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Vibrational Spectra of Group VIII Sulphito Complexes

J. P. HALL and W. P. GRIFFITH

Inorganic Chemistry Research Laboratories, Department of Chemistry, Imperial College, London SW7, U.K.

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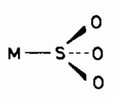
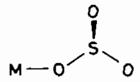
Raman and infrared spectra are reported for $Pd(SO_3)(NH_3)_3$ *and salts containing* $[Ir(SO_3)_2Cl_4]^{5-}$ $[Ir(SO_3)_2(NH_3)_2Cl_2]^{3-}$, $[Rh(SO_3)_3(NH_3)_3]^{3-}$, $[Ir(SO_3)_3(NH_3)_3]^{3-}$, $[Pt(SO_3)_4]^{6-}$, $[Ir(SO_3)_4Cl_2]^{7-}$ *and* $[OsO_2(SO_3)_4]^{6-}$. *The results suggest that these contain metal–sulphur bonds and this also appears to be the case for the new complexes* $Os(SO_3)(NH_3)_4Cl$, $[Os(SO_3)_3(H_2O)_3]^{4-}$ *and* $[Os_2N(SO_3)(NH_3)_8(H_2O)]^{3+}$. *The spectra of all these differ considerably from those of* $[Fe(OSO_2)_6]^{9-}$ *which is known to contain Fe–O bonds.*

Introduction

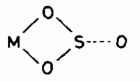
The sulphite group (SO_3^{2-}) can coordinate as a monodentate sulphur(I) or oxygen(II) donor, or in bidentate fashion *via* oxygen(III) or oxygen and sulphur (IV). It may also function as a bridge between metal atoms, but complexes containing this type of bonding are not considered here.



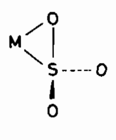
(I) C_{2v}



(II) C_s



(III) C_s



(IV) C_1

Attempts have been made using infrared spectra to distinguish between these possibilities by using the local symmetries as shown above [1–5]; infrared spectra have also been used to study bridged sulphito complexes [6]. However, infrared spectra of sulphito complexes show multiple splitting and it is difficult to draw conclusions as to the mode of bonding involved. We present here both Raman and infrared data on complexes of types (I), (II) and (IV), and show that, by using the full symmetry of the complex, reasonable assignments of modes can be made. The Raman spectra are usually much simpler than the infrared spectra and may have more diagnostic value than the latter for structural conclusions.

Experimental

Preparation of Compounds

Analytical data are given in Table I.

Mono-sulphito Complexes

Sulphito tri-ammino palladium, $Pd(SO_3)(NH_3)_3$

The aquo complex, $Pd(SO_3)(H_2O)_3$ was prepared as described in the literature [7], from $PdCl_2$, Ag_2SO_3 and water. Addition of conc. NH_4OH to aqueous $Pd(SO_3)(H_2O)_3$ produced a white precipitate of the ammine complex. In ^2H_2O solution, $Pd(SO_3)(H_2O)_3$ with $N^2H_4O^2H$ gave $[Pd(SO_3)(N^2H_3)_3]$.

Sulphito tetra-ammino chloro osmium, $Os(SO_3)(NH_3)_4Cl$

This new complex was prepared by treatment of a hot (75 °C) solution of $[Os(NH_3)_5Cl]Cl_2$ (0.3 g in 15 cm^3 water) with $Na_2S_2O_5$ (0.5 g) and SO_2 for six hours giving a red-brown solution. After removal by centrifugation of a small amount of brown material, addition of ethanol precipitated the pink-brown $Os(SO_3)(NH_3)_4Cl$. (Magnetic moment μ_{eff} = 1.45 BM at 294 K).

Sulphito aquo octa-ammino μ-nitrido di-osmium trichloride, $[Os_2N(SO_3)(NH_3)_8(H_2O)]Cl_3$

This new yellow-brown complex was precipitated on addition of ethanol to a solution of $[Os_2N(NH_3)_8Cl_2]Cl_3$ (prepared as in [8], 0.2 g dimer in 30 cm^3 water) treated with sulphur dioxide for 15 min.

