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Mixed Trihalocobaltates(II)

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Tetraethylammonium dichloromonoiodo cobaltate(II) and dibromomonoiodo cobaltate(II) have been isolated and characterised. Their electronic and i.r. spectral, magnetic and conductance studies are reported. It has been concluded from these studies that cobalt is tetrahedrally coordinated in these mixed trihalocobaltates(II).

Introduction

Among the trihalocobaltates(II) only trichloro and tribromocompounds are known to have been isolated and studied [1–3]. In solid trichlorocobaltates(II) studied so far by X-ray crystallography the cobalt atom is octahedrally surrounded by six halogens [1, 4]; no single crystal X-ray work has been reported for tribromocobaltates(II). Mixed trihalocobaltates(II) have been given little attention, *e.g.* only the isolation of dichloromonobromocobaltates(II) has been reported in two patented methods [5] where it has been claimed that these compounds can be used as pesticides. In the present article we are reporting the isolation of two mixed trihalocobaltates(II), namely dichloromonoiodo- and dibromomonoiodocobaltates(II) and their electronic and i.r. spectral, magnetic and conductance studies.

Experimental

Preparation

The reactants weighed in stoichiometric amounts according to the equation

$$RY + CoX_2\cdot 6H_2O = R(CoX_2Y) + 6H_2O$$

where X and Y are halogens and R = $(C_2H_5)_4N^+$, were mixed together and heated on a steam bath. The green paste obtained was cooled inside a desiccator, crystallized from ethanol by slow evaporation inside a vacuum desiccator, filtered, washed with benzene and dried.

Analysis

The complexes were analyzed potentiometrically for their halogen contents following a procedure mentioned earlier [6]. Analysis for carbon and hydrogen was carried out by the Microanalytical Laboratories of the Central Drug Research Institute, Lucknow, India. The analytical results and the melting points are given below.

$[(C_2H_5)_4N][CoCl_2I]$: % Found C, 23.45; H, 5.50; Cl, 17.36; I, 30.80. % Calculated C, 24.80; H, 5.17; Cl, 18.35; I, 32.82, M.P., 100 °C. $[(C_2H_5)_4N][CoBr_2I]$: % Found C, 19.05; H, 4.90; Br, 31.56; I, 25.51. % Calculated C, 20.17; H, 4.20; Br, 33.61; I, 26.68. M.P. 158 °C.

Electronic Spectra

A Unicam SP-700 spectrophotometer was used to record the spectra from 370 to 2500 nm. Diffuse reflectance spectra were recorded in the range 370–2200 nm using magnesium oxide as reference; in no case could the spectra be recorded up to 2500 nm. Nujol mull spectra could be recorded up to 2500 nm. Solution spectra in acetonitrile were also recorded in the range 370–2500 nm using one-cm matched silica cells. Since the samples were transparent in the region 370–600 nm, the figures are shown starting from about 600 nm only.

Far I.R. Spectra

Spectra were recorded in the range 400–100 cm^{-1} at the Chemistry Department, University of Leicester, U.K., by courtesy of Dr. D. M. Adams.

Magnetic Moments

Magnetic susceptibilities were measured at room temperature on a Gouy Balance using $Hg[Co(CNS)_4]$ as standard. The magnetic moments μ_{eff} were calculated from the measured molar susceptibility corrected for diamagnetic effects [7] of the atoms surrounding the metal ion and for the temperature independent paramagnetism [8].

Conductance Measurements

Measurements of conductance of the complexes in acetonitrile (BDH, purified by the method of Walden

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TABLE I. Centres of Gravity of ν_3 and ν_2 Bands and Ligand Field Parameters.

Compound E = $(C_2H_5)_4N^+$	ν_2 (cm^{-1})	ν_3 (cm^{-1})	10Dq (cm^{-1})	B' (cm^{-1})	β	$-\lambda'$ (cm^{-1})
		(Nujol Mull spectra)				
E($CoCl_2I$)	5025	13700	2878	673	0.693	86
E($CoBr_2I$)	4750	13245	2718	656	0.676	93
		(Diffuse reflectance spectra)				
E($CoCl_2I$)	–	14327	–	–	–	–
E($CoBr_2I$)	–	13889	–	–	–	–
		(Solution spectra in acetonitrile)				
E($CoCl_2I$)	–	15430	–	–	–	–
E($CoBr_2I$)	–	14810	–	–	–	–

