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Mixed Tetrahalocobaltates(II)

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Some new mixed tetrahalocobaltates(II) of the general formula $A_2(CoX_2Y_2)$, *where* $A = (C_2H_5)_4N^+$ *and* X *and* Y = *Cl, Br, I, have been isolated and characterized by their chemical analyses, far i.r. spectra, magnetic moments and X-ray powder diffractograms. In all the complexes, Co(II) has been found to be tetrahedrally surrounded by halogens.*

Introduction

Compared to the large number of studies reported on pure** tetrahalocobaltates(II) (*e.g.*, [1–5]) the literature available on mixed tetrahalocobaltates(II) seems to be scanty [6–8] and most of it deals only with studies on $(\mathrm{CoCl_2Br_2})^{=}$ species. Only recently Islam *et al.* [9] have studied the electronic spectrum of $(\mathrm{CoCl_2I_2})^{=}$ species formed in molten state. Interestingly enough, even for $(\mathrm{CoCl_2Br_2})^{=}$ species no direct method of isolation from the constituents involved appears and as far as $(\mathrm{CoCl_2I_2})^{=}$ and $(\mathrm{CoBr_2I_2})^{=}$ species are concerned, Baranovskii *et al.* [10] report that these species with pyridinium ion could not be isolated since when the components, mixed together in ethanol, were crystallized, less soluble chloride or bromide was the first to come out. It is in this context that we report here isolation and characterization of a few mixed tetrahalocobaltates(II).

TABLE I. Elemental Analysis and the Melting Points.

Compounds	Elements	%Found	%Calcd.	Melting points
$M_2(CoCl_4)$	C	27.40	27.51	No visible change up to 360 °C
	H	6.80	6.88	
	Cl	40.95	40.70	
$E_2(CoCl_4)$	C	40.80	41.65	Decomp. >315 °C
	H	8.44	8.68	
	Cl	30.47	30.80	
$E_2(CoCl_2Br_2)$	C	–	34.91	Decomp. >310 °C
	H	–	7.27	
	Cl	12.46	12.89	
	Br	29.15	29.05	
$E_2(CoCl_2I_2)$	C	29.80	29.82	280 °C
	H	6.25	6.21	
	Cl	10.86	11.03	
	I	39.47	39.44	
$E_2(CoBr_2I_2)$	C	26.30	26.19	262 °C
	H	5.30	5.46	
	Br	22.31	21.83	
	I	33.49	34.65	
$M_2(CoBr_4)$	C	18.01	18.22	No visible change up to 360 °C
	H	4.60	4.51	
	Br	60.42	60.72	

$E = (C_2H_5)_4N^+$ $M = (CH_3)_4N^+$

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**The complexes having the same halogens as ligands (*e.g.*, $\mathrm{CoCl_4^{=}}$) are referred to as pure halocobaltates(II) and those having different halogens as ligands (*e.g.* $(\mathrm{CoCl_2Br_2})^{=}$), as mixed halocobaltates(II).

Experimental

Preparation

The complexes, pure as well as mixed (Table I), were prepared by the following two methods:

Solution Method: Stoichiometric amounts of the reacting constituents (substituted ammonium halide and hydrated cobalt halide) according to eqn. (1) were dissolved separately in ethanol and mixed together, the solution was concentrated, allowed to cool inside a desiccator over anhydrous calcium chloride and the blue (in case of chloro-bromo complexes) or green (in case of chloro-iodo or bromo-iodo complexes) crystals were filtered, washed with benzene and dried in an air oven at 80–90 °C.

$$2RY + CoX_2{\cdot}6H_2O \longrightarrow R_2[CoX_2Y_2] + 6H_2O \qquad (1)$$

where $R = (C_2H_5)_4N^+$ or $(CH_3)_4N^+$ & X and Y = Cl, Br, I.

