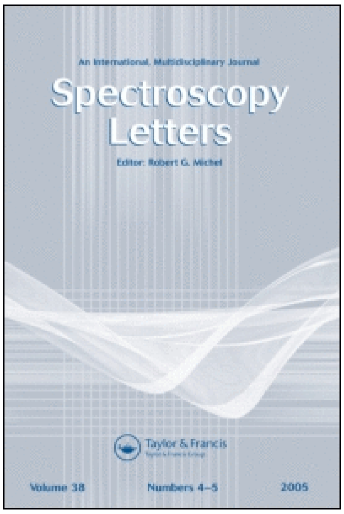

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THE VIBRATIONAL SPECTRUM OF THE ReO_5^{3-} ANION

Key words: pentaoxorhenate (VII), infrared spectrum, Raman spectrum, force constants, bond properties

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ABSTRACT

The infrared and laser-Raman spectra of crystalline $Ba_5(ReO_5)_3Br$ are reported and an assignment for the internal vibrations of the square pyramidal ReO_5^{3-} anion is proposed. Force constants, bond orders and mean amplitudes of vibration are calculated. Some comparisons with other rhenium compounds are made.

Recently, some new apatite-like phases of the type $Ba_5(ReO_5)_3X$ (X = Cl, Br, I) have been prepared[1,2]. An especially interesting aspect of these compounds is the presence of isolated square pyramidal ReO_5^{3-} anions.

As vibrational data on pentaoxometallates are very scarce[3,4], we have prepared the phase $Ba_5(ReO_5)_3Br$ in order to investigate the spectroscopic behaviour of this rhenium anion which, therefore, is the first oxoanion of this type that could be fully characterized from this point of view.

For an isolated square pyramidal anion of symmetry C_{4v} nine fundamental vibrations should be observed. These are classified as $3A_1 + 2B_1 + B_2 + 3E$. All nine modes should be Raman active, whereas only the A_1 and E species should be infrared active.

In the solid compound $Ba_5(ReO_5)_3Br$ (space group $P6_3cm$ and Z = 2)[1], the symmetry of the ReO_5^{3-} moieties is lowered to C_s. This lowering of the symmetry can produce a splitting of the double degenerate E modes into their components, and the activation of the i.r. forbiden modes B_1 and B_2. Furthermore, as the unit cell contains six rhenate anions, the number of observable internal modes can increase additionally due to the so called factor group splittings[4].

The meassured infrared spectrum of $Ba_5(ReO_5)_3Br$ is reproduced in Fig.1. The corresponding Raman spectrum shows two very strong doublets in the 950-800 cm^{-1} region, a series of weak lines in the middle region and a strong doublet at 350 cm^{-1}. The meassured i.r. and Raman frequencies as well as the proposed assignments are shown in Table 1.

According to the structural analysis[1], the ReO_5^{3-} anion has one short Re-O bond of 1.679 Å and four longer ones with an average distance of 1.86 Å. Therefore, the strong Raman doublet at 914/908 cm^{-1} and the corresponding i.r. doublet can be assigned to the stretching of the shorter Re-O bond.

The next higher frequency band arises from the symmetric in plane ReO_4 stretching mode. The corresponding antisymmetric stretching mode, $\nu_7(E)$, is expected as a very strong band in the infrared and therefore, the very broad

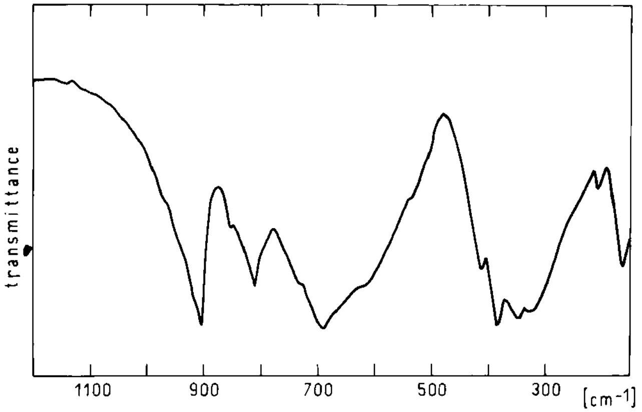

Figure 1 : **IR-Spectrum of $Ba_5(ReO_5)_3Br$**

band centered at 690 cm^{-1} is assigned to this mode, which is seen as a very weak doublet in the Raman effect.

The last stretching mode, the symmetric out of phase ReO$_4$-stretch, $\nu_4(B_1)$, has been assigned to the weak 640/625 cm^{-1} Raman doublet, which appears only as a weak shoulder around 620 cm^{-1} in the infrared spectrum.

The assignment of the five deformation modes is not so easy. The most intense Raman line which remains to be assigned, the 340/350 cm^{-1} doublet, can be assigned confidently to the O'ReO$_4$ deformation mode $\nu_8(E)$ which has is counterpart in the medium intensity 347 cm^{-1} i.r. band.

The $\nu_6(B_2)$ mode, which is the symmetric in plane deformation, has been assigned to the weak 526 cm^{-1} Raman line by comparison with the position of the ν_5 vibration of the ReO$_6^{6-}$ anion[5].

