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Structural Distortions in CrO_4^{2-} Ion in $3CdSO_4 \cdot 8H_2O$ Crystals from IR Studies

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The IR spectrum of CrO_4^{2-} doped $3CdSO_4 \cdot 8H_2O$ crystals has been analyzed in comparison with the IR spectra of $3CdSO_4 \cdot 8H_2O$ and K_2CrO_4. The spectrum consists of seven absorption bands whose relative positions are shifted toward higher frequencies. These bands have been attributed to the CrO_4^{2-} ion. The results suggest that the site symmetry of the CrO_4^{2-} ion is lowered to D_{2d} due to structural distortions. The observed shift in the bands has been discussed in terms of structural compressions and development of new chemical bonds.

Introduction

The study of vibrational spectra of compounds containing complex ions in a crystalline state provides important information not only about the structural distortion of the ion but also about the chemical nature of the ligand environment in the lattice. Such effects of an alien crystal field environment on the infrared (IR) spectra of the chromate (CrO_4^{2-}) ion have been studied mostly in alkali halides (*1–3*) and in a few alkali sulphates (*4, 5*) by isomorphous substitution. However, the study of IR spectra of CrO_4^{2-} ion in sulphates was confined to the correlation of vibrational progressions observed in the electronic spectra with the vibrational modes of the chromate ion (*4*) or to the observation of isotopic shifts in the fundamental frequencies (*5*).

There appear to be few studies made on the IR spectra of the chromate ion in sulphates, either alkali or other sulphates, with the aim of understanding the site symmetry and hence the structural distortions that the tetroxy-anion undergoes due to the changes in the crysal field perturbations. Our recent study (*6*) on a structurally interesting and chemically unique (*7*) system, $3CdSO_4 \cdot 8H_2O$, indicated a nearly unperturbed tetrahedral (T_d) site for the SO_4^{2-} ion in the lattice. The conclusions were in agreement with the crystal structure data (8–10) and Raman spectral data (*11*).

When the isostructural, isovalent CrO_4^{2-} ion substitutes for the SO_4^{2-} ion, the chromate ion is likely to be distorted locally, as the size of the CrO_4^{2-} ion is slightly larger (ionic radius 3 Å) compared to the size of the sulphate ion (ionic radius 2.95 Å) (*3, 12, 13*). The study of electronic absorption spectra (*14*) is not very helpful in verifying and understanding such local distortions, as the spectra involve only the charge transfer

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bands of CrO_4^{2-} (metal in d^0 configuration) which are mostly unaffected by the ligand fields and the local microsymmetry of the ion. In our recent study of the electronic absorption spectra (*15*) of the irradiated CrO_4^{2-} doped $3CdSO_4 \cdot 8H_2O$ crystals, the assignments of the ligand field bands due to the CrO_4^{3-} ion (metal in d^1 configuration) suggested that the possible highest site symmetry for the hypochromate ion is D_{2d}, as against T_d of SO_4^{2-} in the pure solid. Since the CrO_4^{3-} ion is derived, by an electron-capture, from the CrO_4^{2-} ion at the same site in the lattice, the site symmetry of the CrO_4^{2-} ion also is expected to be D_{2d}. One of the methods of confirming the site symmetry of the chromate ion in $3CdSO_4 \cdot 8H_2O$ is to analyze the vibrational spectra of CrO_4^{2-} doped $3CdSO_4 \cdot 8H_2O$ crystals by separating them from the IR absorption due to the host SO_4^{2-} ion. Therefore, an attempt has been made to analyze the IR spectra of chromate doped $3CdSO_4 \cdot 8H_2O$, with the main objective of arriving at the most probable site symmetry of CrO_4^{2-} ion and hence understanding the possible distortions causing it in the lattice.

Experimental

The $3CdSO_4 \cdot 8H_2O$ crystals were grown by the method of slow evaporation of an undersaturated solution of the salt (AR grade, BDH make) at a consant temperature of 35°C. The doped crystals were grown by similar method by adding 2% by weight of K_2CrO_4 (AR grade, BDH make) to the host solution. Fairly large size (4 mm × 4 mm × 2 mm) crystals of well-defined morphology were obtained after about a fortnight. These crystals belong to monoclinic system with space group $C_{2/c}$ (C_{2h}^6).