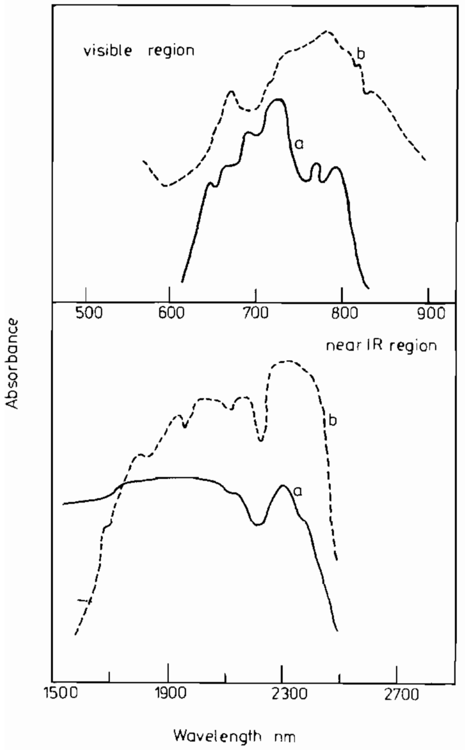


Figure 1. Electronic spectra of (a) $[(C_2H_5)_4N][CoCl_2I]$ and (b) $[(C_2H_5)_4N][CoBr_2I]$ (nujol mull).

and Birr [9]) were carried out at 25 ± 0.5 °C on a W. G. Pye Conductance Unit. The solutions used were $\sim 10^{-3}$ *M*.

Results and Discussion

The trihalocobaltates(II) (halo = chloro or bromo) are reported to have been isolated by (i) dehydrating the hydrated trihalocobaltates(II) from aqueous medium [3, 4], (ii) fusing the constituents under vacuum or in presence of the appropriate hydrogen halide gas [4, 10] or (iii) mixing the constituents in a non-aqueous medium [2]. In the present work the two mixed trihalocobaltates(II) were obtained directly by using hydrated cobalt halides instead of the anhydrous ones. Attempts to prepare these complexes from non aqueous medium using hydrated cobalt halides failed.

Electronic Spectra

The electronic spectrum of solid caesium trichlorocobaltate(II) has been interpreted [11, 12] in terms of the octahedral environment around Co(II) and as mentioned earlier, single crystal X-ray work has also shown the presence of octahedrally surrounded Co(II). So, by analogy, the two mixed trihalocobaltates(II) under discussion may be assumed to contain octahedrally coordinated cobalt(II). This assumption will now be examined in the light of the observed spectra.

Diffuse Reflectance and Nujol Mull Spectra

The centres of gravity of the composite bands in the two spectra are given in Table I and the Nujol mull spectra are shown in Fig. 1. Supposing that these mixed trihalocobaltate(II) have octahedral cobalt the following features must not be absent in their spectra:

(a) Considering the band observed in the near i.r. region to be the ν_1 (*i.e.* $^4T_{2g} \leftarrow {}^4T_{1g}$) transition of an octahedrally coordinated Co(II), theoretically then ν_2 transition ($^4A_{2g} \leftarrow {}^4T_{1g}$) must occur at $\sim 2.1 \times \nu_1$ cm^{-1} [13a]. In case of cobalt chloride [13b], cobalt bromide [13b] and trichlorocobaltate(II) [11] all of which have been shown to have octahedral Co(II), the ν_2 band is rightly observed at the calculated position approximately. But no such band was observed at the required position in case of $(CoCl_2I)^-$ and $(CoBr_2I)^-$ (Table I).

TABLE II. Assignment of the Components of ν_3 Band.

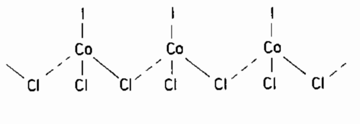
Compound $E = (C_2H_5)_4N^+$	Type of Spectra	$^2E(G) \leftarrow {}^4A_2(F)$ (cm^{-1})	$^4T_1(P) \leftarrow {}^4A_2(F)$ (cm^{-1})	$^2A_1(G) + {}^2T_1(G) + {}^4T_1^a(P) \leftarrow {}^4A_2(F)$ (cm^{-1})		$^2T_2(G) \leftarrow {}^4A_2(F)$ (cm^{-1})
E(CoCl$_2$I)	N.M	12658	12987	13889	14993 14925sh	15385
	D.R.	13158	14493	14749sh	15625	16340sh
	Soln.	14925	15198sh	15823sh	16529	16807sh
E(CoBr$_2$I)	N.M.	11976	12225	12469sh 12821	13605sh 14045sh	14925
	D.R.	12903	13700	14600sh	15625	–
	Soln.	14535	14881sh	15083sh	15674sh	16129

sh = shoulder, N.M. = nujol mull, D.R. = diffuse reflectance, soln. = acetonitrile solution.
[a] Some components of $^4T_1(P)$ term; transitions to the remaining components are shown in column 4.

