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Vibrational Spectra of Xanthate Complexes

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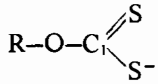
Vibrational spectra of xanthates have been studied and potential constants are determined by Wilson's GF matrix method using Urey-Bradely force field. The empirical assignments made by earlier workers are compared with those of the normal coordinate analysis. Regions of four bands characteristic of $COCS_2$ group have been identified.

Introduction

The structure of metal xanthate complexes have been the subject of investigation by the infrared[1-4] and the crystallographic[5-7] methods. Vibrational bands of these metal salts have so far been assigned on empirical basis by various workers.[1-4] However, there seems to be some controversy about the assignments of the bands appearing in the 1000-1300 cm^{-1} range.

In continuation of our current program of the study of the vibrational spectrum of various sulfur ligands and their metal complexes[8,9] results are reported here on the assignments of several vibrational frequencies of nickel(II) complex of ethyl xanthate using normal coordinate analysis. The system is treated as a seven body problem.

It has been found that all the bands in  $R{-}O{-}C_1\begin{array}{l}/\!\!/ S\\ \backslash S^-\end{array}$ groups are highly coupled. Further, it appears that the group has four characteristic bands around 1250 cm^{-1}, 1100 cm^{-1}, 1020 cm^{-1}, and 550 cm^{-1} which may be called the xanthate bands. These are mixed bands, mainly due to $\nu(C=S)$, $\nu(C{-}O)$, $\nu(C{-}S)$, and $\nu(R{-}O)$.

Experimental Section

Potassium and sodium salts of ethyl xanthate were prepared by the methods available in the literature.[6,7] These alkali metal salts were used to prepare Ni^{2+}, Co^{3+}, and Cr^{3+} complexes of xanthate by the Watt and McCormick procedure.[10]

The i.r. spectra of alkali metal salts of xanthates and their cobalt(III), nickel(II), and chromium(III) complexes were recorded on a Perkin-Elmer model No. 521 diffraction grating double beam recording spectrophotometer in the region 3500 cm^{-1}-250 cm^{-1}. Samples were prepared as KBr pellets.

Calculations

The Nickel complex of ethyl xanthate is known by crystallographic evidence to be a planar molecule of C_{2h} symmetry. However, the model chosen for these calculations is one half of the molecule with a C_s symmetry as shown in Figure 1. The structural data* are given in Table I. In this model, the methylene and methyl** groups were taken as point masses of 14 and 15 atomic units respectively, and calculations were performed treating the system as a seven body problem. Wilson's GF method[13] has been used. Since the symmetry of this model is C_s, the fifteen vibrations are grouped into two classes ($11A'+4A''$). In this paper only the A′ vibrations are calculated.

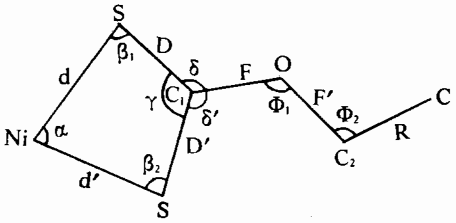


Figure 1.

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(1) L. H. Little, G. W. Poling, and J. Leja, *Can. J. Chem.*, *39*, 1783 (1961).
(2) L. H. Little, G. W. Poling, and J. Leja, *ibid.*, *39*, 745 (1961).
(3) M. L. Shankaranarayana and C. C. Patel, *ibid.*, *39*, 1633 (1961).
(4) G. W. Watt and B. J. McCormick, *Spectrochim. Acta*, *21*, 753 (1965).
(5) G. Carrai and G. Gottardi, *Z. Krist.*, *113*, 373 (1960).
(6) F. Mazzi and C. T. Tadini, *ibid.*, *118*, 378 (1963).
(7) M. Franzini, *ibid.*, *118*, 393 (1963).
(8) Umesh Agarwala and P. Bhaskara Rao, *Ind. J. Pure and Applied Phys.* (accepted for publication).
(9) R. K. Gosavi, U. Agarwala, and C. N. R. Rao, *J. Am. Chem. Soc.*, *89*, 235 (1967).
(10) G. W. Watt and B. J. McCormick, *J. Inorg. Nucl. Chem.*, *27*, 898 (1965).

(*) The value 1.38 Å for F and F' (Figure 1) may be in slight error due to poor X-ray study. However, slight differences in bond distances and bond angles do not cause serious error in the calculation, since the values of the force constants are the main factors in determining the frequencies.[11]

(**) There might be a little mixing of δ(C—H) mode with some of the characteristic frequencies of xanthate group, but for the sake of simplicity of calculations, CH_2 and CH_3 have been taken as unit masses. Also, bending, twisting, rocking, etc., frequencies connected with CH_3 and CH_2 groups are well known.[12] These are not taken into considerations in our calculations which will not affect our assignments of xanthate group frequencies.