For the purpose of recording IR spectra of the CrO_4^{2-} doped crystals (yellow in color), a small crystal was taken; it was crushed, ground, and made into a KBr pellet. The pressures (~15 MPa) applied were within the range of pressures that do not cause polymorphic changes in the sample. Therefore, it is assumed that the unit cell structure of the sample in the pellet is retained. The IR spectrum of the pure $3CdSO_4 \cdot 8H_2O$ crystals was recorded by a similar pellet-sample technique.

Results

The IR spectrum of CrO_4^{2-} doped $3CdSO_4 \cdot 8H_2O$ crystals is shown in Fig. 1 by the solid line, curve (i). Although the IR frequencies of normal modes in free chromate ion (*16, 17*) and K_2CrO_4 crystalline samples (*18*) have been reported in the literature, we have recorded the IR spectrum of K_2CrO_4 crystalline samples to bring about the resolution capability of our instrument, which seems to be accurate within ± 2 cm^{-1}. Such a spectrum of K_2CrO_4 together with the spectrum of pure $3CdSO_4 \cdot 8H_2O$ has been superposed on the spectrum of doped samples for proper comparison of the nature and positions of the bands and are shown by the dash–dot curve (ii) and dotted curve (iii), respectively, in Fig. 1. It may be noted that in Fig. 1 the range of spectra has been limited to 1500 cm^{-1} 200 cm^{-1}, which includes the range of interest of the present investigation. Since a study of the environment of various atoms in $3CdSO_4 \cdot 8H_2O$ suggests (*8*) that there are strong forces between cadmiums and SO_4^{2-} groups and that much weaker ones are involved in the contacts of the water molecule, the region beyond 1500 cm^{-1} is considered unimportant to the present study.

Discussion

It is evident from Fig. 1 that the spectrum (curve i) of CrO_4^{2-} doped $3CdSO_4 \cdot 8H_2O$ is markedly different from the spectra of K_2CrO_4 and $3CdSO_4 \cdot 8H_2O$ samples. Curve (iii) belonging to $3CdSO_4 \cdot 8H_2O$ consists of two strong bands at 1103 and 610 cm^{-1}, and

