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A Search for $^4T_2(F) \xleftarrow{\nu_1} {}^4A_2(F)$ Transition in Tetrahalocobaltates(II)

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For CoX_4^{2-} species (X = Cl, Br, I) which have been shown to be tetrahedral in structure [1–3], three electronic transitions, namely

$$^4T_1(P) \xleftarrow{\nu_3} {}^4A_2(F),\ {}^4T_1(F) \xleftarrow{\nu_2} {}^4A_2(F) \text{ and}$$

$$^4T_2(F) \xleftarrow{\nu_1} {}^4A_2(F),$$

are possible. While a number of studies have been reported [4–9] on ν_3 and ν_2 transitions (including some in which these two transitions have been utilized to calculate the 10 Dq values), only a few cases where the CoX_4^{2-} species have been isolated with caesium cation, the ν_1 transition, which directly gives the value of 10 Dq, has been identified [10]. However, when the cation is an organic one, especially tetraalkylammonium, the ν_1 transition may be obscured by its vibrational absorptions. But in the wake of some workers' attempt [10, 11] to locate and successfully report it even when the cation happened to be a tetraalkylammonium, we here report the results of an attempt made during a study on tetrahalocobaltates(II) to locate the ν_1 band in complexes of the type R_2CoX_4 (R = $(CH_3)_4N^+$, $(C_2H_5)_4N^+$; X = Cl, Br).

Experimental

R_2MX_4 complexes (R = $(CH_3)_4N^+$, $(C_2H_5)_4N^+$; M = Mn, Co, Zn) were prepared according to the method of Gill and Taylor [12]. IR spectra in the region 4000–3200 cm^{-1} were recorded as HCBD mull (speed: 30 minutes per revolution spanning 4000–650 cm^{-1}) for all the complexes prepared and for the corresponding tetraalkylammonium halides on a Hilger–Watts. H 800.306 spectrophotometer.

Discussion

While Andreev and Smirnova [10] do not specify the method they used to identify the ν_1 band in case of R_2CoX_4 complexes (R = $(CH_3)_4N^+$, $(C_2H_5)_4N^+$; X = Cl, Br, I), Smith and Quinn [11], limiting their study to only $CoCl_4^{2-}$ species with $(CH_3)_4N^+$, $(C_2H_5)_4N^+$, PyH$^+$ and QH$^+$ cations (Py = pyridine; Q = quinoline), identified the ν_1 band as a peak of medium intensity having no counterpart in the spectra of $MnCl_4^{2-}$ and $ZnCl_4^{2-}$ species with the same cation in the region 4000–3200 cm^{-1}; the latter two anions are not expected to have any electronic absorption in this region. However, in case of $[PyH]_2/[QH]_2[COCl_4]$ they found the spectra to be almost similar to those of $[PyH]_2[MnCl_4]/[ZnCl_4]$ and $[QH]_2[MnCl_4]/[ZnCl_4]$, respectively, and failed to identify the ν_1 band.

In the present work we thought it better to compare the spectrum of a given tetrahalocobaltate(II) with that of the corresponding tetraalkylammonium halide. In addition, the spectrum of R_2CoCl_4 was compared with those of R_2ZnCl_4 and R_2MnCl_4 (R = $(CH_3)_4N^+$). This was done with the view that (i) there should be very little difference in the spectra of R_2MX_4 and RX (R = $(CH_3)_4N^+$, $(C_2H_5)_4N^+$; M = Mn, Co, Zn; X = Cl, Br) in the region 4000–3200 cm^{-1} if the expected weak electronic band in R_2CoCl_4 is obscured by the vibrational absorptions of the cation and if account is taken of the fact that $MnCl_4^{2-}$ and $ZnCl_4^{2-}$ are not expected to have electronic transition in this region; (ii) if, on comparison of the spectrum of R_2CoX_4 with that of either R_2MnX_4 or R_2ZnX_4, a peak assignable to the ν_1 band is distinguishable in the above mentioned region (4000–3200 cm^{-1}), the same should be evident when the spectrum of R_2CoX_4 is compared with that of RX since the spectra of RX and R_2MX_4 (M = Mn, Zn) must be similar in any case.

