

Infrared Spectra of Cs_3CoCl_5

MAHADEVA NATARAJAN, JOHN QUINN, AND ETALO A. SECCO¹

*Department of Chemistry, St. Francis Xavier University, Antigonish,
Nova Scotia B2G 1C0, Canada*

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The infrared spectra, transmittance, and polarized reflectance of Cs_3CoCl_5 are reported. The group theoretical analysis was executed and a vibrational assignment proposed on the basis of D_{4h} symmetry. Factor group and site effects are discussed.

Introduction

A number of studies have been carried out on complex salts of the form $R_2(\text{MX}_4)$, where R = univalent organic cation, M = bivalent first row transition metal, and X = halogen, with the aim of determining the structural dependence of the complex anion MX_4^{2-} , i.e., its distortion from a regular tetrahedral configuration, in its dependence on the nature of different organic cation environments. The availability of the compound Cs_3CoCl_5 , tricesium tetrachlorocobaltate II chloride, containing a CoCl_4^{2-} core in an inorganic cation environment, induced us to record its infrared spectra, the transmittance and polarized reflectance, for polycrystalline and single crystal samples, and to analyze the spectra using the factor group analysis.

Reynolds *et al.* (3) determined the crystal structure of Cs_3CoCl_5 to be tetragonal, $I4/mcm$, with unit cell dimensions $a = 9.231 \text{ \AA}$ and $c = 14.553 \text{ \AA}$. The two separate types

of Cs^+ ions, a Cl^- anion, and a CoCl_4^{2-} anion, are arranged in a layer-like structure of alternating 2Cs^+ and Cl^- layers and Cs^+ and CoCl_4^{2-} layers (4). The CoCl_4 units are tetrahedrally distorted with Cl-Co-Cl bond angles of 106.1° and 111.2° while maintaining a constant Co-Cl bond length of 2.252 \AA . This type of deviation from strict tetrahedral symmetry is similar to that in Cs_2CoCl_4 (5). In Cs_3CoCl_5 , the tetrahedra of CoCl_4^{2-} ions are arranged about the 001 plane and interact in the a (b) direction (4).

Experimental

Crystals of Cs_3CoCl_5 were grown by slow evaporation of aqueous solutions using distilled water and stock reagents supplied by J. T. Baker ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) and the British Drug Houses (CsCl) of stated purity $\geq 99.9\%$. Crushed smaller crystals were used as the polycrystalline sample and larger single crystals in the form of a regular tetragonal prism, $\sim 3 \text{ mm}$ long and 2 mm^2 cross section, were used as the single crys-

¹ To whom all correspondence should be addressed.

tal sample. All samples were confirmed by X-ray diffraction.

The infrared transmittance spectra were recorded with a Perkin-Elmer 180 double beam spectrophotometer on polycrystalline samples in Nujol mull between polyethylene windows. Reflectance spectra of single crystals were recorded with AgBr polarizer on the reflectance accessory. The far infrared region, 40–350 cm^{-1} , was investigated.

Factor Group Analysis

Cs_3CoCl_5 crystallizes in a tetragonal system with space group $I4/mcm$ (D_{4h}^{18}) containing four formula units within the unit cell (3). The primitive cell has two CoCl_4^{2-} units of D_{2d} symmetry. Using standard correlation mapping procedures (6) the correlation of the internal modes for the CoCl_4 units of Cs_3CoCl_5 from the free CoCl_4^{2-} ion group to the factor group with the site effects is given in Table I.

The total number of normal modes for the two formula units of Cs_3CoCl_5 in the

Bravais cell is 54 which includes 18 internal vibrations of CoCl_4^{2-} ions (Table I), 12 external modes of CoCl_4^{2-} ions, viz., A_{2g} , B_{2g} , $2E_g$, A_{2u} , B_{2u} , and $2E_u$, along with 18 external or lattice modes for six Cs^+ ions, viz., A_{1g} , $2A_{2g}$, B_{1g} , B_{2g} , $2E_g$, $2A_{2u}$, B_{1u} , and $3E_u$, and 6 external or lattice modes for two Cl^- ions, viz., A_{1u} , B_{2u} , and $2E_u$. Of these, 15 modes are infrared active, i.e., $6A_{2u}$ and $9E_u$.

Results and Discussion

The recorded infrared transmittance spectrum for polycrystalline and the reflectance spectra for single crystal samples of Cs_3CoCl_5 are shown in Figs. 1 and 2, respectively; the vibrational frequencies are tabulated in Table II with their assignments. The reported infrared spectra can be divided into two main regions, viz., 250–350 and 40–160 cm^{-1} .

The strong broad band centered near 310 cm^{-1} in Fig. 1 is interpreted as resulting from two overlapping absorptions at 309

TABLE I

| Free ion T_d | Site D_{2d} | Crystal D_{4h} |
|--------------------|------------------|---------------------|
| $\nu_1 A_1$ | $2A_1$ | $2A_{1g}$ |
| $\nu_2 E$ | B_1 | B_{1g} |
| $\nu_3, \nu_4 F_2$ | $2E$ | $2B_{2g}$ |
| | $2B_2$ | $2E_g$ |
| | | A_{1u} |
| | | $2A_{2u}$ |
| | | $2B_{1u}$ |
| | | $2E_u$ |