The antisymmetric out of plane deformation $\nu_5(B_1)$ is expected to lie close to the symmetric out of plane defor-

TABLE 1

Vibrational Spectrum of ReO_5^{3-} (values in cm^{-1})

Infrared	Raman	Assignment	
915 sh 908 vs	914 sh 908 vs	$\nu_1(A_1)$	$\nu(ReO')$
810 vs	823 vs 812 vs	$\nu_2(A_1)$	$\nu_s(ReO_4)$
410 m	- -	$\nu_3(A_1)$	δ_s(out of plane ReO_4)
~620 sh	640 w 625 vw	$\nu_4(B_1)$	ν_s(out of phase ReO_4)
382 m	- -	$\nu_5(B_1)$	δ_{as}(out of phase ReO_4)
~530 sh	526 w	$\nu_6(B_2)$	δ_s(in plane ReO_4)
690 s	688 vw 671 vw	$\nu_7(E)$	$\nu_{as}(ReO_4)$
347 m	350 s 340 s	$\nu_8(E)$	$\delta(O'ReO_4)$
332 w 318 w	- -	$\nu_9(E)$	δ_{as}(in plane ReO_4)

vs = very strong; s = strong; m = medium; w = weak;
vw = very weak; sh = shoulder

mation $\nu_3(A_1)$ and, in accordance with this, we have assigned to these vibrations the medium intensity i.r. bands lying at 382 and 410 cm^{-1} respectively, assuming that also here ν_3 must lie at higher frequency as ν_5, similarly to that proposed in the case of the square pyramidal interhalogen molecules[6], the corresponding chalcogenate fluorides[7] and the $XeOF_4$ molecule[6].

Finally, the weak i.r.doublet at 332/318 cm^{-1}, which is seen as a part of the strong band located between 300 and 400 cm^{-1}, has been assigned to the antisymmetric in plane deformation ν_9(E).

The appearance of most of the observed bands as doublets may probably be explained as a manifestation of the correlation field splittings, inasmuch as the differences between the doublet components are generally very small.

The weak i.r. shoulders at 852 and 737 cm^{-1} probably arise from overtones or combinations of the fundamentals described above, whereas the bands at 210 and 164 cm^{-1} as well as the Raman lines located at 168 (s), 152 (s), 126 (s), 120 (m), 94 (vs) and 78 (s) cm^{-1} can be assigned to external (lattice) vibrations.

In order to check the plausibility of the above assignments and also to obtain a wider insight into the bond characteristics of the ReO_5^{3-} anion, we have made a calculation of their force constants.

The G- and F- matrix elements proposed by Begun et al.[6] have been used, assuming all the angles equal to 90° and using the values of 1.68 Å and 1.86 Å for the Re-O' and Re-O bonds respectively[1]. The following frequency values were used to solve the secular equation: $\nu_1 = 911$, $\nu_2 = 817$, $\nu_3 = 410$, $\nu_4 = 630$, $\nu_5 = 382$, $\nu_6 = 526$, $\nu_7 = 690$, $\nu_8 = 345$ and $\nu_9 = 325$ cm^{-1}.

The calculated symmetry and internal force constants are given in Table 2. In this table, R refers to the Re-O' bond, r to the Re-O bonds, α to the OReO angles and β to the O'ReO angles. The primed values refer to interactions between opposite coordinates, and the unprimed to interactions between adjacent coordinates. All stretch/bend interactions as well as the interactions between opposite angles ($f'_{\alpha\alpha}$) were put equal to zero.

TABLE 2

Symmetry and Internal Force Constants for the ReO_5^{3-} Ion

(values in mdyn/Å)

$F_{11} = f_R = 7.16$

$F_{22} = f_r + 2f_{rr} + f'_{rr} = 6.29$

$F_{33} = f_\beta + 2f_{\beta\beta} + f'_{\beta\beta} = 1.21$

$F_{44} = f_r - 2f_{rr} + f'_{rr} = 3.74$

$F_{55} = f_\beta - 2f_{\beta\beta} + f'_{\beta\beta} = 1.37$

$F_{66} = f_\alpha - 2f_{\alpha\alpha} + f'_{\alpha\alpha} = 0.65$

$F_{77} = f_r - f'_{rr} = 3.79$

$F_{88} = f_\beta - f'_{\beta\beta} = 0.36$

$F_{99} = f_\alpha - f'_{\alpha\alpha} = 0.46$

$f_R = 7.16$ $f_\beta = 0.83$

$f_r = 4.40$ $f_{\beta\beta} = -0.04$

$f_{rr} = 0.64$ $f'_{\beta\beta} = 0.46$

$f'_{rr} = 0.61$ $f_\alpha = 0.46$

$f_{\alpha\alpha} = -0.10$

The obtained set of force constants gives an exact fit between the observed and computed frequencies. The potential energy distribution showed that all the vibrations of the ReO_5^{3-} anion were highly characteristic, except the two E-bands of lower frequency.

