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Tetrahedral Sulphur Containing Mo^{VI} and W^{VI} Chromophores*

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The spectroscopic studies on simple thioanions and oxythioanions have been in recent years dealt with in a number of papers of which particular attention deserve the papers by Müller[1-4], Tridot[5-6], and Kaufmann[7-9]. Although the subject has been discussed in detail, some points are not clear enough and in this paper we offer a more detailled interpretation of the electronic transition in the above ions.

Experimental Section

Preparation of Mo^{VI} and W^{VI} thio- and oxythiosalts.
Ammonium salts were prepared according to methods described in detail in literature and checked by numerous authors. $(NH_4)_2 MoS_4$ was synthesied according to Berzielius[10], $(NH_4)_2 MoO_2S_2$ by the Kruss method[11], $(NH_4)_2WS_4$ and $(NH_4)_2WO_2S_2$ by the method of Corleiss[12]. Piperidinium salt of tetrathiomolybdate was prepared according to the method given by Debucquet and Velluz[13].

Electronic absorption spectra. The electronic spectra over the range 200-1000 nm have been performed in a Unicam SP 700 recording spectrophotometer and in a VSU-2 Zeiss apparatus.

Results and Discussion

The electronic spectra of molybdates and tungstates and of the corresponding thioanions are well known as published in many papers. The spectrum of the tetrathiomolybdatepiperdinium salt was as yet not studied and it is shown in the Fig. 1. In Table 1

transition energies, molar extinction coefficients and band-widhts were given for $(NH_4)_2MoS_4$ and $(NH_4)_2WS_4$ absorption spectra. These values were obtained by means of Gaussian analysis.
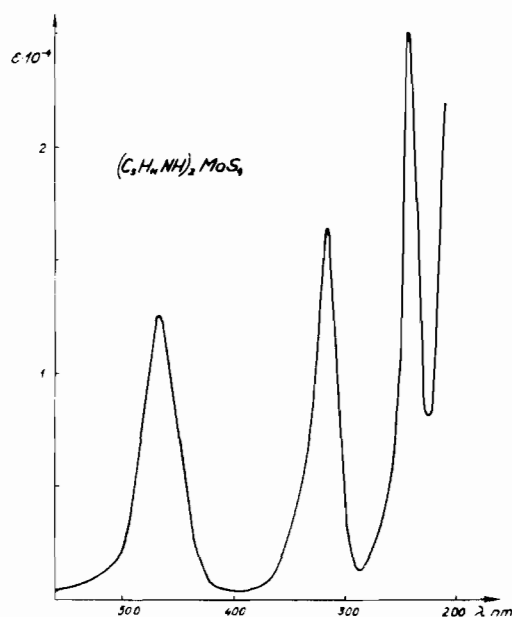

Figure 1. Absorption spectrum of $(C_5H_{11}NH)_2MoS_4$ in water $(c = 10^{-4}m)$.

There exist distinct differences between the electronic spectra of molybdates and tungstates and the corresponding thioanions. These differences result from following factors: 1) bathochromic shift of the bands 2) higher (in general) number of bands 3) higher intensities and 4) characteristic bands structure. The least evident and clear is factor 2. We note for instance in the case of MoS_4^{2-} four intense absorption bands but in thiotungstate only three.

On the basis of any of the known molecular orbital schemes, this fact could not be explicitly cleared up. With an undistorted T$_d$ structure in the tetrathioanions the reason for a higher number of bands in the UV and visible region may be the destabilization of the lower molecular orbitals from which the transition occur. Such a destabilization is justificable in the case of the t_1 orbital which is a non-bonding π-orbital centered on the sulphur atom. The reason for this change with respect to energy of the oxygen

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Table I. Absorption bands in the electronic spectra of $(NH_4)_2MoS_4$ and $(NH_4)_2WS_4$ (Gaussian analysis).

(NH₄)₂MoS₄				(NH₄)₂WS₄				E_W-E_{Mo}
Transition energy (cm⁻¹)	ε_{max}	Half-width (cm⁻¹)	f	Transition energy (cm⁻¹)	ε_{max}	Half-width (cm⁻¹)	f	
19,150	900	1,700	0.007	23,100	1,050	1,600	0.008	3,950
21,400	11,800	1,600	0.087	25,450	13,700	1,700	0.107	4,050
22,700	2,200	1,200	0.012	26,750	1,760	1,100	0.009	4,050
25,500	700	2,800	0.009	30,200	1,400	3,300	0.021	4,700
29,000	2,600	2,000	0.024	34,000	5,800	1,800	0.048	5,000
31,600	15,750	2,600	0.188	36,100	20,700	2,100	0.200	4,500
37,500	3,200	2,600	0.038	41,450	4,200	4,600	0.089	3,950
41,400	23,700	3,000	0.327	46,900	26,100	4,800	0.576	5,500
48,500								E_W-E_{Mo} 4,500

atom in oxyanions is the lower electronegativity of the sulphur atom. The energy changes, however, in higher orbitals which may participate in these transition could not be explicitly predicted without accurate calculations and ma vary for various central atoms.

