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INFRARED AND RAMAN INVESTIGATION OF THE STRUCTURAL BEHAVIOUR OF THE $S_2O_3^=$ ION IN CADMIUM THIOSULFATE DIHYDRATE, $CdS_2O_3.2H_2O$ (1)

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Solid state infrared and Raman spectra of cadmium thiosulfate dihydrate, $CdS_2O_3.2H_2O$, have been examined. The splittings and the shifts of the internal frequencies of the coordinated S_2O_3 anions were found to characterize bridging thiosulfate groups binding two cadmium ions through the external sulfur atom.

We have recently synthetised a great number of new compounds containing thiosulfate anion, cadmium and either another metallic ion or an organic ligand (2). Infrared and Raman investigations revealed that, in such compounds, the S_2O_3 groups can bind cadmium ions either as bridging ligands (I), monodentate through terminal sulfur (II) or as bidentate with bridging (III) or chelate (IV) framework (Fig. 1).

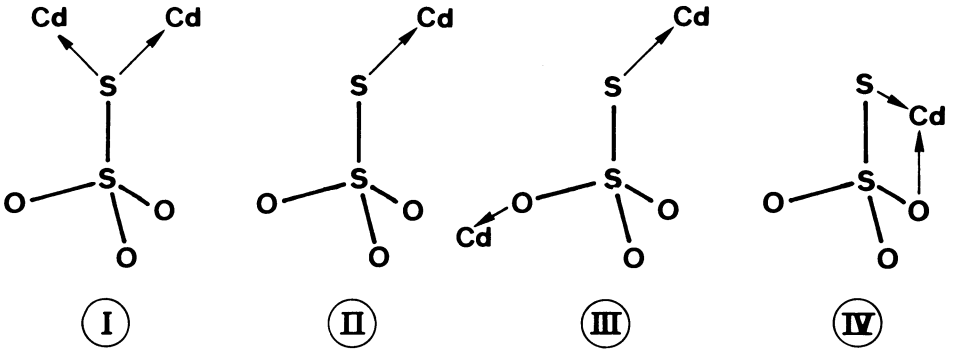


Figure 1

We report here the solid state infrared and Raman spectra of the simpliest compound containing cadmium and thiosulfate ions, $CdS_2O_3.2H_2O$, in order to throw some light on the structural behaviour of the S_2O_3 entity towards cadmium in absence of perturbing effects due to other host ions or ligands.

EXPERIMENTAL

$CdS_2O_3.2H_2O$ has been synthesized as described earlier (3). Infrared spectra in the range 4000-200 cm^{-1} have been measured using a Beckman IR-12 spectrometer. As the samples undergo reaction when alkali halide disks are used or even when pressed into corresponding pellets (4), Nujol mulls between Tl_2BrI plates have been used. Raman spectra in the range 4000-20 cm^{-1} were measured directly on crystalline powders in a glass capillary using a Coderg PHO monochromator equipped with a 50 mw Spectra Physics He-Ne Laser.

RESULTS AND DISCUSSION

In a previous study the vibrational behaviour of the $S_2O_3^=$ ion in a number of solid inorganic thiosulfates involving various metal-$S_2O_3^=$ associations has been examined in the light of their known or proposed structures $^{(2,5)}$. A systematic study of the splittings and the shifts of the six thiosulfate fundamental frequencies with respect to those for the free unperturbed anion lead to a consistent set of spectra-structure correlations. General criteria could be established and used to make clear the structural behaviour of the S_2O_3 entity by means of infrared and Raman spectroscopy for compounds not yet submitted to a X-ray crystallographic study.

These criteria are used here to elucidate the coordination of the thiosulfate ion in $CdS_2O_3.2H_2O$.

The geometry changes of the S_2O_3 pyramid as well as the SO and SS bond order perturbations due to thiosulfate-metal interactions in the crystal will considerably influence the vibrational spectra of the coordinated anions. In the 300-1250 cm^{-1} region, nine i.r. bands and Raman peaks are observed (Table I).

Table I : Infrared and Raman frequencies (cm^{-1}) for $CdS_2O_3.2H_2O$ and their assignments

$CdS_2O_3.2H_2O$		free $S_2O_3^{=}$(10)	Assignments
IR	Raman		
	95 m		lattice modes including ν(Cd-S) and ν(Cd-S-Cd)
	127 m		
	153 w		
	180 w		
	209 w		
	297 w		
330 w	330 w	339	$\rho(SO_3) = \nu_6(E)$
353 w	355 m		
425 w	424 vs	448	$\nu(SS) = \nu_3(A_1)$
530 m	527 m	538	$\delta_{as}(SO) = \nu_5(E)$
556 m	550 w		
635 s	628 m	671	$\delta_{sym}(SO) = \nu_2(A_1)$
1019 s	1017 vs	999	$\nu_{sym}(SO) = \nu_1(A_1)$
1157 m	1150 m	1126	$\nu_{as}(SO) = \nu_4(E)$
1212 m	1210 m		

The three degenerate (E) modes of the free ion are found split into doublets indicating that the S_2O_3 C_{3v} point group symmetry has been lowered (C_s or C_1).
This splitting can result either from a S_2O_3 distortion upon coordination or from a local low symmetry field created by the surrounding ions (site splitting effect). When both effects are present the former is always predominant. On the other hand, we have found that a briging-type coordination generally causes a greater distortion of the S_2O_3 geometry than a simple sulfur to metal bond. The magnitude of the distortion can be evaluated by the frequency separation (Δ) between the two doublets. In the case of $CdS_2O_3.2H_2O$ an important splitting of the degenerate modes is observed (Table I) and the Δ values measured (Table II) tend to support a bridging thiosulfate coordination.