Solid–Solid State Interaction Method: Stoichiometric amounts of the reactants, according to eqn. (1), were ground to a fine powder separately and then thoroughly mixed together so as to obtain a homogeneous mixture which was heated on a steam bath. A paste , blue coloured in case of chloro-bromo and green coloured in case of chloro-iodo or bromo-iodo complexes, so obtained was cooled inside the desiccator over anhydrous calcium chloride, dissolved in ethanol or nitromethane and crystallized therefrom; the crystals were washed with benzene and dried as in the *Solution Method*. In case of pure halo and the chloro-bromo complexes, the constituents reacted just on grinding and no heating was required; however, in case of complexes containing iodine the mixture, as also mentioned earlier, had to be heated for the reaction to reach completion.

Analysis

All the complexes were decomposed with water and the halogen contents were determined potentiometrically. However, since the chloro-iodo and bromo-iodo complexes produced brown coloured particles on reacting with water which were tested to be free iodine, they were decomposed by a dilute solution of sodium hydroxide, heated slightly to convert the bluish cobaltous hydroxide to cobaltous oxide which settled down; the solution was then made acidic with acetic acid and titrated potentiometrically for halide determination.

Analysis for carbon and hydrogen contents of the complexes was carried out by the Microanalytical Laboratories of the Central Drug Research Institute, Lucknow, India.

Melting points were determined using an electrothermal melting point apparatus. The analytical results and melting points of the complexes are given in Table I.

Far I.R. Spectra

Far i.r. spectra for two of the mixed halocobaltates(II) were recorded in the range 400–100 cm^{-1} at the University of Leicester, U.K., by courtesy of Dr. D. M. Adams. For the rest, the recording was done in our laboratories on a Grubb–Parsons DM-2 spectrophotometer in the range 400–200 cm^{-1}, using HCBD mulls.

Magnetic Moment

Room temperature values of the magnetic moments were calculated by measuring the magnetic susceptibilities on a Gouy Balance using $HgCo(CNS)_4$ as standard. The magnetic moments, μ_{eff}, were calculated as $\mu_{eff} = 2.84\sqrt{\chi_M^{corr} \times T}$ where χ_M^{corr} is the molar susceptibility corrected for the diamagnetic effects of the atoms [11] surrounding the metal ion and for the temperature independent paramagnetism [1]. The 10Dq values involved in the calculation of temperature independent paramagnetism of these compounds have been reported elsewhere [12].

X-ray Powder Diffraction

X-ray powder diffractograms for some of the tetrahalocobaltates(II) were recorded at the X-ray laboratory of the Indian Institute of Petroleum, Dehradun, India. The values of 2θ were read out directly from the diffractograms and values of d and $1/d^2$ were obtained by a computer program using the equation $\lambda = 2d\sin\theta$, where $\lambda = 1.5418$ Å. The intensities of the peaks were obtained by noting their heights in the diffractograms. These intensities are reported in arbitrary units taking the value of the most intense peak as 100 in a given diffractogram. The X-ray powder data are shown in Tables V and VI.

Results and Discussion

Far I.R. Spectra

Table II shows the stretching modes for $CoCl_4^=$ and $CoBr_4^=$ species and they are in agreement with the values reported earlier [13–15]. Spectra of the pure tetrahalocobaltates(II) were recorded for comparison purpose. Now, as far as the mixed tetrahalocobaltates(II) are concerned, they are derived from the pure $CoX_4^=$ species which have been shown to be tetrahedral [3, 16] and, therefore, their geometry remains tetrahedral although the formal symmetry comes down to C_{2v}. On this basis, the degenerate vibrations in case of $CoX_4^=$ with nearly exact T_d symmetry are split up and give rise to a total of eight i.r. active vibrations [17] for a $(CoX_2Y_2)^=$ complex derived from $CoX_4^=$ (X and Y are different halogens).

TABLE II. Peak Positions and Assignments in Far I.R. Spectra.

