater than 3000 cm$^{-1}$, assignable to $\nu$(NH) vibration, and the presence of bands at 3400, 3350, 3205, 1605 and 605 cm$^{-1}$, characteristic of coordinated water [2], in the monoprotonated 1-methylpiperazine ligand indicate that strong hydrogen bonding exists between the secondary "uncharged" nitrogen atom of the cation-ligand and the water molecule. By complex formation all the bands of the water disappear and two sharp bands appear at 3150–60 and 2740–50 cm$^{-1}$ assignable to the vibrations of the coordinated NH group and uncoordinated $\overset{+}{N}HCH_3$ group, respectively.

It can be noted that the $\overset{+}{N}H$ or $\overset{+}{N}H_2$ stretching frequencies vary only slightly with the halides, indicating that these groups are not involved in hydrogen bonding and that the zwitterion complexes have a highly ordered crystalline structure.

### *Far-infrared Spectra*

We have paid particular attention to the far-i.r. spectra of these complexes, as poor data are reported in literature for complexes having these types of coordination [1, 3, 18]. The known data regard the cobalt–chlorine stretching vibrations, found at 322–5 and 304–12 cm$^{-1}$ [1, 3, 18].

Table IV illustrates the correlation table for the normal modes of vibration in $T_d$ symmetry and its lower symmetry analogs ($C_{3v}$, $C_{2v}$ and $C_s$).

The bands of the cation-ligands in the 400–60 cm$^{-1}$ region disappear on complexation or are masked by the more intense vibrations of the complexes (Table V). This is suggested by the fact that all the

TABLE V. Far-i.r. Spectra (400–60 cm$^{-1}$) of the Monoprotonated Ligands and of the Complexes.

| | $\nu$(Co–Cl) | | $\nu$(Co–Br) | | $\nu$(Co–I) | | $\nu$Co–N) | Other Far-i.r. Bands |
|---|---|---|---|---|---|---|---|---|
| $(1L_N)HBr \cdot H_2O$ | | | | | | | | 365m 269m 238m 152ms 112ms 64s |
| $(1L_N)HI \cdot H_2O$ | | | | | | | | 334m 208m 122ms 86ms |
| $CoCl_3(1L_N^+)$ | 325vs | 311vs | | | | | 256w | 279s 220w 168ms 153s 130w 110vs 89vs 86w |
| $CoBr_3(1L_N^+)$ | | | 251vs | 241vs | | | 260sh | 198m 159m 124s 80s |
| $CoI_3(1L_N^+)$ | | | | | 219sh | 213vs | 256m | 190m 126m 116vs 60m |
| $CoCl_2Br(1L_N^+)$ | 324vs | 316vs | 252ms | | | | 266sh | 296w 280w 235w 210w 184sh 164m 148ms 108s |
| $CoClBr_2(1L_N^+)$ | 313vs | | 252m | 246sh | | | 264sh | 294w 280vw 221vw 208w 162sh 146m 134ms 102m |
| $CoCl_2I(1L_N^+)$ | 322vs | 310vs | | | 212m | | 255w | 290w 280w 164m 150s 138sh 110s |
| $CoBr_2I(1L_N^+)$ | | | 254vs | 244sh | 228m | | 264sh | 202m 156sh 134sh 124s 80ms |
| $(2L_N)HBr$ | | | | | | | | 370w 318w 308sh 300ms 278vs 194vs 135m 117vs 91vs 64vs |
| $(2L_N)HI$ | | | | | | | | 364m 315w 306m 296ms 269vs 188vs 158w 128m 109sh 102s 81vs 64s |
| $CoCl_3(2L_N^+)$ | 332s | 307vs | | | | | 270sh | 320w 288sh 284s 212ms 154sh 136s 118sh |
| $CoBr_3(2L_N^+)$ | | | 256s | 242vs | | | 280mw | 320w 224m 172m 112ms 96w 80w |
| $CoI_3(2L_N^+)$ | | | | | 217vs | 206sh | 280mw | 320w 134s 120w 82ms |
| $CoCl_2Br(2L_N^+)$ | 328s | 306vs | 240m | | | | 284m | 320m 186m 156sh 132ms 96w 86m |
| $CoCl_2I(2L_N^+)$ | 334s | 304vs | | | 224m | | 284w | 322m 187m 148sh 124m 68m |
| $CoBr_2I(2L_N^+)$ | | | 260m | 236vs | 222sh | | 284m | 318m 177m 162w 148sh 110vs 88w 78w 60w |

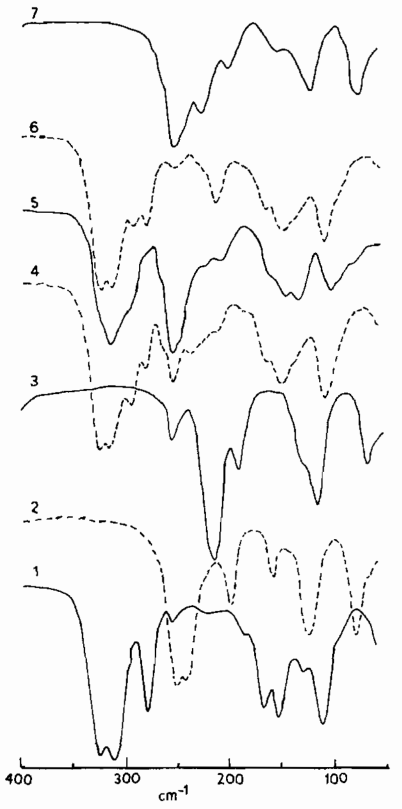

Figure 3. Exemplifying far-i.r. spectra of the pseudotetrahedral $CoCl_3(1L_N^+)$ (1), $CoBr_3(1L_N^+)$ (2), $CoI_3(1L_N^+)$ (3), $CoCl_2Br(1L_N^+)$ (4), $CoClBr_2(1L_N^+)$ (5), $CoCl_2I(1L_N^+)$ (6), $CoBr_2I(1L_N^+)$ (7) complexes.

bands found in the far-i.r. spectra of the complexes are halogen dependent, except a band at 320 cm$^{-1}$ in the $2L_N^+$ complexes (Fig. 3).

Since several sets of compounds of the same stereochemistry are available in which the halogen varied from Cl to Br to I, the assignment of the cobalt–halogen stretching vibrations is made with a reasonable certainty; on the contrary, the assignment of the cobalt–nitrogen stretching vibrations is only tentative. This band is assigned in Table V on the assumption that for a series of compounds of the same stereochemistry the $\nu$(M–L) 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 $\nu$(M–X) vibrations, and by comparison with other pseudotetrahedral complexes of cobalt(II) with pyrazine [22], thiazole [23], 4-methylthiazole[23] and pyridizines [24] for which the $\nu$(Co–N) was found in the same spectral region.

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