The Infrared Spectra of Complex
Sulphates of the Type $M^I M^{III}(SO_4)_2$

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*A group of isomorphous trigonal complex sulphates,
of the type $M^I M^{III}(SO_4)_2$, where $M^{III} = Al$, Ga, In, Cr,
or Fe have been prepared and the infrared spectra in
the range 4000-20 cm^{-1} have been recorded. The fac-
tor group analysis was performed and the absorption
bands have been assigned. The vibrational frequen-
cies were correlated to the ionic radii of M^I and M^{III}.
A good correlation was found in the case of M^I, which
is ascribed to the lattice contraction effect and a less
profound one in the case of M^{III}, showing that other
characteristics of M^{III} ions are operative. The infrared
spectra, together with the results of an X-ray structure
determination show that the sulfate ion acts probably
as a triply bridging ligand.*

Introduction

The complex sulphates of general formula $M^I M^{III}$-
$(SO_4)_2$ have been described in the literature. These
compounds have been of prime interest in the past
since they were considered to be the final dehydration
products of the corresponding alums. Vegard and
Maurstad[1,2] have performed the X-ray diffraction ana-
lysis of $KAl(SO_4)_2$, $NH_4Al(SO_4)_2$, $KCr(SO_4)_2$, and NH_4-
$Fe(SO_4)_2$ on the basis of powder diagrams. Franke
and Henning[3] have analysed the X-ray diffraction pat-
terns of a series of analogous compounds and have
shown that these compounds are isostructural with the
above-mentioned compounds. Recently, Manoli, Her-
pin, and Pannetier[4] have performed the analysis of the
X-ray diffraction patterns of a single crystal of KAl-
$(SO_4)_2$. Essentially, they have confirmed the results
of Vegard and Maurstad[1,2] but the coordinates of atoms
lying on general positions had to be corrected. Our
Guinier powder diagrams of all other compounds in-
vestigated show them to be isostructural with those
mentioned above.

We decided to investigate the infrared spectra of
the compounds in order to elucidate the nature of
the chemical bond between M^{III} and sulphate ions.

Experimental Section

The complex sulphates were obtained, by de-
hydration of the corresponding alums, which were

prepared by well known methods. The alums were
dehydrated in a drying pistol in the vacuum of a
rotary pump with a heating rate of 5°/min up to 210
°C, their temperature being held constant for 24 hours.
Preliminary infrared spectra showed the strong in-
fluence of lattice defects and therefore the samples
were annealed at 450 °C for another 5 to 6 hours
in air. Further annealing did not improve the spectra.
The samples were analytically controlled by standard
methods. Deviations from theoretical composition
were found within experimental error in all cases.
The infrared spectra were recorded on a Perkin-Elmer
Model 521 Infrared Grating Spectrophotometer, and
the far infrared spectra were obtained on a Beckman
Model IR-11 Grating Infrared Spectrophotometer (us-
ed in the range 350-59 cm^{-1}) and a Research and
Industrial Instruments Co. Model FS-720 Fourier
Transform Spectrophotometer (in the range 70-20
cm^{-1}) in conjunction with a Research and Industrial
Instruments Co. FTC-100 Fourier transform compu-
tor. All spectra have been recorded with the samples
prepared in the form of Nujol mulls. In the range
4000-250 cm^{-1} a demountable cell, equipped with
cesium bromide windows, was used, while in the 350-
20 cm^{-1} range similar cells, equipped with polyethy-
lene windows, were used. The spectra of some sam-
ples were measured in other mulling agents. However,
no additional absorption bands were found.

Results

Representative spectra are reproduced in Figures 1
and 2 (that of $KAl(SO_4)_2$). The measured bands in
wave numbers for all compounds investigated are list-
ed in Table I.
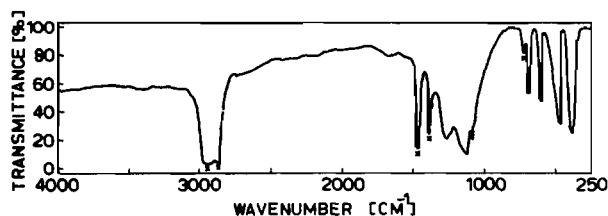

Figure 1. Infrared spectrum of $KAl(SO_4)_2$.