(11) K. Nakamoto and A. E. Martell, *J. Chem. Phys.*, *32*, 588 (1960).
(12) C. N. R. Rao, «Chemical Applications of Infrared Spectroscopy», Aacdemic Press, New York (1963).

Table I. Molecular parameters and force constants

Internal coordinates	Bond distance Å	Stretching force constant m.d./Å	Internal coordinates	Bond angles (deg)	Bending force constants m.d./Å	Repulsive force constants m.d./Å	
d	2.24	1.4	α	80.0	0.65	S--S	0.40
d'	2.23	1.4	β_1	83.0	0.6	Ni--C_1	0.30
D	1.65	3.7	β_2	81.0	0.6	S--O	0.25
D'	1.73	3.2	γ	116.0	0.4	S--O	0.25
F	1.38 [a]	4.1	δ	124.5	0.5	C_1--C_2	0.25
F'	1.38 [a]	5.6	δ'	119.5	0.5	C--O	0.2
R	1.48	3.0	Φ_1	123.0	0.55		
			Φ_2	108.5	0.4		

[a] Reference 11.

Table II. Comparison of observed and calculated frequencies

K^+(exan) cm^{-1}	Cr^{3+}(exan)$_3$ cm^{-1}	Co^{3+}(exan)$_3$ cm^{-1}	Ni^{II} ethyl xanthate exp. cm^{-1}	Ni^{II} ethyl xanthate Calculated cm^{-1}	Percent dev. [a]
1145	1250	1258	1268	1264	0.3
1122	1120	1134	1115	1092	2.1
1015	1032	1035	1025	1024	0.1
840	861	865	857	866	1.0
540	563	549	563	580	3.0
447	442	441	437	443	1.3
350	361	358	383	389	1.5
308	340	340	351	347	1.0
290	296	—	281	274	2.5

[a] Percent deviations are obtained with reference to nickel complex.

Table III. Potential Energy distribution for Ni Xanthate

Calc. cm^{-1}	M-S	M-S	C_1-S	C_1-S	C_1-O	O-C_2	Internal coordinates S-M-S	C_1-S-M	C_1-S-M	S-C_1-S	S-C_1-O	S-C_1-O	C_1-O-C_2	C_2-C	O-C_2-C
580	—	1	16	43	15	1	2	—	—	1	1	—	10	2	7
866	—	—	—	2	—	1	—	—	—	—	—	—	2	92	4
347	32	51	—	2	—	—	1	6	3	—	1	1	1	—	2
102	1	2	—	—	—	—	—	1	—	1	21	14	50	1	9
389	24	8	15	—	4	1	6	—	—	1	3	8	15	1	12
250	1	4	—	—	5	—	8	11	8	9	9	—	1	—	44
1092	—	—	3	13	28	42	—	1	—	3	—	5	3	—	—
274	11	—	2	4	2	2	7	3	12	5	7	25	5	—	16
1263	—	—	7	1	43	44	—	—	1	1	3	—	—	—	—
443	23	24	4	—	—	—	—	6	4	12	—	1	9	1	8
1024	—	—	46	30	—	5	—	1	1	—	6	5	4	1	—

The internal coordinates are shown in Figure 1. The GF matrix was symmetrized by the standard method[14] and the symmetrized GF matrix was diagonalized. The matrix secular equation, $|GF-E\lambda| = 0$[13], was solved. The L matrix was obtained by the procedure after Miyazawa.[14] The distribution of potential energy among various coordinates was expressed as $\frac{1}{2}F_{ii}L_{ia}^2\lambda_a$ for the ith coordinate whereby the percentage distribution was obtained.

Although infrared spectra were measured for sodium(I), potassium(I), cobalt(III), nickel(II), and chromium(III) xanthates, the calculations were carried out on only the Ni^{2+} complex. In order to express the potential energy, the Urey-Bradley force field was employed.[15] The force constants were transferred from other molecules.[16,17] After several trials the best set of force constants, listed in Table I, was obtained. In Table II, the calculated frequencies obtained by using this set of force constants are compared with the experimental values of the metal ion complexes.