(b) Comparing the reported ν_3 value (observed in the visible region) for trichlorocobaltate(II) [11], *i.e.* 17020 cm^{-1}, with those reported in Table I for mixed trihalocobaltates(II), it is observed that the latter are far below the expected values, taking into account the presence of Br$^-$ and I$^-$ instead of Cl$^-$ in the coordination sphere and thus, they seem to be outside the range for octahedral complexes of Co(II).

Therefore, it may be concluded that the coordination of Co(II) is not octahedral in these mixed trihalocobaltates(II) and the close proximity of their ν_3 and ν_2 values to those reported for tetrahedral Co(II) complexes [8, 13b] leads one to conclude that the coordination, in fact, may be tetrahedral in these complexes. The tetrahedral geometry around Co(II) in a trihalocobaltate(II) may be attained in the solid state by a bridging halogen atom. Since smaller size and high electronegativity are the requisites of a good bridging atom, bridging through chlorine in $(CoCl_2I)^-$ and through bromine in $(CoBr_2I)^-$ may be occurring.

The structure may be a chain type (I). However, a structure consisting of dimeric units (II) will also satisfy the tetrahedral geometry around Co(II).



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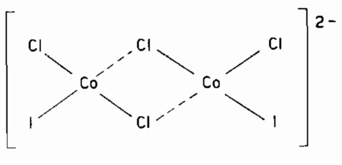

II

To decide between the two possibilities on a tentative basis, the following step was taken.

Dimeric halocobaltates(II), $(Co_2Cl_6)^=$ and $(Co_2Br_6)^=$ have been isolated by Gentile *et al.* [14] with $Co(DA)^{+2}$ (DA = diacetamide) cation. [Co(DA)]-[CoX$_4$] (X=Cl or Br) was refluxed in acetic anhydride to obtain these complexes which were characterized by chemical analysis and were shown by electronic spectral and magnetic studies to contain tetrahedral Co(II). In a bid to see whether $[(C_2H_5)_4N]_2[CoCl_4]$ on being given a similar treatment gives $[(C_2H_5)_4N]_2[Co_2Cl_6]$ or not, it was found that even on refluxing, no white tetraethylammonium chloride, according to the equation given below,

$$2\,[(C_2H_5)_4N]_2[CoCl_4] \xrightarrow[\text{Reflux}]{Ac_2O} [(C_2H_5)_4N]_2[Co_2Cl_6] + 2(C_2H_5)_4NCl$$

appeared and also the blue substance that was crystallized gave a chlorine content which fitted $[(C_2H_5)_4N]_2[CoCl_4]$ very well.

This experiment gave an indication that the dimeric species may not be stable in the solid state with the monovalent cation and hence the mixed trihalocobaltates(II) may preferably have the chain structure(I) and not the dimeric unit structure(II).

The spectra in Fig. 1 show much structured and broad bands for both ν_3 and ν_2 absorptions. It may be noted that notwithstanding the increased splitting these bands still retain the profile of the spectra observed for mixed tetrahalocobaltates(II) which have been shown [6], on the basis of electronic, far i.r. and magnetic studies, to be tetrahedral. This supports the contention that the two mixed trihalocobaltates(II) are of tetrahedral geometry, distorted though it may be.

The splitting in the ν_3 bands may be due to lower formal symmetry coupled with the mixing of the ^4P

TABLE III. Doublets and Their Assignment.

Compound E = $(C_2H_5)_4N^+$	$^2G^a \leftarrow {}^4A_2(F)$ nm	 cm^{-1}	$^2P + {}^2H \leftarrow {}^4A_2(F)$ nm	 cm^{-1}
E($CoCl_2I$)	530b	18868b	475sh	21058sh
			450	22222
E($CoBr_2I$)	610	16399	490sh	20408sh
	575sh	17391sh	480	20833
	550sh	18182sh		

sh = shoulder, b = broad.