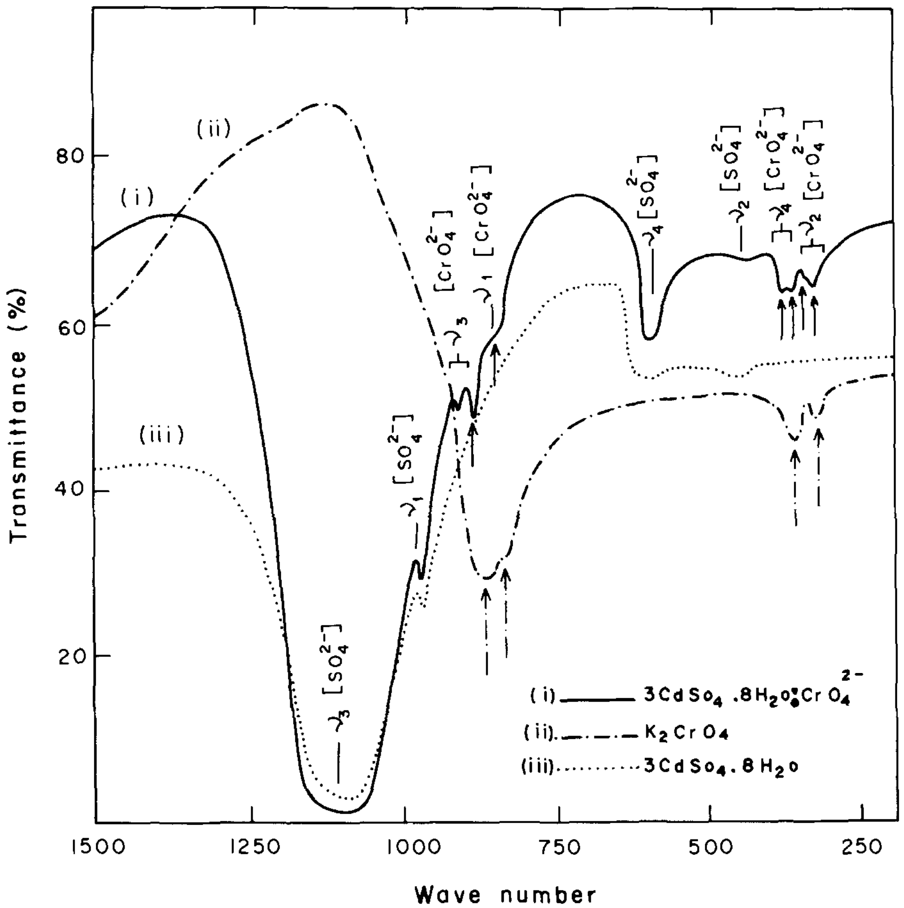

FIG. 1. IR bands observed in chromate doped $3CdSO_4 \cdot 8H_2O$ lattice: curve (i), solid line, gives the spectrum of the CrO_4^{2-} doped sample; curve (ii), dash–dot line, corresponds to the IR spectrum of K_2CrO_4. The IR spectrum of $3CdSO_4 \cdot 8H_2O$ [curve (iii), dotted line] is given for comparison.

these have been attributed to the IR active modes of SO_4^{2-} ion $\nu_3(F_2)$ and $\nu_4(F_2)$ under perfect T_d symmetry. The very weak bands at 980 and 453 cm^{-1} are due to the IR inactive modes $\nu_1(A_1)$ and $\nu_2(E)$, respectively, as reported earlier (*6*). Relative to these sulphate bands, the usually observed (*16–18*) four bands of the chromate ion are observed at 847 cm^{-1} due to $\nu_1(A_1)$ mode, 348 cm^{-1} due to $\nu_2(E)$ mode, 884 cm^{-1} due to $\nu_3(F_2)$ mode, and at 368 cm^{-1} due to $\nu_4(F_2)$ mode, as indicated by curve (ii) belonging to K_2CrO_4. In contrast to these spectra, the spectrum of chromate doped $3CdSO_4 \cdot 8H_2O$ crystals (curve i) consists of two prominent bands at 920 and 890 cm^{-1}, a well-defined shoulder at 855 cm^{-1}; two weak but well-resolved bands at 388 and 378 cm^{-1}, and lastly a shoulder at 360 cm^{-1} on the weak band peaking at 345 cm^{-1}. Thus the IR spectrum of chromate doped $3CdSO_4 \cdot 8H_2O$ consists of seven distinct bands, besides the usual sulphate bands of the host-lattice. These results are summarized in Table I, which includes, for comparison, the bands observed for the CrO_4^{2-} ion doped in other

TABLE I

VIBRATIONAL FREQUENCIES (cm^{-1}) OBSERVED FOR CrO_4^{2-} ION UNDER DIFFERENT SITE SYMMETRIES IN VARIOUS CRYSTALLINE MATRICES

Crystal	Dopant	Site symmetry	$\nu_1(A_1)$	$\nu_2(E)$	$\nu_3(F_2)$	$\nu_4(F_2)$	Reference
K_2CrO_4	—	T_d	847	348	884	368	(*18*)
K_2SO_4	K_2CrO_4	T_d	869	340	907	380	(*4*)
Na_2SO_4	K_2CrO_4	T_d	860	335	904	390	(*4*)
$(NH_4)_2SO_4$	K_2CrO_4	T_d	865	335	905	390	(*4*)
K_2SO_4	Cs_2CrO_4	*	*	*	931	*	(*5*)
					911		
					906		
Rb_2SO_4	Cs_2CrO_4	*	*	*	919	*	(*5*)
					903		
					898		
$3CdSO_4 \cdot 8H_2O$	K_2CrO_4	D_{2d}	855	360	920	388	(present work)
				345	890	378	
Cs_2SO_4	Cs_2CrO_4	*	*	*	905	390	(*5*)
					892	382	
					887	380	

Note. Asterisk (*) indicates not reported.

lattices. It is seen from Table I that the average positions of the four modes A_1, E, F_2, and F_2 of the CrO_4^{2-} in the doped crystals are shifted toward higher frequency.