Cadmium ion (soft acid) is expected to interact with S_2O_3 entities through the terminal sulfur atom (soft base) rather than through the oxygen atoms which have a hard basic character. The resulting SO and SS bond order perturbations will then cause a shift of the SO symmetric and asymetric stretching modes towards higher frequencies together with a decrease of ν(SS) frequency. Any Cd-oxygen interaction is expected to cause the same frequency shifts in the opposite direction while a mixed O and S bidentate coordination (Schemes III and IV) should be characterized by a quite different and typical vibrational pattern (2,6).

Table II

Coordination	Characteristic frequency position (cm^{-1}) for some normal vibrations				Magnitude of the splittings of the degenerate modes (cm^{-1})		
	νSS	ν_{sym}(SO)	ν_{as}(SO)	ν(SO)aver.	$\Delta\nu_4$	$\Delta\nu_5$	$\Delta\nu_6$
Free $S_2O_3^=$ (10)	448	999	1126	1084	-	-	-
Cd-S-SO_3 (2) monodentate	425-435	1005-1012	1150-1170	1105-1125	20-50	15-25	<20
Cd\\ S-SO_3 (2) Cd/ bridging	<425	1015-1028	1170-1200	>1125	45-80	20-40	>20
$CdS_2O_4.2H_2O$ IR	425	1019	1187	1132	50	26	23
R	423	1017	1185	1130	60	23	25

The infrared and Raman frequencies of the thiosulfate ions involved in $CdS_2O_3.2H_2O$ are reported in Table I and compared with the position of the fundamental frequencies arising from the free $S_2O_3^=$ ion. The important shifts observed for ν_{sym}(SO), ν_{as}(SO) and ν(SS) clearly suggest a cadmium-sulfur association.

We have also shown (2) that the magnitude of the shifts mentioned above could prove a useful criterion for distinguishing between a sulfur bridging (Scheme I) and a sulfur-monodentate (Scheme II) thiosulfate groups. Two electron-acceptor cadmium ions will perturb the SO and SS bond orders in a larger extent than only one ion and the corresponding shifts of the ν_{sym}(SO), ν_{as}(SO) and ν(SS) modes are expected to be more pronounced in the former case.

Typical positions of the ν_{sym}(SO), ν_{as}(SO) and ν(SS) vibrations, the values of the average SO stretching frequency calculated using the Lehman's (7) formula :

$$\nu(SO)\ av. = 1/3\ [\ \nu_{sym}(SO) + 2\ \nu_{as}(SO)\ ]$$

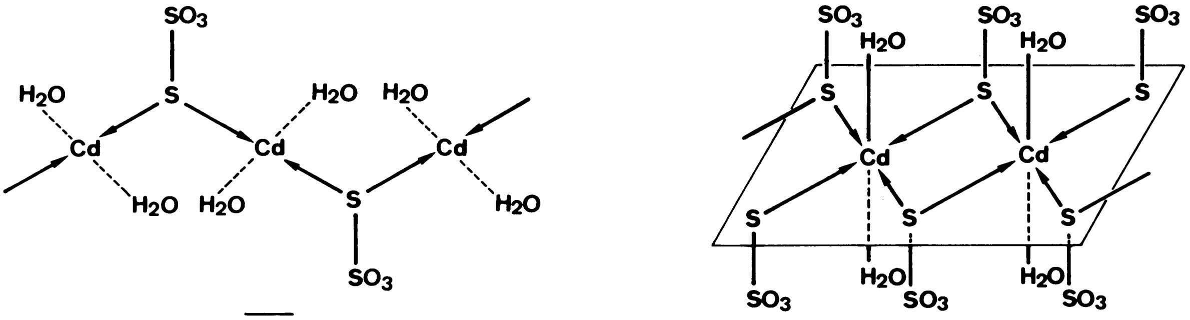
for both bridging and S-monodentate S_2O_3 ions associated to cadmium are given in Table II and compared with the same parameters obtained in the case of $CdS_2O_3.2H_2O$.

All the values do fall within the frequency range defined for a bridging thiosulfate group and confirm the preliminary conclusions derived from the Δ values.

For a sulfur atom interacting with two different cadmium ions in the bridging position, two possible schematic structures for $CdS_2O_3.2H_2O$ could be proposed :

(i) cadmium thiosulfate is a simple salt. The Cd atom is then tetrahedrally surrounded by 2S and $2H_2O$, the whole framework consisting in a polymeric chain (Scheme V, Fig. 2).

(ii) cadmium thiosulfate is an autocomplex salt of the type $Cd[Cd(S_2O_3)_2(H_2O)_2].\ 2H_2O$ (cadmium bis-aquo-bis-thiosulfato-cadmate dihydrate). The structure of the $[Cd(S_2O_3)_2(H_2O)_2]^{=}$ anions will consist in polymeric chains with the Cd atoms octahedrally surrounded by 4S and $2H_2O$ (Scheme VI, Fig. 2).



V.

VI.

Figure 2

Although several authors have mentioned previously the possible existence of bridging S_2O_3 groups in solution containing soft acidic cations such as cadmium (8) or both cadmium and mercury (9) the present work reports the first example of solely bridging thiosulfato groups coordinated to cadmium ions in the solid state.

An X-ray crystallographic study of $CdS_2O_3.2H_2O$ is at present under investigation.

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