^{a}Some of the components of ^2G were incorporated in ν_3 band (Table II).

and ^2G components due to spin–orbit coupling. It may be remarked here that the structure of the ν_3 band in case of pure* as well as mixed tetrahalocobaltates(II) has been attributed to the latter factor only [6, 15, 16]. Assignment, – tentative and approximate one – of the various components of the ν_3 bands (Table II) has been made on the same basis as in the case of mixed tetrahalocobaltates(II) [6].

As in the case of mixed tetrahalocobaltates(II) [6], doublets were observed on the higher energy side of the ν_3 band in these complexes also but they were ill-defined and only a part of the expected bands were observed. Further, the doublets could be observed only in diffuse reflectance and not in the Nujol Mull spectra. The approximate assignments of the observed doublets are given in Table III.

The ν_2 bands again show more structures than were observed for the mixed tetrahalocobaltates(II) [6] and since in the latter cases these were explained on the basis of spin–orbit coupling accompanied by vibrational progression, in the mixed trihalocobaltates(II) they may be due to a combined effect of lower symmetry, spin–orbit coupling and vibrational progression.

Ligand Field Parameters

Since the overall shapes of the bands are almost similar to those for pure and mixed tetrahalocobaltates(II), 10Dq, B′, β and λ' values (Table I) were calculated using the relations given by Underhill and Billing [17]. These could be calculated from the nujol mull spectra only.

As expected, the 10 Dq value for $(CoCl_2I)^-$ is higher than that for $(CoBr_2I)^-$ since the former contains chlorine in place of bromine (in the latter) and chlorine occupies a higher position in the spectrochemical series. Some contribution to these 10 Dq values may be due to the distortion present in these complexes owing to halogen bridging. It is of interest to compare these 10Dq values with those of mixed tetrahalocobaltates(II) [6]. Considering $(CoCl_2I)^-$ to be $(CoCl_3I)^=$ and $(CoBr_2I)^-$ to be $(CoBr_3I)^=$ on the basis of bridging structure (I), the 10Dq value of the former is higher than that of $(CoCl_2I_2)^=$ and of the latter than that of $(CoBr_2I_2)^=$ and this is expected in view of the position of the ligands in the spectrochemical series.

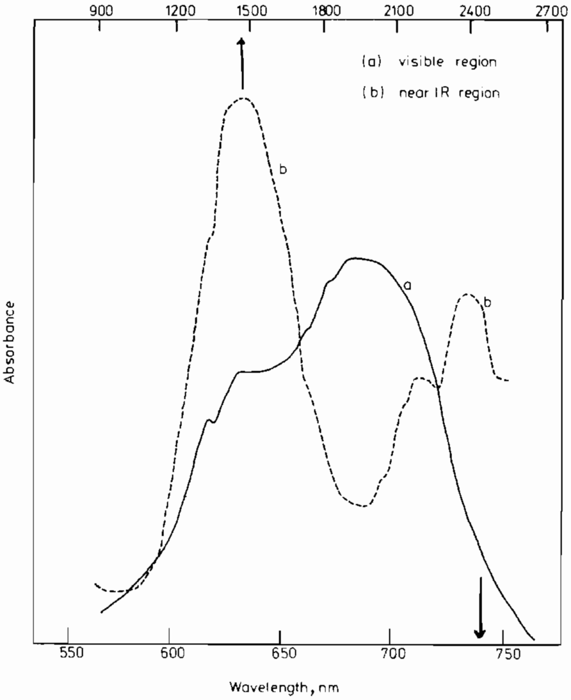

Figure 2. Electronic spectrum of $[(C_2H_5)_4N][CoBr_2I]$ in acetonitrile.

The B′ values also fall in order, the lower values of B′ or β for $(CoBr_2I)^-$ showing more orbital overlap and hence more covalency. The values of the spin–orbit coupling constant, –86 for $(CoCl_2I)^-$ and –93 for $(CoBr_2I)^-$, are low since the magnetic moments were also lower than the normal value for tetrahalocobaltates(II) (*q.v.*). However, the values of λ' are as expected, in the order of increasing covalency in going from $(CoCl_2I)^-$ to $(CoBr_2I)^-$.