In order to clarify the t_1 orbital destabilization and the bathochromic shift of the first and second absorption bands in thioanions one can assign them to the same type of transitions as in the oxyanions. For instance the Ballhausen-Liehr (BL) scheme was adopted in some papers[1,4]. It seems, however, that the situation is somewhat different in the thioanions where a considerable contribution of the covalent bond appears depending on the central atom.

In the BL scheme the first two absorptions bands correspond to the transitions from the t_1 to 2e and 3t₂ orbitals. Hence th eenergy difference of the above bands is equal to the tetrahedral 10Dq parameter. While however, these differences decrease with the increasing ionic radii of the metal atom in oxyanions they increase in the thioanions (Fig. 2).

The importance of these facts is connected with the following considerations. In a previous announcement Bartecki[14] has discussed in detail the rela-

tionship given by Teltow[15] and Symons and al.[16]. According to these authors the energy of the first long-wave absorption band is a linear function of the central metal ionic radius in the tetraoxyanions, However, it was shown that this function is also obeyed by the second, short-wave band in oxyanions[14]. In this way two linear equations can be given for both transition energies not only in oxyanions but - extending this idea - also in thioanions. From the equations for oxyanions it follows that the differences between the second and first transition energies decrease considerably from ab. 14kK in MnO_4^- to 1.8 kK in WO_4^{2-}. However, contrary to all other anions the last figure cannot be compared with the experimental one as in the tungstate ion only one band is known up to now. Hence, the value of 1.8 kK follows from the theoretical equations. The necessary data for thioanions have been taken from our own studies (for Mo and W) and from Müller's results[17]. The discrepancy for Re is not clear but it is interesting to note a similar situation in the case of ReO_4^-. Since an increase of the ionic radius correspond to an increase of the atomic number for the same group of elements then an increase of the tetrahedral splitting, that is, of the difference between orbitals 3t₂—2e would be thus explained. On the other hand the reverse is true for tetrahedral oxyanions and an analogous assignment could not be correct. It seems, therefore reasonable not to apply the BL scheme simultanously to oxyanions and thioanions, but rather, to assume different schemes or, at least, different assignments for these systems.

The band number problem becomes complicated if the oxythioanions will also be taken into consideration. Owing to the symmetry decrease in the MeO_3S^{2-} and $MeO_2S_2^{2-}$ ions down to C_{3v} and C_{2v} even more bands should be expected. The dioxydithioanions exhibit, however, less bands than the $MeOS_3^{2-}$ species. This may be explained by the fact that the total removal of degeneracy in the ions with C_{2v} symmetry leads to the formation of levels with energies very close each to other. On the other hand, in the C_{3v} symmetry the number of splitting products is lower but the corresponding bands do not overlap and appear separately. It is worth while to mention here that according to Wolfsberg and Helmholz such a
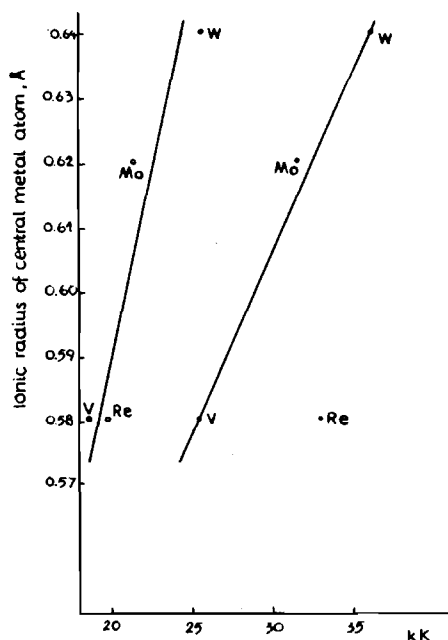
Figure 2. Plots of the two absorption maxima of some MS_4^{2-} thioanions against the ionic radii central metal atom.