Bis-sulphito and -hydrosulphito Complexes

Penta-potassium di-sulphito tetrachloro iridium hexahydrate, $K_5[Ir(SO_3)_2Cl_4]\cdot 6H_2O$

This is the first report of the potassium salt, though the sodium analogue is known [9]. Warming a solution of $K_3[IrCl_6]$ (0.64 g in 9 cm^3 water) with potassium sulphite solution (0.33 K_2CO_3 in water saturated with SO_2) for two hours led to formation of the salt as a light orange solid.

Tri-sodium di-sulphito dichloro di-ammino iridium hexahydrate, $Na_3[Ir(SO_3)_2Cl_2(NH_3)_2]\cdot 6H_2O$

A tetrahydrate of this salt has been reported [10] but the following procedure gives the hexahydrate. The salt $(NH_4)_2[IrCl_6]$ (1 g) was dissolved in ammonium bisulphite solution (1 g $(NH_4)_2CO_3$ in 12 cm^3 water, saturated with SO_2). The product formed on standing the orange solution overnight was redissolved in warm water, and sodium tetraphenylborate solution added to precipitate the ammonium ions. The pale yellow $Na_3[Ir(SO_3)_2Cl_2(NH_3)_2]\cdot 6H_2O$ was precipitated from the solution with acetone.

Bis-hydrogen-sulphito tetra-ammido ruthenium, $Ru(NH_3)_4(HSO_3)_2$

The complex, prepared by using the literature method [11], was obtained by reacting $[Ru(NH_3)_5Cl]Cl_2$ with $Na_2S_2O_5$ and SO_2 in aqueous solution.

Tris-sulphito Complexes

Tri-sodium tri-sulphito tri-ammino iridium heptahydrate, $Na_3[Ir(SO_3)_3(NH_3)_3]\cdot 7H_2O$

As described in the literature [12], $Na_7[Ir(SO_3)_4Cl_2]\cdot 7H_2O$ with excess ammonia solution yields the white ammine complex. Evaporation to dryness *in vacuo* of a solution in ^2H_2O produced the deuteriated material.

Tri-ammonium tri-sulphito tri-ammino rhodium sesqui-hydrate, $(NH_4)_3[Rh(SO_3)_3(NH_3)_3]\cdot 1\frac{1}{2}H_2O$

This was made by a modification of the literature procedure [13]. A hot solution of $RhCl_3$ (1 g in 1.5 cm^3 water and 1 cm^3 concentrated hydrochloric acid) was warmed until colourless with ammonium bisulphite solution (10 cm^3, 50% w/v SO_2). Discarding the first crop of crystals, $(NH_4)_2SO_3$, from the cooled solution, the white solid obtained next was recrystallised from water/acetone as white needle crystals of the complex. A deuteriated sample was prepared by evaporation to dryness *in vacuo* of a solution in ^2H_2O.

Tripotassium tri-sulphito rhodium dihydrate, $K_3[Rh(SO_3)_3]\cdot 2H_2O$

The product, as a yellow powder, was obtained by reaction of a hydrochloric acid solution of $RhCl_3$ with aqueous $K_2S_2O_5$, as described in the literature [14].

Tetra-potassium tri-sulphito tri-aquo osmium, $K_4[Os(SO_3)_3(H_2O)_3]$

This new complex was collected on cooling a mixture of $K_2[OsCl_6]$ (1.65 g) and potassium bisulphite (5 g $K_2S_2O_5$ in 25 cm^3 water) which had been warmed to 70 °C for two hours. The diamagnetism of the complex (mass susceptibility $\chi_g = -4.95 \times 10^{-9}$ m^3 kg^{-1} at 294 K) suggests the presence of octahedral osmium(II) (d^6). It is light-brown.

Tetrakis-sulphito Complexes

Hexa-potassium tetrasulphito platinum, $K_6[Pt(SO_3)_4]$

Using the literature method [15], white crystals of the complex were obtained on cooling a warmed mixture of aqueous solutions of $K_2[PtCl_4]$ and $KHSO_3$.

Hexa-sodium tetra-sulphito dioxo-osmium dihydrate, $Na_6[OsO_2(SO_3)_4]\cdot 2H_2O$

The complex was obtained as a tan precipitate from the reaction of sulphur dioxide with a cooled solution of osmium tetroxide (0.66 g) in sodium hydroxide (2.6 g in 35 cm^3 water), as described in the literature [16].