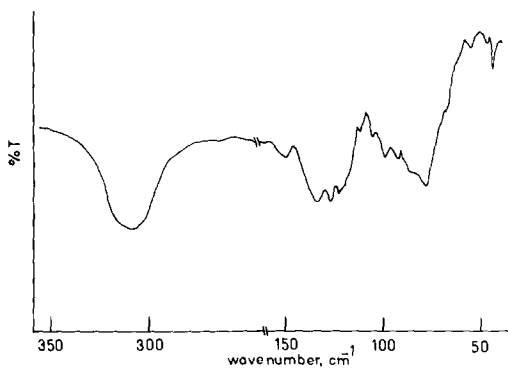


FIG. 1. Infrared transmittance spectrum of Cs_3CoCl_5 .

and 316 cm^{-1} . This interpretation is supported by the two discernible peaks at 312 and 316 cm^{-1} in the unpolarized spectrum, A_{2u} mode, and at 310 and 314 cm^{-1} in the 90° polarized spectrum E_u mode, Fig. 2. These group factor splittings along with the weak splittings, $\sim 4\text{ cm}^{-1}$, are assigned to the $\nu_3(F_2)$ mode of the two CoCl_4^{2-} ions residing in the primitive unit cell. The number of weak absorptions present in the single crystal spectra, but absent in the polycrystalline spectrum, raises the question as to the nature of these modes in the single crystal, these features may have been eliminated by grinding the material to form the polycrystalline state.

The transmittance and reflectance frequencies in the range $120\text{--}135\text{ cm}^{-1}$ are assigned to the factor group splitting of the

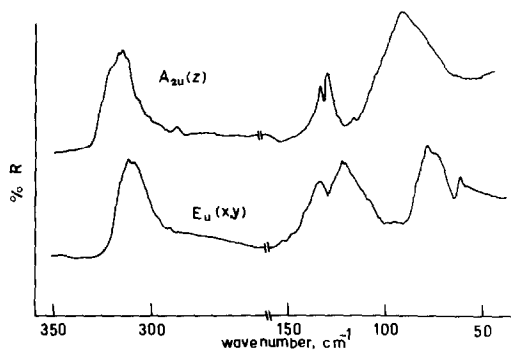


FIG. 2. Infrared reflectance spectra, polarized and unpolarized, of Cs_3CoCl_5 .

TABLE II
INFRARED VIBRATIONAL FREQUENCIES AND
ASSIGNMENTS OF Cs_3CoCl_5

| Frequencies of free CoCl_4^{2-} ion (cm^{-1}) | Transmittance frequency (cm^{-1}) | Reflectance frequency (cm^{-1}) | Assignment |
|---|--|--|------------------------------------|
| $\nu_1, ? (A_1)$ | | | Symmetric stretching |
| $\nu_2, 82 (E)$ | | | Symmetric bending |
| $\nu_3, 297 (F_2)$ | 309 316 | 310, 312 314, 316 | Asymmetric stretching |
| $\nu_4, 130 (F_2)$ | 120, 123 127, 134 106 112, 150 | 121, 123 131, 135 117 | Asymmetric bending Combinations |
| | 94, 87, 78, 68 100, 56, 48, 45 | 91, 80 75, 62 | External and lattice modes |

asymmetric bending $\nu_4(F_2)$ mode. Similar splitting of the $\nu_4(F_2)$ mode had been reported for CoCl_4^{2-} at 118 and 136 cm^{-1} (1). In addition to the predicted factor group splitting for the two CoCl_4^{2-} units, a further possible separation of the transverse and the longitudinal optic modes, i.e., A_{2uL} , A_{2uT} , E_{uL} , E_{uT} on the basis of dipolar coupling factors, is attributed to the vibrational doublets (7, 8).

The remaining observed peaks in the region $45\text{--}100\text{ cm}^{-1}$ are attributed to the external and lattice modes of CoCl_4^{2-} , Cs^+ , and Cl^- species. In general, the rotational modes are expected to appear at higher frequencies with higher intensities relative to the translational modes. Furthermore, the external mode frequencies are expected to decrease in the sequence $\text{Cl}^- > \text{Cs}^+ > \text{CoCl}_4^{2-}$ on the basis of the mass factor alone.

The peaks at $106, 112$ and 150 cm^{-1} , recorded in the transmittance spectrum but not observed in the single crystal spectra, are tentatively assigned to a combination of external modes, viz., $A_{2u} + E_u$.

In summary, we observed all the internal modes predicted by factor group analysis for CoCl_4^{2-} in Cs_3CoCl_5 along with a multi-

plet structure arising from internal optic modes. Also recorded were many of the external modes for CoCl_4^{2-} , Cs^+ , and Cl^- .

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References

1. SABATINI AND L. SACCONI, *J. Amer. Chem. Soc.* **86**, 17 (1964) and references therein.
2. R. J. H. CLARK AND T. M. DUNN, *J. Chem. Soc.*, 1198 (1963).
3. P. A. REYNOLDS, B. N. FIGGIS, AND A. H. WHITE, *Acta Crystallogr. Sect. B* **37**, 508 (1981).
4. B. N. FIGGIS, G. M. GERLOCH, AND R. MASON, *Acta Crystallogr.* **17**, 506 (1964).
5. M. A. BORAI-KOSHITS, *Kristallografiya* **1**, 291 (1956); *Tr. Inst. Kristallogr., Akad. Nauk SSSR* **10**, 117 (1954).
6. J. R. FERRARO AND J. S. ZIOMEK "Introductory Group Theory and its Applications to Molecular Structure," Plenum, New York (1975).
7. R. FRECH, *J. Chem. Phys.* **58**, 5067 (1973).
8. G. J. WU AND R. FRECH, *J. Chem. Phys.* **66**, 1352 (1977).