Average Ligand Field Approximation

10Dq and B′ values for these complexes were calculated using average ligand field approximation; $(CoCl_2I)^-$ was assumed to be $(CoCl_3I)^=$ (chlorine-bridged) and $(CoBr_2I)^-$ to be $(CoBr_3I)^=$ (bromine bridged). A good agreement is observed between the 10Dq values calculated from this approximation (2883 cm^{-1} for $(CoCl_2I)^-$ and 2718 cm^{-1} for $(CoBr_2I)^-$) and those calculated from the experimental data (2878 cm^{-1} for $(CoCl_2I)^-$ and 2718 cm^{-1} for $(CoBr_2I)^-$) but a large difference exists between B′ values obtained from the two routes [$(CoCl_2I^-)$: calc.

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*Pure means those having the same halogens in the coordination sphere *e.g.* $CoCl_4^=$ and 'mixed' means those having different halogens in the coordination sphere *e.g.* $(CoCl_2Br_2)^=$.

TABLE IV. Electronic Spectral Data (Acetonitrile Solution; figures in parentheses denote ϵ_{max} values).

Compound $E = (C_2H_5)_4H^a$	${}^4T_1(P) \xleftarrow{\nu_3} {}^4A_2(F)$		${}^4T_1(F) \xleftarrow{\nu_2} {}^4A_2(F)$	
	nm	cm^{-1}	nm	cm^{-1}
$E(CoCl_2I)$	595sh	16807sh	1350sh	7407sh
	605	16529	1420	7042
	(260)	(260)	(67)	(67)
	632sh	15823sh	1950	5128
	658sh	15198sh	(35)	(35)
	670	14925	2050sh	4878sh
	(360)	(360)	2150	4651
			(46)	(46)
			2260sh	4425sh
			2470	4049
			(44)	(44)
$E(CoBr_2I)$	620	16129	1340sh	7463sh
	(280)	(280)	1450	6897
	638sh	15674sh	(74)	(74)
	663sh	15083sh	2050sh	4878sh
	672sh	14881sh	2140sh	4673sh
	688	14535	2200	4546
	(516)	(516)	(36)	(36)
			2390	4184
			(47)	(47)

714 cm^{-1}, exp. 673 cm^{-1} and $CoBr_2I^-$: calc. 695 cm^{-1}, exp. 656 cm^{-1}].

Solution Spectra

The spectrum of $(CoBr_2I)^-$ in acetonitrile is shown in Fig. 2 and ϵ_{max} values for various components of the bands for both the complexes are presented in Table IV. The c.g.'s of ν_3 band are shown in Table I. Regarding the structure of the complexes in solution, shapes of the ν_3 bands, being akin to those for $CoX_4^=$ in acetonitrile [6] suggest that they are tetrahedral in nature. In solid state their tetrahedral structure is maintained by bridging halogen but in solution the solvent may break up the bridge and enter itself into the fourth coordination site. This assumption is supported by the fact that ν_3 values in diffuse reflectance and in nujol mull spectra are lower than in acetonitrile spectra (Table I) (CH_3CN occupies a higher position in spectrochemical series than the halides). Moreover, the ϵ_{max} values for the ν_3 bands are well within the range expected for tetrahedral Co(II) complexes (13c). Incidently, CoX_3^- (X = Cl, Br, I) species are also known to be tetrahedral in solution with a solvent molecule occupying the fourth coordination site [18].

Doublets on the higher energy side of ν_3 band were not observed in acetonitrile solutions. The ν_2 bands were not observed in full up to 2500 nm, hence neither their centres of gravity are reported nor the ligand field parameters could be calculated from the solution spectra. Assignments of various absorption peaks of the ν_3 band are given in Table II.

Far IR Spectra

Spectra from 400–100 cm^{-1} are shown in Figs. 3 and 4 and the positions of various peaks along with their assignments are given in Table V.