Compound	Absorption Values (cm^{-1})	Assignments
$M_2(CoCl_4)$	300sh, 295vs	ν(Co–Cl)
$M_2(CoBr_4)$	232vs	ν(Co–Br)
$E_2(CoCl_2Br_2)$	303sh, 295vs	ν(Co–Cl)
	230sh, 220vs	ν(Co–Br)
$E_2(CoCl_2I_2)$	310vs, 297sh	ν(Co–Cl)
	188s, 160w	ν(Co–I)
	135m, 112m	δ(Cl–Co–Cl)
	105m	Cation Translation
$E_2(CoBr_2I_2)$	230vs, 218sh	ν(Co–Br)
	202sh, 192vs	
	171w, 165w	ν(Co–I)
	141sh, 132w	
	110w	–
	105w	Cation Translation

$E = (C_2H_5)_4N^+$; $M = (CH_3)_4N^+$

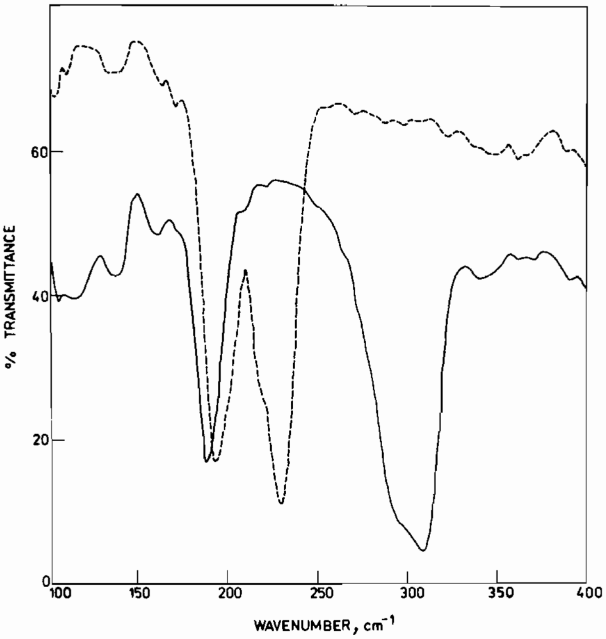

Figure. Far IR spectra of mixed tetrahalocobaltates(II). ——$[(C_2H_5)_4N]_2[CoCl_2I_2]$; ------$[(C_2H_5)_4N]_2[CoBr_2I_2]$.

Out of these eight i.r. active vibrations, two stretching modes each for (Co–X) and (Co–Y) and one bending mode each for (X–Co–X) and (Y–Co–Y) should be observed.

Some of the spectra are shown in the Figure.

Now coming to the spectrum of $(CoCl_2Br_2)^=$ (Table II), two stretching modes each for (Co–Cl) and (Co–Br) are, as expected, observed. Bending modes (Br–Co–Br) and (Cl–Co–Cl) which have been reported [10, 15] to appear below 200 cm^{-1} could not be observed. Mundie *et al.* [18] have reported the far i.r. spectrum of $(Py)_2(CoCl_2Br_2)$ (Py = pyridine), but they observed only one stretching mode each for (Co–Cl) and (Co–Br) although the bending mode (Cl–Co–Cl) was split into two.

Taking the case of $(CoCl_2I_2)^=$, again the expected two (Co–Cl) stretchings are observed at 310 cm^{-1} and 297sh cm^{-1} (Table II) and (Co–I) stretching modes at 188 cm^{-1} and 160 cm^{-1}. The (Co–I) stretching frequency in $CoI_4^=$ has been reported at 203 cm^{-1} by Baranovskii and Mazo [10] and at (197, 192sh) cm^{-1} by Sabatini and Sacconi [15]. The peaks at 135 and 112 cm^{-1} may be attributed to (Cl–Co–Cl) bending mode. Other workers [15] have also reported almost similar values for this mode. Bending mode (I–Co–I) which is reported [10] to appear below 100 cm^{-1} could not be observed. The weak peak at 105 cm^{-1} may be ascribed to cation translation [15].

In case of $(CoBr_2I_2)^=$, the absorptions at 230 cm^{-1} and 218sh cm^{-1} are due to (Co–Br) stretchings while the (Co–I) stretchings are observed at (192, 202sh) cm^{-1} and (165, 171) cm^{-1} [10, 15]. The weak peak at 105 cm^{-1} may be attributed, as in case of $(CoCl_2I_2)^=$, to cation translation [15]. The peaks at 110 cm^{-1} and (132, 141sh) cm^{-1} were difficult to assign. They may arise from different reasons, *e.g.*, they may represent rocking, twisting or wagging modes [17] or some combination bands. It may be interesting to observe that in case of $(CoCl_2I_2)^=$ also strong peaks appeared at these positions but they could be, then, easily assigned. Similar unassigned bands have been reported by other workers [19, 20] also in case of mixed tetrahaloferrates(III) and thallates(III). Bending modes could not be observed for either (I–Co–I) or (Br–Co–Br) since both are expected to appear [10] below 100 cm^{-1}. Assignments of the spectra for mixed tetrahaloferrates(III) and zincates(II) have been reported along similar lines [19, 21].