It is seen both from Fig. 1 and Table I that the triply degenerate bands $\nu_3(F_2)$ and $\nu_4(F_2)$ of the SO_4^{2-} ion in $3CdSO_4 \cdot 8H_2O$ are not only appreciably separated from each other but are also appreciably away from the triply degenerate $\nu_3(F_2)$ and $\nu_4(F_2)$ band positions of the CrO_4^{2-} ion in K_2CrO_4. This facilitates one to observe any site group splittings in these degenerate vibrations of the chromate ion in the host crystal. It is seen from Fig. 1 (curve i) that indeed such splittings occur clearly in the ν_3 and ν_4 bands, besides the band due to $\nu_2(E)$ at ~350 cm^{-1} showing a weak splitting. Since the separation between these split components of the bands does not exceed ~40 cm^{-1} in all the three modes, they are most probably not due to any correlation field splittings (*19*) which give rise to combinational bands. Thus, all seven bands observed for chromate doped $3CdSO_4 \cdot 8H_2O$ crystals, excluding the host sulphate bands, are unambiguously assigned to the CrO_4^{2-} complex.

The features such as splitting of degenerate modes and shifting of the band positions toward higher frequency observed for chromate doped $3CdSO_4 \cdot 8H_2O$ crystals are to be explained in terms of site symmetry and lattice effects on the CrO_4^{2-} ion. When the tetrahedral chromate ion occupies the SO_4^{2-} site, which is nearly of T_d symmetry (*6, 8*), it is subjected to perturbations due to a different environment, besides the compression arising from the slight incompatibility in ion sizes. The different environment may mean development of bonds between the CrO_4^{2-} ion and the surrounding Cd^{2+} metal ion.

The bonding, slight compression, and such other solid state chemical interactions lead to a situation where the crystal field experienced by CrO_4^{2-} in the host $3CdSO_4 \cdot 8H_2O$ is different from what the ion experiences in the K_2CrO_4 lattice. It is quite likely, therefore, that the CrO_4^{2-} ion undergoes structural distortions involving changes in bond lengths and angles of Cr–O bonds. Such distortions in MX_4 type tetrahedral ions have been reported in the literature (*20*). Therefore, the observed IR spectra have to be interpreted in terms of a site symmetry lower than T_d. In case the distortion leads to elimination of the C_3 symmetry element, the probable site symmetry for the ion will be D_{2d}. On the other hand, if distortions are such that the C_2 and S_4 symmetry elements of the T_d point group are lost, the site symmetry will be lowered to C_{3v} (*19, 21, 22*). Since the crystal structure data indicate that the site of SO_4^{2-} in $3CdSO_4 \cdot 8H_2O$ is of nearly T_d symmetry, it is quite unlikely that the site symmetry of the CrO_4^{2-} ion is lowered further below C_{3v}. Therefore, other point groups for the site need not be considered.

Under D_{2d} symmetry, the degeneracy of $\nu_3(F_2)$ and $\nu_4(F_2)$ are partially removed and the degeneracy of $\nu_2(E)$ is completely lifted. On the other hand, under C_{3v} symmetry, while the degeneracies of ν_3 (F_2) and ν_4 (F_2) are removed to the same extent, no lifting of degeneracy of the ν_2 (E) mode occurs. The correlation between the various symmetry species under the T_d, D_{2d}, and C_{3v} point groups, along with the relative shifts in the energies of the corresponding vibrations, are summarized in Fig. 2. A close look at curve (i) of Fig. 1 indicates that the band at ~350 cm^{-1} with a shoulder corresponds to the non-degenerate vibrations of the $\nu_2(E)$ mode which transform under D_{2d} as $\nu_2(A_1)$ and $\nu_2(B_1)$. This observation favors D_{2d} rather than C_{3v} site symmetry for the CrO_4^{2-} ion in 3Cd $SO_4 \cdot 8H_2O$. Therefore, the structural distortions are not probably as high as to cause the lowering of T_d symmetry to C_{3v}. Since the seven band spectrum of curve (i) in Fig. 1 fits well into the D_{2d} point group, (Fig. 2) we believe that the chromate ion in the $3CdSO_4 \cdot 8H_2O$ crystal is distorted to a flattened tetrahedron and its site symmetry is most probably D_{2d}.