Hepta-sodium tetra-sulphito dichloro iridium heptahydrate, $Na_7[Ir(SO_3)_4Cl_2]\cdot 7H_2O$

The literature method [17], warming $Na_3[IrCl_6]$ (0.5 g) with sodium bisulphite solution (6 g $NaHCO_3$ in 60 cm^3 water, saturated with SO_2) at 75 °C for two hours, produced the complex as a pale yellow microcrystalline solid.

Hexakis-sulphito Complexes

Nona-ammonium hexa-sulphito iron, $(NH_4)_9[Fe(OSO_2)_6]$

Orange microcrystals of the salt were obtained after treatment of a cold ammoniacal suspension of $Fe(OH)_3$ with sulphur dioxide as described in the literature [18].

Physical Measurements

Raman spectra were measured (100–1400 cm^{-1}) on a Spex Ramalog 5 (14018) double monochromator instrument, with a DPC-2 detector, using exciting radiation from a Coherent Radiation model 52 krypton ion laser. Colourless solids were run in capillaries, lightly coloured and slightly photosensitive samples 1:1 with potassium bromide in a spinning KBr disc, using excitation wavelengths remote from electronic absorption bands. Solution spectra were run using a spinning cell.

TABLE I. Analytical Data.

Complex	Found %					Required %				
	H	N	S	Cl	K	H	N	S	Cl	K
Mono-sulphito										
$[Pd(SO_3)(NH_3)_3]$	3.9	16.4	13.4	–	–	3.8	17.7	13.5	–	–
$[Os(NH_3)_4(SO_3)Cl]$	3.4	15.1	8.6	8.0	–	3.2	15.0	8.6	9.5	–
$[Os_2N(NH_3)_8(SO_3)(H_2O)]Cl_3$	3.5	16.6	5.0	14.0	–	3.6	17.2	4.4	14.5	–
Bis-sulphito and hydrosulphito										
$K_5[Ir(SO_3)_2Cl_4]\cdot 6H_2O$	1.4	–	7.8	17.7	22.3	1.5	–	8.0	17.8	24.5
$Na_3[Ir(SO_3)_2(NH_3)_2Cl_2]\cdot 6H_2O$	2.8	3.9	9.9	10.8	–	2.9	4.4	10.1	11.2	–
$[Ru(NH_3)_4(HSO_3)_2]$	4.2	16.7	18.4	–	–	4.3	16.9	19.3	–	–
Tris sulphito										
$Na_3[Ir(SO_3)_3(NH_3)_3]\cdot 7H_2O$	2.2	6.2	13.1	–	–	3.4	6.2	14.2	–	–
$(NH_4)_3[Rh(SO_3)_3(NH_3)_3]\cdot 1\frac{1}{2}H_2O$	4.6	16.6	20.6	–	a	5.1	17.7	20.2	–	a
$K_3[Rh(SO_3)_3]\cdot 2H_2O$	0.8	–	18.9	–	24.0	0.8	–	19.4	–	23.6
$K_4[Os(SO_3)_3(H_2O)_3]$	0.9	–	14.6	–	23.4	0.9	–	15.0	–	24.4
Tetra sulphito										
$K_6[Pt(SO_3)_4]\cdot 2H_2O$	0.5	–	14.7	–	29.3	0.5	–	16.3	–	29.9
$Na_6[OsO_2(SO_3)_4]\cdot 2H_2O$	0.5	–	14.0	–	–	0.5	–	17.9	–	–
$Na_7[Ir(SO_3)_4Cl_2]\cdot 7H_2O$	1.0	–	13.9	8.4	–	1.6	–	14.7	8.2	–
Hexa-sulphito										
$(NH_4)_9[Fe(OSO_2)_6]$	4.9	17.1	27.3	–	–	5.2	18.1	27.5	–	–

[a] NH_4^+, found 11.1%, required 11.4%.

Infrared spectra of mulls in liquid paraffin, between caesium iodide plates, or of samples in potassium bromide discs were measured on Perkin-Elmer 457 and 597 instruments (2000–200 cm^{-1}).