Magnetic Moments

Values of the effective magnetic moments measured at room temperature (Table III) show that they fall within the accepted range for tetrahedral and pseudotetrahedral complexes of Co(II) (*i.e.*, 4.08–4.98 B.M.) [7]. A gradual increase in the value of magnetic moment is also observed as more polarisable halide ion is introduced into the co-ordination sphere. This may be explained as due to increased orbital contribution to the singlet ground state on passing from chlorine to iodine.

Table IV shows the values of the magnetic moments calculated for the mixed tetrahalocobaltates(II) on the basis of average environment rule. The rule was applied as the electronic spectra at room temperature of these complexes did not differ to any appreciable extent from those of the pure tetrahalocobaltates(II) [12]. There is a good agreement

TABLE III. Magnetic Data.

Compound	Temp. °K	Diamag. Correction × 10^6 cgsu	T.I.P. Correction × 10^6 cgsu	χ_M^{corr} × 10^6 cgsu	μ_{eff} B.M.
$M_2(CoCl_4)$	311.0	−236	700	7919	4.45
$E_2(CoCl_2Br_2)$	311.5	−353	731	8217	4.54
$E_2(CoCl_2I_2)$	309.7	−385	762	8477	4.60
$E_2(CoBr_2I_2)$	309.2	−408	791	9056	4.75
$M_2(CoBr_4)$	311.0	−281	758	8796	4.70

$E = (C_2H_5)_4N^+$; $M = (CH_3)_4N^+$

TABLE IV. Average Environment Calculations for Magnetic Moments.

$B = (n\text{-}C_4H_9)_4N^+$; $E = (C_2H_5)_4N^+$

Compound	μ_{eff} Observed (B.M.)	μ_{eff} Calculated (B.M.)
$E_2(CoCl_2Br_2)$	4.54	4.58
$E_2(CoCl_2I_2)^a$	4.60	4.65
$E_2(CoBr_2I_2)^a$	4.75	4.78

[a] Value of μ_{eff} for $CoI_4^=$ was taken for the compound $B_2(CoI_4)$ [1].

in the experimentally observed values and those calculated on the basis of this rule.

X-ray Powder Diffractograms

Tables V and VI show the indexing of the peaks observed in the diffractograms of $[(C_2H_5)_4N]_2[CoCl_2Br_2]$ and $[(C_2H_5)_4N]_2[CoBr_2I_2]$. While for the former the diffraction pattern has been indexed on the basis of tetragonal unit cell with a = 9.02 Å and c = 15.81 Å, the latter was indexed with an orthorhombic unit cell with a = 12.60 Å, b = 11.11 Å and c = 15.81 Å. X-ray powder diffractogram for the already known compound $[(CH_3)_4N]_2[CoCl_4]$ was also recorded and indexed on the basis of an orthorhombic unit cell with a = 12.27 Å, b = 9.00 Å and c = 15.40 Å. These are in agreement with the unit cell dimensions reported for the same compound by Wiesner *et al.* [3] through single crystal X-ray study.