(1) L. Vegard and A. Maurstad, *Skr. Akad. Oslo*, Nr. 7 (1928).
(2) L. Vegard and A. Maurstad, *Z. Krystall.*, *69*, 519 (1929).
(3) W. Franke and G. Henning, *Acta Cryst.*, *19*, 870 (1965).

(4) J. M. Manoli, P. Herpin, and G. Pannetier, *Bull. Soc. Chim.
France*, 98 (1970).

**Table I.** I.R. frequencies (cm⁻¹) for the complex sulphates $M^IM^{III}(SO_4)_2$

KAl(SO₄)₂	1255	1115	1075	685	605	475	500	387	282	182	126	109
RbAl(SO₄)₂	1250	1110	1070	685	600	470	500	377	275	186	99	87
CsAl(SO₄)₂	1245	1115	1073	685	600	465	500	380	270	188	87	76
TlAl(SO₄)₂	1235	1120	1070	685	600	463	510	380	277	180	75	59
KGa(SO₄)₂	1240	1090	1045	668	590	460	378	255	245	152	120	101
RbGa(SO₄)₂	1235	1090	1045	667	590	460	370	260	240	156	96	82
CsGa(SO₄)₂	1232	1090	1045	664	590	455	367	260	235	156	85	70
KIn(SO₄)₂	1250	1075	1022	655	593	455	345	230	182	116		84
RbIn(SO₄)₂	1240	1075	1022	650	590	453	340	240	175	113	86	72
CsIn(SO₄)₂	1225	1073	1025	650	590	450	335	240	170	112	74	63
KCr(SO₄)₂	1237	1060	1035	670	583	463	447	335	255	157	117	103
RbCr(SO₄)₂	1235	1060	1040	668	585	465	440	335	252	160	92	83
CsCr(SO₄)₂	1232	1060	1040	665	583	463	440	335	245	163	83	72
TlCr(SO₄)₂	1220	1057	1035	,665	583	463	440	335	250	150	72	59
NH₄Fe(SO₄)₂	1220	1065	1030	665	585	445	385	280	223	189	122	
RbFe(SO₄)₂	1230	1055	1035	655	585	447	380	280	220	151	92	80
CsFe(SO₄)₂	1225	1050	1035	655	585	445	375	273	210	152	82	69

Table II.

D_3	n_i		K—Al—(SO₄)₂				SO₄AlSO₄—K		SO₄AlSO₄			
		T	T′	R′	n_i'	T″	R″	T′—T″	R′—R″	ν(S—O)	δ(O—S—O)
A_1	5	0	1	1	3	0	0	1	1	2	1(2*)
A_2	7	1	2	1	3	1	1	1	0	2	1(2*)
E	12	1	3	2	6	1	1	2	1	2	4

* Redundancy condition.

Factor group analysis. KAl(SO₄)₂ crystallises in the hexagonal space group D_3^2 (*P*321 or *C*32) with Z = 1[1,2,4]. The primitive unit cell contains one molecule of the compound. Factor group analysis, *i.e.* the finding of the number of normal vibrations belonging to a given irreducible representation has been obtained from Halford's[5] formula.
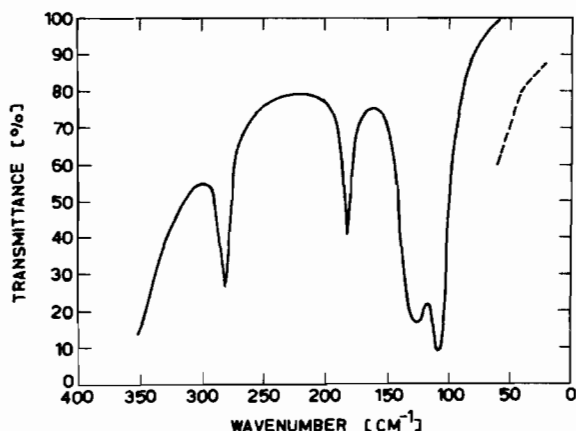
Figure 2. Far infrared spectrum of KAl(SO₄)₂.