Microanalyses were performed by the Microanalytical Laboratory, Imperial College. Ammonium and potassium were determined gravimetrically as their tetraphenylborate salts.

Results and Discussion

The Raman and infrared spectra of some Group VIII complexes are listed in Table II; a number of the complexes listed therein are new. As in previous work [1–5] on the infrared spectra of sulphito complexes, the four vibrational modes ν_1–ν_4 of the free SO_3^{2-} ion are used as approximate descriptions of the vibrations of the coordinated ligand. For free SO_3^{2-} in solution (Raman data [19]) the four modes are the symmetric and asymmetric stretches ν_1 (a_1) 967 cm^{-1} and ν_3 (e) 933 cm^{-1} and the symmetric and asymmetric deformations ν_2 (a_1) 620 cm^{-1} and ν_4 (e) 469 cm^{-1}. The strongest Raman modes are assumed to arise from symmetric rather than asymmetric vibrations. Deuteriation has been used in three cases $[Pd(SO_3)(NH_3)_3]$ and $(NH_4)_3[M(SO_3)_3(NH_3)_3]$ (M = Rh, Ir), the SO_3^{2-} vibrations being relatively unaffected while the NH_3 modes are greatly shifted.

Mono-sulphito Complexes

The X-ray crystal structures of $Pd(SO_3)(NH_3)_3$ [20] and of *trans*$[Rh(SO_3)(CN)(NH_3)_4]\cdot 2H_2O$ [21] show that in both of these the SO_3^{2-} coordinates *via* its sulphur atom rather than an oxygen atom. Infrared spectra of $Pd(SO_3)(NH_3)_3$ and other palladium sulphito complexes have already been reported and interpreted in terms of monodentate S-bonded sulphite ligands [4]. The Raman and infrared spectra of $Pd(SO_3)(NH_3)_3$ are consistent with the overall C_s symmetry of the square planar ion (taking the ammine ligands as point masses): the degeneracy of the e modes ν_3 and ν_4 is lifted and they split into

TABLE II. Vibrational Spectra of Sulphito Complexes.

Complex		SO_3 modes				ν(M–S)	Other ligand bands
		ν_1	ν_2	ν_3	ν_4		
Mono-sulphito							
$[Pd(SO_3)(NH_3)_3]$	IR	977s	633ms	1060vs,br	518mw, 505m		ν(Pd–N) 415mw
(C_s)	IR*	976m	625m, 615mw	1068vs,br	515m, 505sh		ν(Pd–N) 390w
	R	978s	640m	1090w, 1075vw	518w	253ms	ν(Pd–N) 478vs, 427mw
$[Os(NH_3)_4(SO_3)Cl]$	IR	965mw	615ms,sp	1090s, 1055s	568w		ν(Os–N) 460mw, 447m
†(C_s) (*trans*)							ν(Os–Cl) 297ms
	R	983ms	620w	1085w, 1060w	570w, 550w		ν(Os–N) 495m, 475mw
$[Os_2N(NH_3)_8(SO_3)(H_2O)]Cl_3$	IR	957m,sp	625m	1090sh, 1045m	508w		$\nu(Os_2N)$ 1108s,
†(C_s) (axial)							ν(Os–N) 465mw
	R	990m	648w	1135m, 1102m	505m		$\nu(Os_2N)$ 285s
							ν(Os–N) 490m
Bis-sulphito and hydrosulphito							
$K_5[Ir(SO_3)_2\cdot Cl_4]\cdot 6H_2O$	IR	975s, 945vs	650sh, 630s	1073vs, 1024vs	520ms		ν(Ir–Cl) 330sh, 318ms
†(C_{2h}) (*trans*)	R	982sh, 972s, 940w	655mw	1090w, 1050mw,b 1030mw	530sh	252m	ν(Ir–Cl) 350m, 312vs
$Na_3[Ir(SO_3)_2(NH_3)_2Cl_2]\cdot 6H_2O$	IR	993ms, 976vs	660s, 635s	1085s, 1050vs	520ms		ν(Ir–Cl) 340m
†(C_{2h}) (*trans*)	R	1000s	670vw	1110w, 1070mw	520vw	258m	ν(Ir–Cl) 318vs
							ν(Ir–N) 465vs
$[Ru(NH_3)_4(HSO_3)_2]$	IR	1000vs,b		1230ms,b, 1000s,b	570vs, 500s,sp		ν(Ru–N) 475sh, 440w
							ν(O–H) 3310s
(*trans*)	R	999s	619mw	1110m	570vw	243ms	ν(Ru–N) 488mw, 458m, 446vw, 417mw
Tris-sulphito							
$Na_3[Ir(SO_3)_3(NH_3)_3]\cdot 7H_2O$	IR	975vs	660sh, 633ms	1100vs, 1050s	520m		
†C_{3v} (*cis*)	IR*	960s	665sh, 637s, 620s	1100vs,b	530m		ν(Ir–N) 450mw
	R	995s, 980sh	620mw	1090m	530mw	250m,b	ν(Ir–N) 460s
$(NH_4)_3[Rh(SO_3)_3(NH_3)_3]\cdot 1\frac{1}{2}H_2O$	IR	938vs	661m,sp 620vs	1120s, 1028vs	532ms		ν(Rh–N) 408m
†(C_{3v}) (*cis*)	IR*	940vs	678mw, 621s	1100vs, 1030vs	520m		
	R	997ms, 963w, 955w	663mw, 630mw	1130vw, 1100vw, 1050w	528mw	247s,b	ν(Rh–N) 474w, 427s, 415sh
	R††	982mw, 963w	660w, 630w	1070mw,b, 1010ms	520w	220ms,b	ν(Rh–N) 430s

