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Abstract

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On the Structure of Complex Compounds with Bidentate Sulfito Groups

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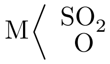
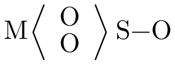
The sulfito group, as is known, can occupy not only one but also two coordination positions in the inner sphere of complexes. For example, in compounds whose composition corresponds to the formula $M_3^I[M(\mathrm{SO_3})_3] \cdot n\mathrm{H_2O}$, where M^I is a monovalent cation and M is trivalent Co or Rh, each sulfito group formally occupies two coordination positions, since the coordination numbers of trivalent Co and Rh are equal to 6. We say formally because it is not known whether the bidentate sulfito group occupies two coordination positions in the inner sphere of mononuclear complexes or whether it is a bridging group. Structural data on this question are lacking. Most investigators assume (see, for example, ($^{1-4}$)) that in complexes with a bidentate sulfito group structure I is realized.



$$\mathrm{M}\left\langle \begin{matrix} \mathrm{SO_2} \\ \mathrm{O} \end{matrix} \right. \qquad (I)$$

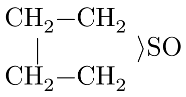


$$\mathrm{M}\left\langle \begin{matrix} \mathrm{O} \\ \mathrm{O} \end{matrix} \right\rangle \mathrm{S{-}O} \qquad (II)$$

However, structure I is rejected (^{5}) already on the basis of consideration of spatial relations. Belluijn (^{6}), on the contrary, regards structure II as the most probable for complex compounds of Co(3+). Consideration of spatial relations (^{5}) permits the existence of structure II, although in this case the corresponding octahedra or squares (Pt(2+) and Pd(2+)) must be substantially distorted. Finally, Ervikker (^{7}), on the basis of a study of the chemical properties of Pd(2+) compounds, came to the conclusion that in Pd(2+) complexes the bidentate group is a bridging group.

To clarify the question of the structure of complexes with formally bidentate sulfito groups, one may use data from the infrared absorption spectra of $\mathrm{Na_3[Co(SO_3)_3] \cdot 4H_2O}$ (^{8}), $\mathrm{K_3[Rh(SO_3)_3]}$ (^{9}), and $\mathrm{(NH_4)_3[Rh(SO_3)_3]}$ (^{9}). It should be expected that, if structures I and II are realized (symmetry of the sulfito groups C_s; all 6 frequencies $(4A' + 2A'')$ are active in infrared absorption), part of the frequencies of the valence vibrations of SO will be lowered in comparison with the sulfite ion because of weakening of the SO bonds whose O atom is bound to the atom of the complex-forming metal. This point of view is confirmed by the experimentally found lowering of the frequencies of the valence vibrations of XO bonds (for the most diverse atoms

X) upon coordination of groups containing these bonds through the O atom (for example, nitrito, nitrato, iodato, perchlorato groups, $(CH_3)_2SO$,



$$\begin{matrix} CH_2-CH_2 \\ | \\ CH_2-CH_2 \end{matrix} \rangle SO$$

and others).

Table 1 gives, according to the works ([8],[9]), the vibrational frequencies found in the infrared spectra of Co(3+) and Rh(3+) complexes with bidentate sulfito groups, and Table 2—according to the same works—the frequency intervals for the sulfite ion and monodentate sulfito groups (the spectra were obtained for complexes in the solid state).

Table 1

	ν(SO), cm^{-1}*	δ(SO), cm^{-1}
$Na_3[Co(SO_3)_3] \cdot 4H_2O$	1100; 1019; 1104; 969; 930 b.	653 b.; 635537 b.; 493
$K_3[Rh(SO_3)_3]$	1139; 1112 b.$ 1069b.; 1051 < br > $971 b.; 942	681; 635552; 526
$(NH_4)_3[Rh(SO_3)_3]$	$ $1159 b.; $ 1138b.; 1111 < br > $1066 b.; 1048; 949	680; 631545; 526

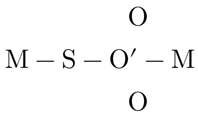
* b. —bend.