Results and Discussion

The i.r. spectra of alkali metal xanthates and transition metal (cobalt(III), nickel(II), and chromium (III)) complexes were found to be exactly the same as those given by Watt and McCormick.[4] There has been a controversy[1-4] regarding the assignments of the bands in the range 1020-1070 cm^{-1} and 1100-1270 cm^{-1}. Little *et al.*[1,2] and Watt and McCormick[4] in recent studies have empirically assigned the 1268 cm^{-1}

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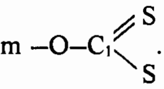
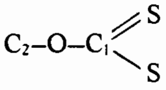
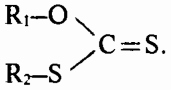
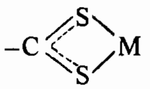
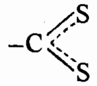
(13) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, «Molecular Vibrations», McGraw Hill, New York (1955).
(14) T. Miyazawa, *J. Chem. Phys.*, *29*, 246 (1958).
(15) T. Shimanouchi, *J. Chem. Phys.*, *17*, 245, 734, 848 (1949).
(16) K. Nakamoto, J. Fujita, R. A. Condrate, and Y. Morimoto, *J. Chem. Phys.*, *39*, 423 (1963).
(17) T. Miyazawa, K. Fukushima, and Y. Ideguchi, *ibid.*, *37*, 2764 (1962).

band, as due to ν(C–O) and 1025 cm^{-1}, as due to ν(C=S), whereas Shankaranarayana and Patel[3] have assigned the bands in the reverse order. It appears that except for the 437 cm^{-1} band, the present calculations generally verify the empirical assignments made by Watt and McCormick.[4] Most of the bands are coupled. The 1268 cm^{-1} absorption has about 90% contribution from the stretching of the C_1–O–C_2 system and the remaining contribution comes from ν(C_1=S). The band at 1115 cm^{-1} has major contributions from ν(C_2–O), ν(C_1–O), and ν(C_1=S)* modes. The 1025 cm^{-1} band has a single major contribution of 60% from the ν(C_1=S) mode. 857 cm^{-1} band is more or less pure ν(C_2–C), which is in agreement with the assignment of Watt and McCormick.[4] 565 cm^{-1} band is highly coupled, but 95 percent of the total contribution comes from the stretching of the three bonds in the system  $-O-C_1\!\begin{smallmatrix}\nearrow S\\ \searrow S\end{smallmatrix}$.

The four highly coupled bands (1268 cm^{-1}, 1115 cm^{-1}, 1025 cm^{-1}, and 565 cm^{-1}), are due to ν(C_1–O), ν(C_2–O), ν(C_1=S), and ν(C_1–S) of  $C_2-O-C_1\!\begin{smallmatrix}\nearrow S\\ \searrow S\end{smallmatrix}$ system. Similar bands are also found in dixanthates[2] and xanthate esters[2]  $\begin{smallmatrix}R_1-O\\ R_2-S\end{smallmatrix}\!\!>C=S$. Thus, one may suggest that there are four characteristic bands for the xanthate group appearing around 1200 cm^{-1}, 1100 cm^{-1}, 1020 cm^{-1}, and 560 cm^{-1}.

The band at 437 cm^{-1}, having some contribution from skeletal deformation has 46% contribution from ν(M–S) with 10% of δ(C_1–O–C_2). Watt and McCormick[4] have assigned this band to δ(C_1–O–C_2). In the light of our studies[8,18] and the Lecomte's work,[19] the assignment of 437 cm^{-1} band to δ(C_1–O–C_2) appears to be high for this mode. Further, comparison with the spectrum of the potassium xanthate, which has a peak in the same region, may not be taken as a supporting evidence for the above assignment. It is just possible that the nature of the metal ligand bond in the complexes may be such as to make the  $-C\!\begin{smallmatrix}\nearrow S\searrow\\ \searrow S\nearrow\end{smallmatrix}\!M$ residue much heavier than  $-C\!\begin{smallmatrix}\nearrow S\\ \searrow S\end{smallmatrix}$ in alkali metal salts and in that case a lowering of the bending frequency, δ(C_1–O–C_2) in metal xanthate is expected due to mass effect. Such an effect has been observed by Watt and McCormick[4] while comparing the metal complexes of methyl and ethyl xanthates. However, this is just a tentative explanation.

The other bands in which ν(M–S) is distributed are 383 cm^{-1} and 351 cm^{-1}. There is apparently a large difference between the two ν(M–S) frequencies (437 cm^{-1} and 383 cm^{-1}, 351 cm^{-1}). However, this seems to be reasonable since the two M–S bonds are next to each other and interact strongly.

The skeletal vibrations δ(C_1–O–C_2) and δ(C–C_2–O) are not observed above 250 cm^{-1}, but they are tentatively assigned to 108 cm^{-1} and 250 cm^{-1}.

Acknowledgments. The authors' thanks are due to the Director, Indian Institute of Technology, Kanpur, for providing the facilities for work.

(*) In 1268 cm^{-1} and 1115 cm^{-1} bands there might be a little mixing due δ(C—H) which we have not taken in our calculation for simplification reasons.

(18) Umesh Agarwala, P. Bhaskara Rao, *Ind. J. of Pure and Applied Phys.* (sent for publication).
(19) J. Lecomte, M. Josien, and J. Lascomb, *Bull. Soc. Chem.*, (France), p. 163 (1956).