$K_4[Os(SO_3)_3(H_2O)_3]$	IR	980s	600m	1120s, 1070s, 1030m	508m		$\nu(Os–OH_2)$ 370m
†(C_{3v}) (*cis*)	R	950m	610vw	1114m, 1082s, 1056sh	500w	255m	
$K_3[Rh(SO_3)_3]\cdot 2H_2O$	IR	970sh, 945s	687m, 640ms	1150s, 1112ms, 1073s, 1053s	550vw, 530mw		
	R	960sh, 937s	690w, 642mw	1160mw,b, 1110ms, 1090sh	560w 525w		$\nu(Rh–S)$ 250ms, $\nu(Rh–O)$ 373mw
Tetrakis-sulphito							
$K_6[Pt(SO_3)_4]\cdot 2H_2O$	IR	968vs	660m, 640ms	1085vs, 1058ms	538m, 527m		
†C_{4h}	R	977mw	690mw, 627w	1077mw, 1066m 1027s	532mw 515m	248vs	
$Na_6[OsO_2(SO_3)_4]\cdot 2H_2O$	IR	977vs	647ms	1115vs, 1077vs	522ms		$\nu(Os=O)$ 842m,sp
†C_{4h} (*trans*)	R	918m,sh	646w,b	1002m,b	496vs	280m,b	$\nu(Os=O)$ 858w,b
$Na_7[Ir(SO_3)_4Cl_2]\cdot 7H_2O$ †C_{4h} (*trans*)	IR	965vs	635s, 625sh	1110ms, 1070s 1053vs, 1030s	525m		$\nu(Ir–Cl)$ 337m,sp
	R	980w	670mw, 640mw	1090m, 1082s	540w	240w	$\nu(Ir–Cl)$ 308s
Hexakis-sulphito							
$(NH_4)_9[Fe(OSO_2)_6]$	IR	815s	638ms	943vs	520mw		$\nu(Fe–O)$ 458m
(oxygen coordinated)	R	828s	638ms	991vs, 967ms	520ms		$\nu(Fe–O)$ 461w

All frequencies in cm^{-1}, *deuteriated sample, †idealised overall symmetry best in agreement with spectra, ††Raman spectra in aqueous solution.

doublets or are broadened, while ν_1 and ν_2 are both Raman and infrared active. A Raman band at 253 cm^{-1} may be the Pd–S stretch; bands in this region are assigned to this mode for $[Pd(thiourea)_4]Cl_2$ [22] and for $Pd(SMe_2)_2Cl_2$ [23]. Similar spectral features are observed for the new complexes $Os(SO_3)(NH_3)_4Cl$ and $[Os_2N(SO_3)(NH_3)_8(H_2O)]Cl_3$ and we suggest that these contain S-bonded sulphite also.