Table 2

	ν_1 (A_1)	ν_2 (A_1)	ν_3 (E)	ν_4 (E)
Sulfite ion	951—998	616—655	897—972	445—527
Sulfito group, Co(3+)	948—1009	618—665	1044—1121	495—530
Sulfito group, Rh(3+)	949—977	628—665	1042—1106	515—525

The spectra of Rh(3+) complexes with bidentate sulfito groups have two distinctive features. First, in the region of the bands assigned to ν(SO), three complex bands of approximately equal (or, in any case, comparable) intensity are found; the magnitude of the splitting is substantial. Second, the frequencies ν(SO) of bidentate (942—1139 cm^{-1}) and monodentate (949—1106 cm^{-1}) sulfito groups are approximately the same. Consequently, the character of the SO bonds in mono- and bidentate sulfito groups is approximately the same. On the basis of these groups one may conclude that the symmetry of bidentate sulfito groups in Rh(3+) complexes is indeed lowered (a substantial splitting of ν(SO)) in comparison with monodentate sulfito groups; however, structure I or II is not realized (there are no ν(SO) frequencies substantially lowered in comparison with the sulfite ion).

The results obtained become readily explicable if one assumes the existence, in the crystalline state, of bridging sulfito groups with nonequivalent metal-ligand bonds: the S—M bond is stronger than the O′—M bond:



(III)

$$\mathrm{M - S - \underset{O}{\overset{O}{O'}} - M}$$

With such a structure the symmetry of the sulfito group is lowered, which leads to splitting of the frequencies; however, since the O′—M bond is weak, no noticeable weakening of the S—O′ bond and the associated lowering of ν(SO) occur. In crystals, structures III may form polymeric chains, which, on going into solution, may break at the site of the O′—M bond; the vacated site will be occupied by solvent molecules or by another substance. This conception fully coincides with the already mentioned view of Erviker (7) on the structure of Pd(2+) complexes. For $Na_3[Co(SO_3)_3] \cdot 4H_2O$ the splitting of ν(SO) is less significant; lowering of the frequencies is also not found. Consequently, for Co(3+) as well, structures I or II are rejected. The smaller splitting of the frequencies indicates that the O′—Co bond (structure III) in this complex is even weaker than the O′—Rh bond. If structures III form polymeric chains, then the corresponding compounds should be poorly soluble. And indeed, complexes containing only monodentate sulfito groups are, as a rule, sparingly soluble in water.

Thus, at least for the complexes of Co(3+) and Rh(3+), the most probable is the existence of bridging sulfito groups of type III, rather than sulfito groups occupying two coordination positions in a mononuclear complex.

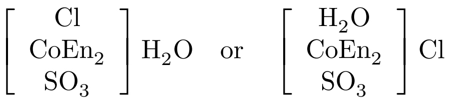
The compounds $[CoEn_2SO_3]X$, where $X = \mathrm{Cl, J}$, or SCN, studied by Beldyugin, are no exception. The properties found for these complexes agree with the bridging structure of formally bidentate sulfito groups that we propose. In this case the complexes in the crystalline state apparently have the structure:

$$\left[\text{ structure with two } \mathrm{CoEn_2} \text{ fragments bridged by } \mathrm{SO_3} \text{ groups }\right]\mathrm{Cl_2},$$

where the cobalt—oxygen bonds are less strong than the cobalt—sulfur bonds. On transfer into solution the cobalt—oxygen bonds are broken; therefore it is not surprising that in aqueous solutions the complexes are monomers. Cleavage of the cobalt—oxygen bonds leads to the formation of ions

$$\left[\text{ mononuclear } \mathrm{CoEn_2SO_3(H_2O)} \text{ ion }\right]^+ \qquad \text{(IV)}$$

Beldyugin found that compounds of this type are less prone to addition of SCN^-, NO_2^-, or SO_3^{2-} than complexes of the type $[CoEn_2SO_3Cl] \cdot H_2O$. This is understandable, since the water molecule in IV is in the trans position to the relatively weakly trans-influencing ethylenediamine and therefore has no special tendency to be replaced by other ligands. Complexes of the type $[CoEn_2SO_3Cl] \cdot H_2O$, however, apparently have a trans structure:



$$\begin{bmatrix} Cl \\ CoEn_2 \\ SO_3 \end{bmatrix} H_2O \quad \text{or} \quad \begin{bmatrix} H_2O \\ CoEn_2 \\ SO_3 \end{bmatrix} Cl$$

In these complexes the chloro ligand (or the water molecule) is in the trans position to the strongly trans-influencing[10] sulfito group, which explains the ease with which substitution reactions occur.

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