A Vibrational Study of the (S–S) Group in Transition-element Compounds

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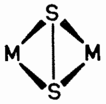
Summary The i.r. spectra of polysulphides MS_3 (M = Ti, Zr, Nb, and U), VS_4, and thiohalides NbS_2X_2 (X = Cl, Br, and I) and the Raman spectra of the latter were investigated to determine the vibrational range of their (S–S) group as distinguishable from pyrites-type (S–S) groups: we show the existence of such groups in $Mo_2S_5Cl_3$ and $Mo_2S_5Br_3$.

SEVERAL polysulphides and thiohalides of transition elements of Groups IV, V, and VI possess an (S–S) group bridging two metallic atoms, as shown in the Figure. We have determined (S–S) vibrational frequencies in these compounds.



FIGURE

The polysulphides MS_3 (M = Ti, Zr, Nb, and U), obtained by known methods[1,2] were identified by chemical and *X*-ray analyses; they are isostructural with $ZrSe_3$:[3] they consist of chains of C_{2v} symmetry trigonal-bipyramids $[M_2S(S–S)]$, with, in the equatorial plane, one sulphur atom and one (S–S) group. For the latter there corresponds an i.r.-active vibration of the species a_1.

The sulphide VS_4 prepared[1] by the interaction of an excess of sulphur with V_2S_3 consists[4] of chains of octahedral $[V_2(S–S)_2]$ cages, the symmetry of which is closely related to D_{2h} type. The thiohalides NbS_2X_2 (X = Cl, Br, and I) were isolated by Schäfer and Beckmann.[5] The chloride and the bromide are isostructural; the iodide probably has the same structure.[6] It consists of octahedral $[Nb_2(S–S)_2]$ cages of C_{2h} symmetry; the niobium atoms are bonded to one another by halogen bridges. For the $[V_2(S–S)_2]$ and $[Nb_2(S–S)_2]$ cages, the a_g type in-phase vibration of the two (S–S) groups will be Raman-active. The i.r. activity will be the related phase-contrast vibration of the b_{2u} and b_u species for the $[V_2(S–S)_2]$ and $[Nb_2(S–S)_2]$ cages respectively.

	TiS_3	ZrS_3	NbS_3	US_3	VS_4	NbS_2Cl_2	NbS_2Br_2	NbS_2I_2	$Mo_2S_5Cl_3$	$Mo_2S_5Br_3$	MnS_2	FeS_2	BaS_2
ν(S–S) I.r. (cm^{-1})	560	529	570	505	555	588	585	575	560	555	Inactive[8]		
ν(S–S) Raman (cm^{-1})	Not recorded					592	585	No result	570	565	490	438	473

The observed i.r. spectra exhibit two distinct ranges: below 400 cm^{-1} M–X modes occur—assigned by means of their shift with the thiohalide considered—and a number of bands assigned to M–S modes: at low frequency there are vibrations which correspond to the rather weak M–S bond. Above 500 cm^{-1}, for all these compounds, there occurs one band assigned to the (S–S) mode: we expect a single vibration, lying at a higher frequency as a result of the small mass of the sulphur atom and the strength of the (S–S) bond. The Raman spectra exhibit the same behaviour. The first results of a vibrational analysis of $[Nb_2(S–S)_2]$, at present under study, are in agreement with our assignments. The strong intensity of the i.r.-active ν(S–S) band for $[M_2(S–S)_2]$ (M = V and Nb), compared with that of MS_3 compounds, is explained by the large dipole moment variation connected with the phase-contrast vibration of the two (S–S) groups.

The thiohalides $Mo_2S_5Cl_3$ and $Mo_2S_5Br_3$ were prepared by the method of Rannou and Sergent.[7] We have also obtained $Mo_2S_5Br_3$ by interaction of sulphur with $MoBr_2$. These compounds as well as the thiohalides of niobium, have i.r. and Raman spectra characterised by a strong band near 550—570 cm^{-1}: they are therefore polysulphides of the type described here.

Our results are summarised in the Table: we also give, for comparison, the ν(S–S)[8] for pyrites-type polysulphides. The vibration of the (S–S) group bridging the metal atoms (Figure) lies above 500 cm^{-1} in the i.r. as well as in the Raman spectrum, *i.e.* at a higher frequency than in pyrites derivatives. The i.r. activity of this group, in contrast with that of pyrites-type compounds, and the fact that it absorbs at such a high frequency, distinguish our polysulphides from pyrites-type compounds.

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