Bis-*sulphito Complexes*

Single-crystal X-ray studies suggest that the complex anion in *trans*-$(NH_4)_5[Ir(SO_3)_2Cl_4]$ has an idealised C_{2h} symmetry [24]. Infrared spectra of $(NH_4)_5[Ir(SO_3)_2Cl_4]$ and of $Na_3(NH_4)_2[Ir(SO_3)_2Cl_4]$ were earlier interpreted on the basis of a *cis* structure for the anion [1]. We find the Raman and infrared spectra of $(NH_4)_5[Ir(SO_3)_2Cl_4]\cdot H_2O$ and $K_5[Ir(SO_3)_2Cl_4]\cdot 6H_2O$ to be very similar, though the Raman spectrum of the ammonium salt was of poor quality. Complex splitting of ν_1, ν_2 and ν_3 is observed; under C_{2h} symmetry, six S–O stretches are expected ($2a_g + b_g + a_u + 2b_{2u}$), three Raman active ($a_g$, b_g) and three infrared (a_u, b_u), as against the four strong Raman and four infrared bands observed. A Raman band at 252 cm^{-1} may be an Ir–S stretching mode.

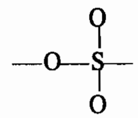
For $Na_3[Ir(SO_3)_2(NH_3)_2Cl_2]\cdot 6H_2O$ three Raman and four infrared active bands are seen in the S–O stretching regions, suggesting a *trans* structure (idealised C_{2h} symmetry). In the Ir–Cl region one Raman band at 318 cm^{-1} and one infrared band at 340 cm^{-1} also indicate a *trans* structure for the anion.

Tris-*sulphito Complexes*

Infrared studies on $Na_5(NH_4)[Ir(SO_3)_3(NH_3)_3]_2$ have been interpreted in terms of the sulphite ligands being bonded with a *fac* configuration [1], and infrared spectra for $K_3[Rh(SO_3)_3]\cdot 3\frac{1}{2}H_2O$ have been interpreted on the basis of S-bonded monodentate sulphite ligands being present [3, 4].

The main features of the infrared and Raman spectra of $Na_3[Ir(SO_3)_3(NH_3)_3]\cdot 7H_2O$, $(NH_4)_3[Rh(SO_3)_3(NH_3)_3]\cdot 1\frac{1}{2}H_2O$ and the new complex $K_4[Os(SO_3)_3(H_2O)_3]$ are similar, suggesting the same basic stereochemistry for the anions. A *fac* structure has been suggested for the anion of $Na_3[Ir(SO_3)_3(NH_3)_3]\cdot 7H_2O$ [12], and for this idealised C_{3v} structure five S–O stretches ($2a_1 + a_2 + 3e$ with a_1 and e modes both infrared and Raman active) are expected. The observed three or four bands are more in agreement with this than the less symmetric *mer* form. Bands at 250 cm^{-1} (Ir), 247 cm^{-1} (Rh) and 255 cm^{-1} (Os) observed in the Raman spectra may be metal–sulphur stretches.

The complex $K_3[Rh(SO_3)_3]\cdot 2H_2O$ may contain bidentate SO_3^{2-} ligands [4], but the complexity of the spectra, together with the very low solubility of the compound and its apparently amorphous character with respect to X-rays suggests a polymeric structure, perhaps with



$$-O-\overset{\displaystyle O}{\underset{\displaystyle O}{S}}-$$

bridges. It is interesting that bands are seen in the same region as for monodentate S-bonded sulphite groups.

Tetrakis-sulphito Complexes

The infrared spectrum of $Na_7[Ir(SO_3)_4Cl_2]$ has been measured, and a *cis* configuration for the anion with monodentate S-bonded sulphite groups suggested [1]. Infrared spectra of $K_6[Pt(SO_3)_4]$ [2], $Na_6[Pd(SO_3)_4]\cdot 2H_2O$ and $K_6[Pt(SO_3)_4]\cdot 6H_2O$ suggest that these too contain S-bonded sulphite ligands [2].