While the bonds between K^+ and CrO_4^{2-} in the K_2CrO_4 lattice are ionic, the bonding that develops between the metal Cd^{2+} and the CrO_4^{2-} ion in $3CdSO_4 \cdot 8H_2O$ is also ionic, but probably with a higher covalent character. The metal ion, Cd^{2+}, in the doped crystal is known to possess greater polarizing power compared to the corresponding polarization in the K_2CrO_4 lattice. The polarization in the doped crystals could be due to higher covalent interactions, particularly, between Cd^{2+} with its higher charge density and O^{2-} of the anion (CrO_4^{2-}). This assumption is well justified by the crystal structure data (*8*), which suggest that the forces between metal atoms (Cd^{2+}) and the SO_4^{2-} (or CrO_4^{2-} in the doped case) ions must be greater, and to a first approximation the structure has been regarded as being composed of Cd atoms and SO_4 groups only. Therefore, the anionic environment in $3CdSO_4 \cdot 8H_2O$ for the dopant CrO_4^{2-} can be considered as constituted mainly by four cadmium ions. Such an anionic environment for the CrO_4^{2-} ion in the $3CdSO_4 \cdot 8H_2O$ lattice and the consequent structural distortions discussed above have been presented schematically in the Fig. 3. Thus, as CrO_4^{2-} replaces SO_4^{2-} in $3CdSO_4 \cdot 8H_2O$, the bonding between the Cd^{2+} and the CrO_4^{2-} ion causes lowering of the symmetry from T_d in K_2CrO_4 to D_{2d} in the $3CdSO_4 \cdot 8H_2O$ crystal (Fig. 3).

This conclusion is in conformity with D_{2d} site symmetry predicted for the CrO_4^{3-} ion from the study of electronic absorption spectra (*15*). In accordance with this D_{2d} site symmetry, the observed seven bands have been assigned to the following symmetry species: ν_1 (A_1) 855 cm^{-1}; ν_2 (E) splits into 360 cm^{-1} (A_1) and 345 cm^{-1} (B_1); $\nu_3(F_2)$ splits into 920 cm^{-1} (B_2) and 890 cm^{-1} (E); and $\nu_4(F_2)$ splits into 388 cm^{-1} (B_2) and 378 cm^{-1} (E).

The shift in the band frequencies of the

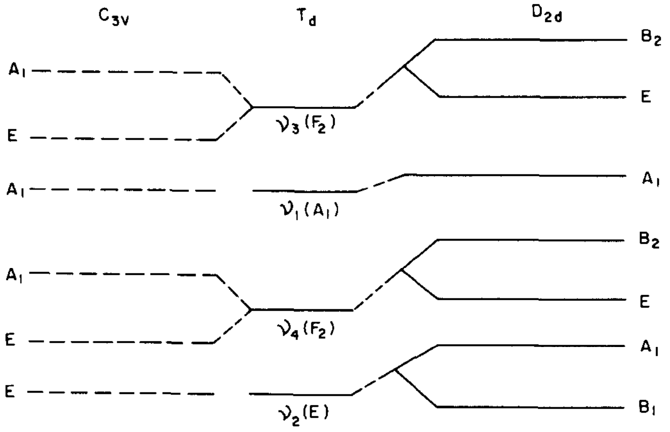

FIG. 2. Correlation map giving the symmetry species corresponding to the normal vibrations of CrO_4^{2-} ion under T_d, D_{2d}, and C_{3v} point groups. The observed shifting of vibrational frequencies in the doped sample is also indicated in terms of relative positions of the symmetry species.

CrO_4^{2-} ion in $3CdSO_4 \cdot 8H_2O$ (Table I) is probably due to the slight compression that the ion undergoes at the host site. Similar shifts were observed in the case of CrO_4^{2-} doped cesium halides and were explained in terms of compression (*3*). However, the shift of IR frequencies of the CrO_4^{2-} ion toward higher frequencies could also be due to the development of bonds between chromate and the Cd^{2+} ion, discussed above. Such effects of host-cation on the vibrational frequencies of CrO_4^{2-} have been re-