If Co is octahedral in $(CoCl_2I)^-$ and $(CoBr_2I)^-$ as it is in $CoCl_3^-$ [1, 4], the stretching frequency for Co–X (X = Cl, Br, I) must be lower than that in the corresponding tetrahedral Co(II) complexes since it is known that the value of Co–X stretching decreases

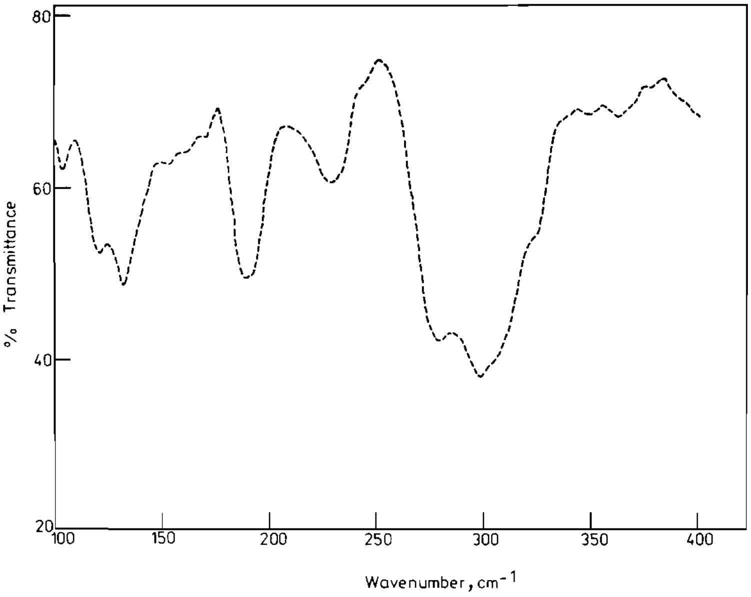

Figure 3. Far I.R. spectrum of $[(C_2H_5)_4N][CoCl_2I]$.

TABLE V. Peak Positions and Assignments in Far I.R. Spectra.[a]

Compound $E = (C_2H_5)_4N^+$	Peak Positions (cm^{-1})	Assignments
$E(CoCl_2I)$	322sh, 299vs, 280vs	ν(Co–Cl) terminal
	228m	ν(Co–Cl) bridging
	190s	ν(Co–I)
	135s, 122s	δ(Cl–Co–Cl)
	105m	Cation translation
$E(CoBr_2I)$	232vs, 215sh	ν(Co–Br) terminal
	200vs	ν(Co–I)
	160m, 150m, 140m	ν(Co–Br) bridging
	122w	–
	105m	Cation translation

[a] vs = very strong, m = medium, sh = shoulder, s = strong, w = weak.

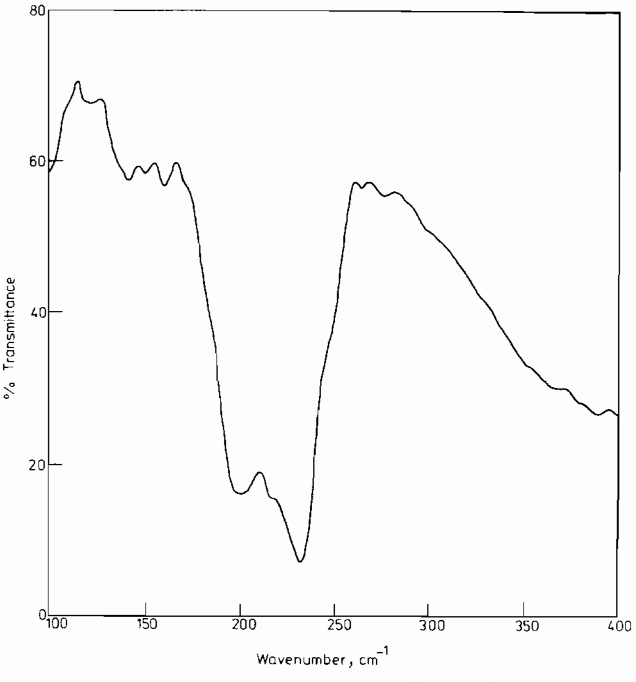

Figure 4. Far I.R. spectrum of $[(C_2H_5)_4N][CoBr_2I]$.

with increasing coordination number [19]. Thus Co–Cl stretching frequency for octahedral $CoCl_3^-$ is 246 cm^{-1} [21] while that for tetrahedral $CoCl_4^{=}$ is 310, 288 sh [21]. Similarly, in trigonal bipyramidal $SnCl_5^-$ the Sn–Cl antisymmetric stretching values are 330 cm^{-1} (axial) and 351 cm^{-1} (equatorial) [22] as against the antisymmetric Sn–Cl stretching values [23] of 403 cm^{-1} for tetrahedral $SnCl_4$. The Co–Cl stretching mode in $(CoCl_2I)^-$ and Co–Br stretching mode in $(CoBr_2I)^-$ appear at ~300 cm^{-1} and ~230 cm^{-1} respectively (Table V), which are almost the same values as for the corresponding stretching modes in $CoX_4^{=}$ species (X=Cl, Br) [21]. Thus it may be concluded that Co(II) has tetrahedral coordination in these complexes.