The spectra of $K_6[Pt(SO_3)_4]$, $Na_6[OsO_2(SO_3)_4]\cdot 2H_2O$ and $Na_7[Ir(SO_3)_4Cl_2]\cdot 7H_2O$ are similar in the S–O region. The platinum complex is expected to have a planar PtS_4 skeleton, and the *trans* arrangement of oxo ligands in the osmium complex (and the consequent planar OsS_4 arrangement) is suggested [25] by the strong infrared band at 842 cm^{-1} and Raman band at 858 cm^{-1}, assigned respectively to asymmetric and symmetric O=Os=O stretches. Although a *cis*-structure has been suggested for the anion in $Na_7[Ir(SO_3)_4Cl_2]\cdot 7H_2O$ [1, 17], the observation of only one infrared active Ir–Cl stretch at 337 cm^{-1} with its symmetric counterpart at 308 cm^{-1} in the Raman suggests a *trans* structure for the anion. For the most symmetric C_{4h} arrangement in these anions $\Gamma_{S-O} = 2a_g + 2b_g + 2e_g + a_u + b_u + 4e_u$, six being Raman active (a_g, b_g, e_g) and five infrared active (a_u, e_u). Though fewer bands are observed (two to four Raman bands and three to five infrared bands) the *cis* (C_{2v}) structure for the anion would be expected to produce a more extensive splitting.

In the Raman spectra bands assigned to ν_{M-S} appear at 248 cm^{-1} (Pt), 280 cm^{-1} (Os) and 240 cm^{-1} (Ir).

Hexa-sulphito Complex

The iron complex $(NH_4)_9[Fe(OSO_2)_6]$ has been shown by an X-ray study [26] to contain monodentate oxygen donor sulphito ligands, the iron being at the centre of an FeO_6 octahedron. The Raman and infrared spectra of this complex differ considerably from all those discussed above, reflecting the different mode of bonding of SO_3^{2-}: thus, both ν_1 and ν_3 drop some 150 cm^{-1} in frequency as compared with the complexes considered above. The bands in the infrared and Raman near 460 cm^{-1} are candidates for assignment to Fe–O stretches.

Hydrosulphito Complex

The complex $Ru(NH_3)_4(HSO_3)_2$ is made [11] from $[Ru(NH_3)_5Cl]Cl_2$, SO_2 and HSO_3^-; no spectroscopic data for it have been reported. Its ready conversion to *trans*-$[RuCl(SO_2)(NH_3)_4]^+$ [11] suggests that there is a *trans* arrangement of HSO_3^- ligands. We suggest, on the basis of the general similarity of the Raman spectra of this complex to those of $K_5[Ir(SO_3)_2Cl_4]\cdot 6H_2O$, that there is metal–sulphur bonding; the Raman band at 243 cm^{-1} may be assigned to ν_{Ru-S}.

New Osmium Sulphito Complexes

$K_4[Os(SO_3)_3(H_2O)_3]$

Attempts to prepare '$K_5H_2[Os(SO_3)_4Cl_4]$' [16] from $K_2[OsCl_6]$ and $KHSO_3$ gave a pale brown diamagnetic salt analysing as $K_4[Os^{II}(SO_3)_3(H_2O)_3]$. We prefer this latter formulation with monodentate S-bonded sulphite groups to the alternative, $K_4[Os(SO_3)_3]\cdot 3H_2O$ with bidentate SO_3^{2-}, because the vibrational spectra are very similar to those for *fac*-$[M(SO_3)_3(NH_3)_3]_3^{3-}$ (M = Rh, Ir) but quite different from those of $K_3[Rh(SO_3)_3]$. For the same reason a *fac* configuration of SO_3^{2-} ligands is suggested.

$Os(SO_3)(NH_3)_4Cl$

Reaction of $[Os(NH_3)_5Cl]Cl_2$ in hot aqueous potassium bisulphite solution with SO_2 gives a pink paramagnetic complex (μ_{eff} 1.45 B.M. at 298 °K). (A related procedure using $[Os(NH_3)_5(H_2O)]^{3+}$, HSO_3^- and SO_2 gives $[Os(NH_3)_5SO_2]Cl_2$ [27]). The vibrational spectra in the SO_3^{2-} region are similar to those of $Pd(SO_3)(NH_3)_3$ and we suggest that, as in the latter complex [20], the SO_3^{2-} ligand is sulphur bonded. The rather low infrared band at 297 cm^{-1} could arise from the chloro ligand *trans* to the sulphite.