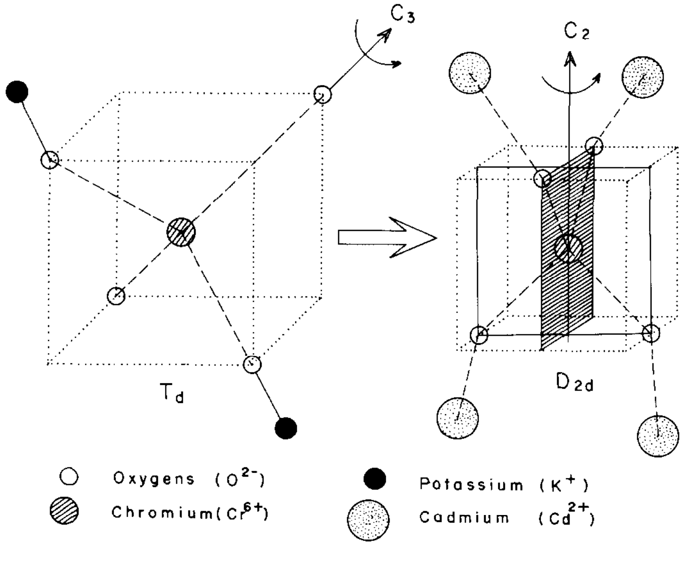

FIG. 3. Schematic diagram showing the change in the anionic environment and the consequent structural distortions of the CrO_4^{2-} ion in the $3CdSO_4 \cdot 8H_2O$ lattice. (On the left, the bonds involved in the K_2CrO_4 molecule only are shown, while on the right bonds involved in the unit cell are shown).

ported (*5, 23*). It is found that as the atomic weight of the host-cation increases, the frequency ν_3 decreases. It is seen from Table I that the vibrational frequencies due to the $\nu_3(F_2)$ mode observed in the present case lie somewhere between the frequencies for CrO_4^{2-} in Rb_2SO_4 and in Cs_2SO_4, understandably due to the fact that the atomic weight of Cd (112.4) lies between those of Rb (85.5) and Cs (132.9). The data obtained in the present study therefore support the observation made by Muller *et al.*(*5*) that in M–CrO_4 complex, as the atomic weight of M^+ (or M^{2+}, as the case may be) increases, the magnitudes of vibrations in the molecular ion decrease.

It is pertinent to mention here that for several tetrahedral ions, certain trends for the vibrational frequencies, besides $\nu_3 > \nu_1$ and $\nu_4 > \nu_2$, have been observed (*20*). The value of ν_3 (asymmetric stretching) frequency is found to depend on the mass of the central atom, decreasing as the latter increases. In the present study, as we go from SO_4^{2-} to CrO_4^{2-}, the mass of the central atom increases from S (32.1) to Cr (52) and the ν_3 magnitude decreases from 1103 to 884 cm^{-1} (Table I). This trend seems to be applicable to the remaining modes also.

In the particular case of tetrahedral tetroxy-anions, it is found that the ratio of totally symmetric stretching frequency to the asymmetric stretching frequency ν_3, i.e., ν_1/ν_3, is found to show some regularity as we go from one compound to the other in the order of increasing mass of the central metal atom (*24*). In fact, it is found that the variations of ν_1/ν_3 frequency ratio could be correlated with the mass and the oxidation number of the central atom. In the present investigation, the ν_1/ν_3 ratio for SO_4^{2-} is 0.89, where S is in the S^{6+} state, and for CrO_4^{2-} in K_2CrO_4 it is found to be 0.95, where Cr is in the Cr^{6+} state. In the case of CrO_4^{2-} doped in $3CdSO_4 \cdot 8H_2O$, the ratio is found to be 0.94, which is almost equal to the ratio observed in K_2CrO_4 and hence supports our assignment of the ν_3 mode whose average value is taken as 905 cm^{-1}.

Conclusions

The analysis of IR spectra of CrO_4^{2-} doped $3CdSO_4 \cdot 8H_2O$ crystals strongly suggests that the site symmetry of the CrO_4^{2-} ion is lowered from T_d in K_2CrO_4 to D_{2d} in the $3CdSO_4 \cdot 8H_2O$ crystal. The lowering is attributed to structural distortions arising mainly from the development of bonds between the Cd^{2+} and the O^{2-} of the chromate ion in the host-lattice. The magnitudes of the observed vibrational frequencies also support such bonding.

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