The results of the factor group analysis are listed in Table II. In the first line the way how the ions in the unit cell are divided is shown. In the next line n_i, T, T′, R′, n_i' indicate the whole numbers of normal modes of the unit cell, translations of the unit cell as an entity, external translations, external rotations, and internal vibrations of the SO_4^{2-} ions in the unit cell, respectively. ν(S—O) and δ(O—S—O) indicate

(5) H. Winston and R. S. Halford, *J. Chem. Phys.*, 17, 607 (1949).

stretching vibrations and deformations of the SO_4^{2-} ions in the unit cell.

In order to find out the internal vibrations of the sulphate ion, we performed the site group analysis for the sulphate ion. Its site group is C_3. In Table III the analysis is shown, where n_i indicates the internal vibrations of the sulphate ions ν(S—O), S—O stretching vibrations, and δ(O—S—O), O—S—O deformation vibrations, respectively.

Table III.

C_3	n_i	ν(S—O)	δ(O—S—O)	IR
A	3	2	1 (2*)	a
E	3	1	2	a

Discussion

The internal vibrations of the sulphate ion have been assigned by Nakamoto *et. al.*[6] In our case the observed infrared absorption bands are in complete agreement with theoretical predictions of the site group analysis (see Table III). The factor group splitting cannot be seen explicitly even at the liquid nitrogen temperature, nevertheless ν(S—O) and δ(O—S—O) vibrations of the symmetry species E of the sulphate ion are broadened considerably. It means that there are no considerable interactions between the two sulphate ions in the unit cell; therefore factor group analysis is just too fine for the treatment of the internal vibrations of the sulphate ion, though being needed for the treatment of the lattice modes. As listed in

(6) K. Nakamoto, J. Fujita, S. Tanaka, and M. Kobayashi, *J. Amer. Chem. Soc.*, 79, 4904 (1957).

Table IV. Description of the infrared spectrum of $KAl(SO_4)_2$ (frequencies in cm^{-1}).

Point group (T_d)	Site group (C_3)		I	Factor group (D_3^2)		Assignment
F_2 1104	A 1255	mbr	s	A_1	(i)	
				A_2	1225	
	E 1115	vbr	vs	E	1115 ^{a}	ν(S—O) stretching modes of the SO_4^{2-} ion
				E		
A (i)	A 1075	vsh	s	A_1	(i)	
				A_2	1075	
F_2 613	E	msh	s	E	685 ^{a}	
				E		
	A 605	sh	ms	A_1	(i)	δ(O—S—O) deformations modes of the SO_4^{2-} ion
				A_2	605	
		sh	mw	A_2	500	$T'-T''$ (SO_4AlSO_4)
E (i)	E 475	msh	vs	E	475 ^{a}	δ(O—S—O) deformations modes of the SO_4^{2-} ion
				E		
		msh	s	E	387 ^{a}	$T'-T''$ (SO_4AlSO_4) symmetric and asymmetric stretching in layer
				E		
		sh	s	E	282	$R'-R''$ (SO_4AlSO_4)
		sh	ms	A_2	182	R'' K—(SO_4AlSO_4)
		mbr	vs	A_2	126	T''' K—(SO_4AlSO_4)
		s	vs	E	109	R'' K—(SO_4AlSO_4)
				E	< 20 ^{b}	T''' K—(SO_4AlSO_4)

I = intensity. *br* broad, *sh* sharp, *vs* very strong, *s* strong, *m* medium, *w* weak. ^{a} unresolved, ^{b} unobserved.

Table IV, the assignment of the bands at 387 and 500 cm^{-1} has been established regarding the strong dependence of these bands on the nature of the trivalent cation and their independence (the regular shifts are within the limits of lattice contraction effect) of the monovalent cation (see Figure 3). The band at 500 cm^{-1} in the spectrum of $KAl(SO_4)_2$ at liquid nitrogen temperature confirmed this assignment.