$[Os_2N(NH_3)_8(SO_3)(H_2O)]Cl_3$

Reaction of $[Os_2N(NH_3)_8Cl_2]Cl_3$ in water with SO_2 yields the yellow-brown product of this formula; the infrared and Raman spectra suggest that the sulphite group is coordinated *via* the sulphur atom. The ready replacement of chloro ligands in $[Os_2N(NH_3)_8Cl_2]^{3+}$ has already been noted [8].

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References

1 A. V. Babaeva, Y. Y. Kharitonov and Z. M. Novozhenyuk, *Russ. J. Inorg. Chem., 6,* 1151 (1961).
2 A. V. Babaeva, Y. Y. Kharitonov and Z. M. Novozhenyuk, *Russ. J. Inorg. Chem., 6,* 1159 (1961).
3 A. V. Babaeva, Y. Y. Kharitonov, and E. V. Shenderetskaya, *Russ. J. Inorg. Chem., 7,* 790 (1961).
4 G. Newman and D. B. Powell, *Spectrochim. Acta, 19,* 213 (1963).
5 M. E. Baldwin, *J. Chem. Soc.,* 3123 (1961).
6 B. Nyberg and R. Larsson, *Acta Chem. Scand., 27,* 63 (1973).
7 G. A. Earwicker, *J. Chem. Soc.,* 2620 (1960).
8 M. J. Cleare and W. P. Griffith, *J. Chem. Soc. (A),* 1117 (1970).
9 V. V. Lebedinskii and M. M. Gurin, *C.R. Acad. Sci. URSS (2), 36,* 22 (1942).
10 V. V. Lebedinskii and Z. M. Novozhenyuk, *Russ. J. Inorg. Chem., 3,* (10) 62 (1958).
11 L. H. Vogt, J. L. Katz and S. E. Wiberley, *Inorg. Chem., 4,* 1157 (1965).
12 V. V. Lebedinskii and M. M. Gurin, *C.R. Acad. Sci. URSS, 33,* 241 (1941).
13 V. V. Lebedinskii and I. A. Fedorov, *Izvest. Inst. Po Izuch. Platin Drugikh. Blagorodnykh. Metallov., 21,* 157 (1948); *22,* 158 (1948).
14 V. V. Lebedinskii and F. V. Shenderetskaya, *Russ. J. Inorg. Chem., 2* (8), 89 (1957).
15 J. Lang, *J. Prakt. Chem., 83,* 417 (1861).
16 A. Rosenheim and E. A. Sasserath, *Z. Anorg. Chem., 21,* 122 (1899).
17 V. V. Lebedinskii and M. M. Gurin, *C.R. Acad. Sci. URSS, 38,* 128 (1943).
18 O. Erametsa, *Ann. Acad. Sci., Fenn., A59,* 5 (1443); *Chem. Abstr., 40,* 6359 (1946).
19 J. C. Evans and H. J. Bernstein, *Can. J. Chem., 33,* 1270 (1955).
20 M. A. Spinnler and L. N. Becka, *J. Chem. Soc. (A),* 1194 (1967).
21 L. M. Dikareva, I. B. Baranovskii and Z. G. Melkhtiev, *Russ. J. Inorg. Chem., 17,* 1772 (1972).
22 D. M. Adams and J. B. Cornell, *J. Chem. Soc. (A),* 884 (1967).
23 J. R. Allkins and P. J. Hendra, *J. Chem. Soc. (A),* 1325 (1967).
24 M. A. Porai-Koshits, S. P. Ionov and Z. M. Novozhenyuk, *J. Struct. Chem. USSR, 6,* 161 (1965).
25 W. P. Griffith, *J. Chem. Soc. (A),* 211 (1969).
26 L. O. Larsson, L. Niinisto, *Acta Chem. Scand., 27,* 859 (1973).
27 J. Sen and H. Taube, *Acta Chem. Scand., A33,* 125 (1979).