From the obtained internal force constants for the two Re-O bonds, an estimation of the respective bond orders has been made using the method of Siebert[8]. For the shorter bond a value of 2.05 is obtained, whereas for the longer ones it lies at 1.40. Both values point to appreciable πcontributions, most important in the case of the shorter bond, which can be considered practically as a double bond.

Such strong metal-oxygen bonds are not rare in the rhenium chemistry. For instance, the high value for the force constant found here is yet overcomed by that of the Re-O bonds of the tetrahedral ReO_4^- ion (7.54 mdyn/Å)[9], the terminal ReO_3 groups of the Re_2O_7 (8.42 mdyn/Å)[10] and that of the ReO_3Cl (8.28 mdyn/Å)[11]. But all the Re-O bonds of the ReO_5^{3-} anion are notably stronger than those of the octahedral ReO_6^{5-} ion, which possesses a force constant of 3.48 mdyn/Å[5].

Finally, we have also made an estimation of the mean amplitudes of vibration using the "Method of the Characteristic Vibrations" (cf.[12-14]). The vibrational assignment to the XY_2 and ZXY "pseudo molecules" was performed using the same criteria as in a previous paper[15]. The results, in the temperature range between 0 and 700 K, are shown in Table 3.

The amplitude values for the shorter Re-O bond lies in a range which is considered characteristic for heptavalent rhenium-oxygen compounds[14,16]. The values for the other four bonds, on the contrary, are clearly higher, pointing to a considerable bond weakening in the "ReO_4 plane".

EXPERIMENTAL

Samples of $Ba_5(ReO_5)_3Br$ have been obtained according to Baud et al.[1], by reaction between metalic rhenium powder and a slight excess of anhidrous $BaBr_2$ working in platinum crucibles, in air and at temperatures around 800°C. The product was deposited in the border of the crucible as very small, light-yellowish, crystalls or powder.

TABLE 3

Mean Amplitudes of Vibration (in Å) for the ReO_5^{3-} Ion

T (K)	u_{ReO}	$u_{ReO'}$	$u_{O...O(sh)}$	$u_{O...O(lg)}$	$u_{O...O'}$
0	0.0402	0.0354	0.066	0.056	0.063
100	0.0402	0.0354	0.066	0.056	0.064
200	0.0405	0.0355	0.069	0.057	0.067
300	0.0416	0.0359	0.075	0.059	0.072
400	0.0436	0.0368	0.081	0.062	0.078
500	0.0459	0.0381	0.088	0.066	0.085
600	0.0485	0.0397	0.094	0.070	0.091
700	0.0511	0.0414	0.101	0.074	0.097

The i.r. analysis of the samples show that they contain also small quantities of $Ba(ReO_4)_2$. Totally pure samples have been obtained by treating the impure product with hot absolute methanol, in which $Ba(ReO_4)_2$ is partially soluble but $Ba_5(ReO_5)_3Br$, similarly as $Ba_5(ReO_5)_2$, is insoluble (cf.for example[17]).

The infrared spectrum has been recorded with a Perkin Elmer 180 model spectrophotometer, dispersing the sample in a CsI pellet. The Raman spectrum has been meassured with a Coderg spectrophotometer (Type PHO) using the 514.4 nm line of an Ar^+ laser as the excitation source.

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REFERENCES

1. G.Baud, J.P.Besse, G.Sueur and R.Chevalier, Mater.Res. Bull. 14, 675 (1979).
2. J.P.Besse, G.Baud, G.Levasseur and R.Chevalier, Acta Crystallogr. B35, 1756 (1979).
3. K.H.Schmidt and A.Müller, Coord.Chem.Rev.14, 115 (1974).
4. A.Müller, E.J.Baran and R.O.Carter, Structure and Bonding 26, 81 (1976).
5. E.J.Baran, Monatsh.Chem. 107, 1327 (1976).
6. G.M.Begun, W.H.Fletcher and D.F.Smith, J.Chem.Physics 42, 2236 (1965).
7. K.O.Christe, E.C.Curtis, C.J.Schack and D.Pilipovich, Inorg.Chem. 11, 1679 (1972).
8. H.Siebert, "Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie". Springer Vlg., Berlin, 1966.
9. A.Müller and B.Krebs, J.Mol.Spectroscopy 24, 180 (1967).
10. E.J.Baran, Anales Asoc.Quím.Argent. 62, 65 (1974).
11. A.Müller, K.H.Schmidt, E.Ahlborn and C.J.L.Lock, Spectrochim.Acta 29A, 1773 (1973).
12. A.Müller, C.J.Peacock, H.Sculze and U.Heidborn, J.Mol. Structure 3, 252 (1969).
13. E.J.Baran, Anales Asoc.Quím.Argent. 61, 141 (1973).
14. A.Müller, E.J.Baran and K.H.Schmidt, "Characteristic Mean Amplitudes of Vibration" in "Molecular Structures and Vibrations" (S.J.Cyvin, Editor). Elsevier Publ. Co., Amsterdam, 1972.

15. E.J.Baran, Z.Naturforsch. 28a, 1376 (1973).
16. E.J.Baran, Afinidad 36, 219 (1979).
17. R.Scholder, Angew.Chem. 70, 583 (1958).

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