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situation exists in the CrO_3F^- ion in comparison to CrO_2Cl_2 where in the first case three and in the second case two absorption bands have been predicted.

To get better information on the electronic transitions in the tetrathioanions the Gaussian analysis was performed. In this way new bands corresponding to forbidden transitions were found. Although these bands were mentioned in the paper no details were given.[17]

As one can see from table I there are four intense and five weak (relative) bands in MoS_4^{2-} ion and three intense and five weak bands in WS_4^{2-}. Considering the smallest molar extinction coefficient in the first case as equal to 700 and in the second case as equal to 1100, these bands are much more intense as ordinary d-d bands. This is quite clear because all transitions discussed are charge transfer transitions. Hence, the weaker bands correspond to singlet-triplet and orbital forbidden transition the first type being probably more important because charge transfer transition cause considerable orbital mixing.

It is worth nothing that all the bands in the spectra of MoS_4^{2-} and WS_4^{2-} are mutually shifted by a nearly constant (mean) value of ab. 4500 cm^{-1}. On the basis of the simple Jørgensen' equation which relates the energy of charge transfer transition to the optical electronegativities it may be concluded that the difference between these values for Mo^{VI} and W^{VI} equals 0,15 unit. This is in full agreement with the data calculated for various Mo^{VI} and W^{VI} ions and provides another evidence that all the bands are due to the charge transfer transition from sulphur orbitals to the metal empty orbitals.

It also is interesting to compare the differences in transition energies of the main bands I and II in the oxy and thiooxyanions. For molybdenum and tungsten the following values have been obtained (Table II).

Table II. Δ_{II-I} values in oxy- and thiooxyanions of Mo^{VI} and W^{VI}.

Ion	MoO_4^{2-}	$MoO_2S_2^{2-}$	$MoOS_3^{2-}$	MoS_4^{2-}
kK	4.1	6.0	8.5*	10.2
Ion	WO_4^{2-}	$WO_2S_2^{2-}$	WOS_3^{2-}	WS_4^{2-}
kK	1.8	6.0	8.7*	10.6

* Data taken from (18). The energy of the band I is the averaged value of v_1 and v_2 in the original paper.

It is evident that these values gradually increase, assuming in the case of MOS_3 the average energy of the two nearly absorption bands which result from splitting as the energy of band I. On the basis of the crystal field model and the concept of a spectrochemical series on the one hand and on the BL model

on the other hand, the reverse direction of changes should be expected. This again means that the same scheme could not be applied to both types of anions.

As we have mentioned earlier, the spectra of the thioanions possess very good enveloped and symmetric bands of relatively low half-widths and considerable intensities. The band structure is well defined by the fact that it is possible to determine both the values of δ_+ and δ_- while it is not possible with the oxyanions of Mo and W. The halfwidth is known to determine the slope of the exited state potential curve at the point corresponding to the equilibrium distance in the ground state. It may be thus concluded that the potential curves of the excited states in the Mo and W thioanions are shifted to a smaller extent with respect to the ground states as in the oxyanions. This statement may also be confirmed by consideration of the band structure showing no evidence of vibronic interaction in thioanions even in organic solvents. Contrary to this, the vibronic structure appears at least in some oxyanions e.g. in MnO_4^- (but not in MoO_4^{2-}) as due to the totally-symmetric vibration. This is consistent with an appreciable shift of the excited state potential curve. On the other hand, it also is known that the band width in the sense of molecular orbital theory depends in a definite transition on the anti-bonding character of the terminal orbital. The corresponding orbitals are then in general less anti-bonding in the thioanions than in the oxyanions.

In the thiooxyanions, as it was expected, the band widths should increase. This could be seen from the Table I. In the other words, the band structure becomes disturbed by introducing the oxygen atoms and greatest disturbance is achieved in the oxyanions.

If, in turn, the band intensities are to be discussed, a considerable increase of the molar extinction coefficients and particularly of the oscillator strengths are observed. On the basis of our data and references (although there are considerable difficulties in obtaining accurate values of the molar coefficients because of the possibility of two or more forms appearing simultaneously) a hyperchromic series may also be suggested which again means that the sulphur atoms increase the transition probability. An important conclusion is drawn out by taking into account the Mulliken postulate that the high absorption band intensities correspond to the 'combination' of states which differ considerably in their ionic bond participation.

Since the contribution of the covalent bond in the ground state is certainly large in the thioanions and much larger than in the oxyanions, the excited states of very strong bands have a stronger ionic character.

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