TABLE V. X-ray Powder Data of $[(C_2H_5)_4N]_2[CoCl_2Br_2]$.

hkl	$1/d^2$		Relative Intensity
	Calc.	Obs.	
002	0.0160	0.0166	100
110	0.0246	0.0250	26
111	0.0286	0.0290	26
112	0.0406	0.0412	32
103	0.0483	0.0490	27
200	0.0492		
201	0.0532	0.0533	21
004	0.0640	0.0638	27
212	0.0775	0.0785	29
203	0.0852	0.0861	94
213	0.0975	0.0985	27
220	0.0984		
300	0.1107	0.1105	16
302	0.1267	0.1275	21
321	0.1639	0.1646	19
322	0.1759	0.1761	17
007	0.1960	0.1959	12
400	0.1968	0.1968	18
402	0.2128	0.2122	15
411	0.2131		
422	0.2620	0.2627	11
118	0.2806	0.2806	10
532	0.4342	0.4341	8
309	0.4347		
634	0.6175	0.6179	6
702	0.6187		
704	0.6667	0.6664	5
722	0.6679	0.6686	6
3212	0.7359	0.7344	4
5011	0.7915	0.7914	6
5111	0.8038	0.8053	8
4212	0.8220	0.8230	5
803	0.8232		
2014	0.8332	0.8325	8

Conclusions

It may be tempting to conclude that these mixed tetrahalocobaltates(II) may, in fact, be a mixture of pure tetrahalocobaltates(II), *e.g.* dibromodichlorocobaltate(II) may be an equimolar mixture of tetrabromocobaltate(II) and tetrachlorocobaltate(II). But the sharp melting points of mixed chloro-iodo and bromo-iodo cobaltates(II) (Table I) and the observation that repeated crystallizations from different solvents like nitromethane and alcohol did not alter the compositions of these compounds irrespective of the solvent employed indicate that these are pure compounds rather than mixtures.

The magnetic data presented here cannot distinguish between the two possibilities. Also the

TABLE VI. X-ray Powder Data of $[(C_2H_5)_4N]_2[CoBr_2I_2]$.

hkl	$1/d^2$		Relative Intensity
	Calc.	Obs.	
100	0.0063	0.0072	21
010	0.0081	0.0082	25
002	0.0160	0.0163	100
111	0.0184	0.0190	21
102	0.0223	0.0216	23
200	0.0252	0.0253	21
210	0.0333	0.0336	22
013	0.0441	0.0442	21
022	0.0484	0.0483	21
212	0.0493		
004	0.0640	0.0632	40
310	0.0648	0.0640	29
311	0.0688	0.0698	27
213	0.0693		
104	0.0703		
104	0.0703	0.0713	21
014	0.0721		
014	0.0721	0.0727	40
302	0.0727		
131	0.0832	0.0845	38
032	0.0889	0.0884	33
320	0.0891		
204	0.0892		
320	0.0891	0.0901	29
204	0.0892		
024	0.0964	0.0968	35
214	0.0973		
411	0.1129	0.1127	18
232	0.1141	0.1146	17
115	0.1144		
133	0.1152		
404	0.1648	0.1642	17
502	0.1735	0.1739	17
430	0.1737		
432	0.1897	0.1893	18
520	0.1899		
341	0.1903		
036	0.2169	0.2161	19
154	0.2728	0.2729	17
046	0.2736		
336	0.2736		
435	0.2737		
060	0.2916	0.2922	17
254	0.2917		

fact that two (Co–X) and two (Co–Y) stretches are observed in the far i.r. region (Table II) according to the theoretical expectation (lowering to C_{2v} from T_d symmetry) may not be conclusive for the existence of $(CoX_2Y_2)^=$ species in these compounds because even for $CoX_4^=$ species in some cases two (Co–X) stretches have been reported which are attributed to solid state interaction or low site symmetry [10, 15]. It is the amount of difference between the two Co–X stretches in these compounds as compared to that in $CoX_4^=$ compounds which points out to the possibility of the presence of $(CoX_2Y_2)^=$ species. Though the difference between the two (Co–Cl) or two (Co–Br) stretches is not very significant, that observed between (Co–I) stretches in the case of mixed bromoiodo and chloroiodo compounds (Table II) is significant enough not to warrant the proposition of the splitting of (Co–I) stretch in a supposedly $CoI_4^=$ species present due to some solid state interaction or due to low site symmetry.

It is likely that the mixing of the pure tetrahalocobaltates(II) in these compounds is at a molecular level in which case the melting point, the crystallization and possibly the far i.r. spectral criteria may not distinguish between the two possibilities. A detailed crystal structure analysis alone would resolve the problem in such a case.

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