The three sharp bands at 282 cm^{-1}, 182 cm^{-1}, and 109 cm^{-1} respectively are assigned as rotational lattice modes. The prime argument for this assignment is their characteristic dependence on the nature of the trivalent cation and their independence of the nature of the monovalent cation.
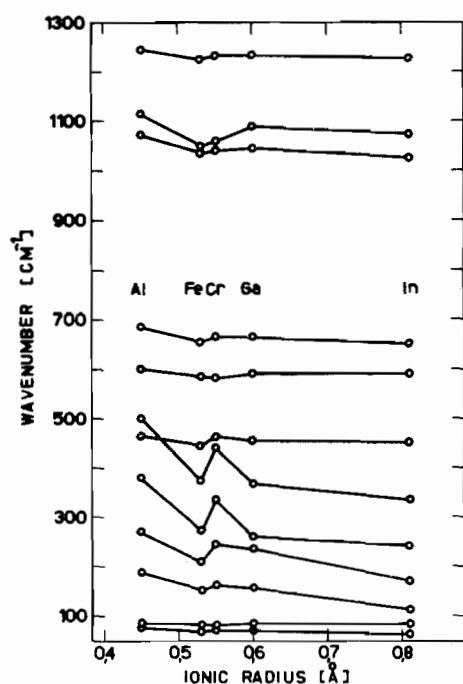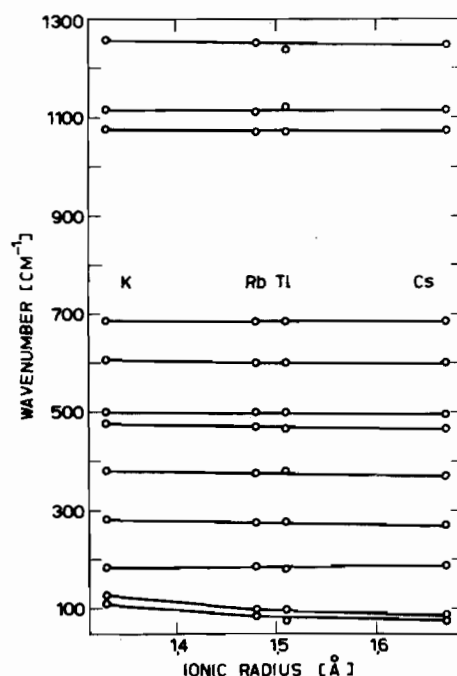

Figure 4. Plots of observed wavenumbers of infrared bands *vs.* Goldschmidt ionic radii of M^I in $M^IAl(SO_4)_2$.

The band at 126 cm^{-1} (A_2) is assigned to a translational lattice mode where the monovalent cation and complex layer (SO_4AlSO_4)$^-$ are involved. The proof thereof is its remarkable frequency independence of the trivalent cation and its dependence on the monovalent cation. Such a significant feature can hardly

Figure 3. Plots of observed wavenumbers of infrared bands *vs.* Goldschmidt ionic radii of M^{III} in $CsM^{III}(SO_4)_2$.

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be expected at such very low wavenumbers and therefore this evidence is much more important.

In regard to the nature of the band T'' K–(SO$_4$Al-SO$_4$) (E) we can but conclude that it occurs below 20 cm^{-1}, this being well beyond the measuring limit of our instrument.

Therefore the infrared spectra have shown the existence in these compounds of triply bridged sulphate ions, which had been forecast from the study of their crystal structures. Splitting of the stretching and deformation modes (F_2 1104 cm^{-1} and F_2 613 cm^{-1}) of the sulphate ion in the crystal spectra indicated that

sulphate ions are coordinatively bound to M^{III} ions. This is also supported with the most interesting frequencies of M^{III}–OSO$_3$ which are found in the range 500-240 cm^{-1}. These frequencies are in good agreement with the data of Ferraro et al.[7] and Gatehouse et al.[8]

The correlation of vibrational frequencies with ionic radii, as shown as an example for M^{I}Al(SO$_4$)$_2$ in Figure 4 clearly shows that the monovalent cation is ionically bound in these compounds and that their influence on vibrational frequencies is expressed exclusively through the lattice contraction effect.

(7) J. R. Ferraro and A. Walker, *J. Chem. Phys.*, **43**, 1278 (1965).

(8) B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm, *J. Chem. Soc.*, 4222 (1957).