So taking $[(CH_3)_4N]_2[CoCl_4]$ first, it is clear from the Table as well as from the Figure that except for some small shifts in the positions of the peaks there is practically no difference between the spectrum of the complex and of $(CH_3)_4NCl$ even if

TABLE. Search for $^4T_2(F) \xleftarrow{\nu_1} {}^4A_2(F)$ Band. E = $(C_2H_5)_4N^+$; M = $(CH_3)_4N^+$.[a]

Compound	Absorption Maxima (cm^{-1})				
$M_2(CoCl_4)$	3535m	3470m	3385m	3310m	3240sh
$M_2(ZnCl_4)$	3550sh	3480m	3400m	3320m	3260sh
$M_2(MnCl_4)$	3540sh	3475m	3400m	3330m	
$M_2(CoBr_4)$	3525sh	3450m	3400m	3340m	3280sh
$E_2(CoCl_4)$	3540sh	3470m	3370m	3295m	3230sh 3200w
MCl	3540sh	3470m	3385m	3330m	3240sh
ECl	3540sh	3420m	3350m	3250sh	
MBr	3560sh	3460m	3370m	3330sh	3260sh

[a] sh = shoulder; m = medium; w = weak.

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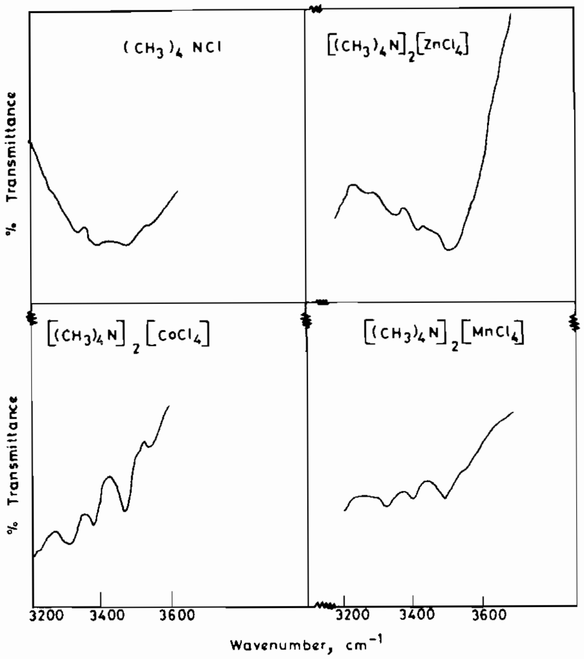

Figure. IR Spectra of $[(CH_3)_4N]_2[MCl_4]$ (M = Mn, Co, Zn) and $(CH_3)_4NCl$.

intensities of the corresponding peaks are compared. This indicates that any electronic transition occurring in this region is obscured by the vibrational absorptions of the cation. Also, a comparison of the spectrum of $[(CH_3)_4N]_2[CoCl_4]$ with that of either $[(CH_3)_4N]_2[MnCl_4]$ or $[(CH_3)_4N]_2[ZnCl_4]$ shows that there is no difference in the two spectra and this is expected as mentioned earlier. Moreover, we could not observe any peak at 3425 cm^{-1} as reported, and identified to be the ν_1 band, by Smith and Quinn [11]. Similarly, in case of $[(CH_3)_4N]_2[CoBr_4]$ there was no difference between its spectrum and that of $(CH_3)_4NBr$.

In the case of $[(C_2H_5)_4N]_2[CoCl_4]$ more peaks were observed compared to $(C_2H_5)_4NCl$ but a good comparison could not be made as the peaks observed for the latter compound were rather broad and, therefore, it was not possible to assign any peak in tetrachlorocobaltate(II) to the ν_1 band.

In this regard it may also be noted that while Andreev and Smirnova [10] have identified the ν_1 bands at 3240 and 3190 cm^{-1} in $[(CH_3)_4N]_2$-$[CoCl_4]$ and $[(C_2H_5)_4N]_2[CoCl_4]$, respectively, Smith and Quinn [11] report these to be at 3425 and 3400 cm^{-1}, respectively. Similarly as against the value of 3370 cm^{-1} for the ν_1 band in case of Cs_2CoCl_4 reported by Andreev and Smirnova [10], Smith and Quinn [11] have quoted van Stapele *et al.* as having found the value to be 3200 cm^{-1} in case of Cs_3CoCl_5 which is known [13] to be $Cs_2CoCl_4 \cdot CsCl$. Thus the value of ν_1 in tetrahalocobaltates(II) seems to be still undecided.

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