Taking $(CoCl_2I)^-$ first, the question as to which atom is bridging to produce a tetrahedral geometry can be decided easily from the fact that two absorptions, one at 300 cm^{-1} (split into three parts) and the other at 228 cm^{-1} are observed. While the first absorption can be assigned to Co–Cl terminal stretching, the second may be ascribed to the Co–Cl bridging stretch since the bridging metal–halogen frequency is always lower than the terminal metal–halogen frequency [19]. It may be remarked here that this also confirms the conclusion arrived at regarding the bridging atom through electronic spectral study. However, by the far i.r. data it cannot be said whether the structure is chain type or dimeric unit type, but on the basis of discussion in the electronic spectra section, the former structure is to be preferred. Of the rest, the absorptions at 135 cm^{-1} and 122 cm^{-1} can be ascribed to the bending mode (Cl–Co–Cl) and the weak peak at 105 cm^{-1} to cation translation. The peak at 190 cm^{-1} is ascribed to Co–I stretching. All these values are in agreement with those reported by other workers [21, 24] for $CoX_4^{=}$ species (X=Cl, I) and $(C_2H_5)_4N^+$ cation translation.

In case of $(CoBr_2I)^-$ the peaks at 232, 215 sh cm^{-1} can be assigned to Co–Br terminal stretching and the peak at 200 cm^{-1} to Co–I stretching. These values agree with those reported by other workers [21, 24] for $CoX_4^{=}$ species (X=Br, I). The broad band around 150 cm^{-1} split into three parts may be assigned to either Co–I or Co–Br bridging stretch. However, the bromine atom being smaller in size and more electronegative than that of iodine, bridging through it is more probable. Thus, the broad band at ~150 cm^{-1} can be assigned to Co–Br bridging stretch. Another weak peak at 122 cm^{-1} may be due to some combination band. In conclusion a structure analogous to $(CoCl_2I)^-$ may be present.

Magnetic Moment

The values of magnetic moments for $(CoCl_2I)^-$ and $(CoBr_2I)^-$ (4.35 and 4.42 B.M. respectively) were obtained after applying diamagnetic and t.i.p. corrections assuming a tetrahedral unit of $(CoCl_3I)^{=}$ and $(CoBr_3I)^{=}$, respectively. Compared to the values of the magnetic moments of other tetrahedral complexes of Co(II) [6, 8, 25] these values seem to be quite low. This may be attributed to two factors, *viz.* (i) increased interaction between the neighbouring Co(II) ions due to chain structure and (ii) the distortion in the tetrahedral structure introduced due to bridging by a halide. It may be remarked here that in case of $CoCl_3^-$ containing octahedral Co(II), the magnetic moments at room temperature have been reported to be 4.77 B.M. for $CsCoCl_3$ [1] and 4.05 B.M. for $KCoCl_3$ [26]. The values, especially the second one, are much lower than the normal values of the magnetic moments for octahedral Co(II) complexes (4.08–5.20 B.M.). This has been attributed to the increased magnetic concentrations and to exchange interactions between the neighbouring paramagnetic atoms [26].

Amongst themselves, the magnetic moment values of the complexes are in the expected order, *i.e.* the complex having the halogen atoms lower in the spectrochemical series has large magnetic moment which may be attributed to the increased orbital contribution.

Conductance Measurement

From the molar conductance values at single concentration (1×10^{-3} *M*) for $[(C_2H_5)_4N][CoCl_2I]$, 145 and for $[(C_2H_5)_4N][CoBr_2I]$, 144, it is evident that these fall within the generally acceptable range (120–160) for a 1:1 electrolyte in acetonitrile [27], thus confirming the presence of ionic species manifest in the molecular formula of the respective complex; of course, as shown by the study of electronic spectra of these species in acetonitrile (discussed above), the fourth site may be occupied by a solvent molecule.

Conclusion

The electronic and far i.r. spectral, magnetic and conductance studies show that the mixed trihalocobaltates(II), $(CoCl_2I)^-$ and $(CoBr_2I)^-$ contain tetrahedrally surrounded Co(II) as against $(CoCl_3)^-$ in which Co(II) has octahedral environment.

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