

Vibrational spectra of sodium paratungstate 26 hydrate, $\text{Na}_{10}(\text{H}_2\text{W}_{12}\text{O}_{42})\cdot 26\text{H}_2\text{O}$

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A great number of polymolybdates and tungstates have been identified and subjected to a series of investigations [1–3]. These types of compounds are interesting in several fields of chemistry including catalysis, solid-state applications and medicine [4–6]. X-ray studies of these phases show the existence of corner- and edge-shared XO_6 octahedra ($\text{X} = \text{Mo}$ and W).

The isopolyanion paradodecatungstate ($\text{H}_2\text{W}_{12}\text{O}_{42}$)¹⁰⁻ has been found in a great number of salts [7–10] and the structure of the title compound has been recently studied by Cruywagen *et al.* [11]. The anion has a centre of symmetry and is built up by 12 WO_6 octahedra joined by either edge or vertices sharings.

In this study an analysis of the infrared and Raman spectra of $\text{Na}_{10}(\text{H}_2\text{W}_{12}\text{O}_{42})\cdot 26\text{H}_2\text{O}$ was carried out not only to understand the vibrational modes of the polyanion, but also to find the characteristics of the water molecules in the lattice.

The $\text{Na}_{10}(\text{H}_2\text{W}_{12}\text{O}_{42})\cdot 26\text{H}_2\text{O}$ was prepared from a 0.1234 M solution in tungstate and 0.1313 M in HCl with a pH of 6.6. The Raman spectrum (50–4000 cm^{-1}) was recorded in the Stokes region of the 488.0 nm line of an Ar-ion laser using a Spex Ramalog 1403 double monochromator spectrometer equipped with a SCAMP data processor. The infrared spectrum (200–4000 cm^{-1}) was obtained on Perkin-Elmer 580B and 983 spectrophotometers with the samples in KBr and polyethylene. The infrared spectrum was also registered at low temperature (about 80 K), using an RIIC cell (VLT-2 model). The X-ray diffraction measurements were registered in a Phillips PW 1730 using Ni-filtered $\text{CuK}\alpha$ radiation.

The $\text{Na}_{10}(\text{H}_2\text{W}_{12}\text{O}_{42})\cdot 26\text{H}_2\text{O}$ compound belongs to the triclinic system, space group $\text{PI} (\text{C}_1^1)$ and $Z = 1$. All atoms in the crystal are in general sites. The 12 W atoms form a polyhedral skeleton with W–W distances ranging from 0.331 nm in edge-sharing to 0.368 nm in corner-sharing octahedra. The W–O bond lengths vary from 0.178 to 0.227 nm. These significant differences suggest considerable octahedral distortions from regular geometry. Although both H atoms were not found in the electron density maps [11], they were located in the related $(\text{NH}_4)_{10}(\text{H}_2\text{W}_{12}\text{O}_{42})\cdot 4\text{H}_2\text{O}$ compound by neutron diffraction [11].

Taking into account the vibrations of the WO_6

groups, factor group analysis [13] predicts 429 normal modes (excluding the three acoustic ones), which split as

$$\Gamma_{429} = 216\text{A}_g(\text{Raman}) + 213\text{A}_u(\text{infrared})$$

Fig. 1 shows the vibrational spectrum of $\text{Na}_{10}(\text{H}_2\text{W}_{12}\text{O}_{42})\cdot 26\text{H}_2\text{O}$ between 1000 and 200 cm^{-1} , together with the infrared spectrum of the anhydrous phase.

It is well known that the stretching and bending vibrations for a free WO_6 octahedron usually occur in the 700–850 and 300–450 cm^{-1} regions, respectively [14]. However, and in comparison with the vibrational analysis of some other isopoly- and

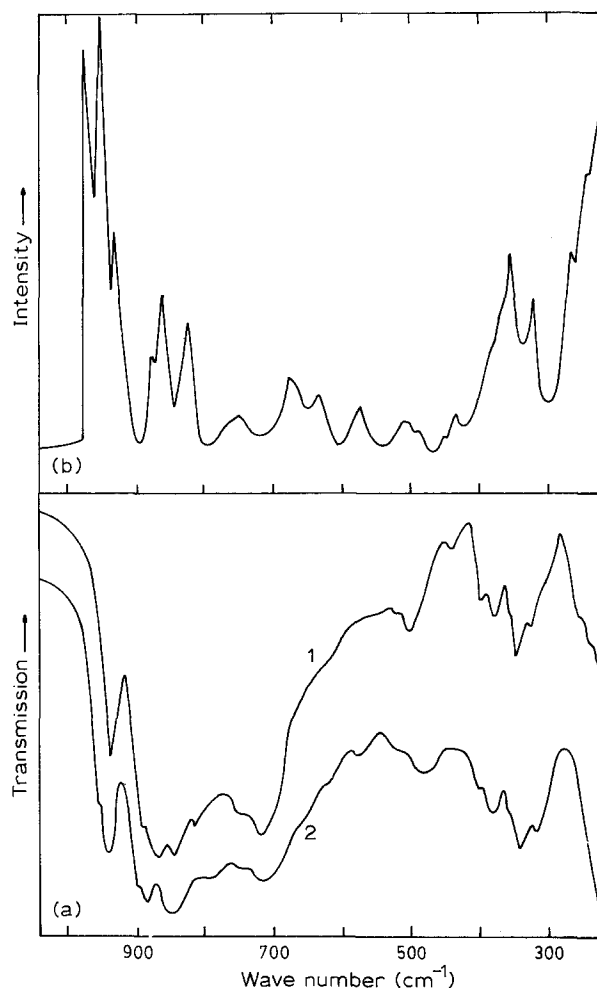


Figure 1 Vibrational behaviour of $\text{Na}_{10}(\text{H}_2\text{W}_{12}\text{O}_{42})\cdot 26\text{H}_2\text{O}$: (a) infrared spectrum (1) at low temperature (about 80 K) and (2) sample heated to 200 °C, and (b) Raman spectrum.

heteropolymetalates [15–22], different types of W–O bonds can be considered in the anion: W–O and W–O₂ terminal groups, (W–O–W)_e octahedral edge sharing, (W–O–W)_c octahedral corner sharing and (W–O–W) octahedral edge and corner sharing. Only the terminal stretchings can be considered as pure vibrations, because the remaining bonds show some bend character [19].

The three most intense Raman lines (967, 950 and 930 cm⁻¹) associated with the infrared shoulder at 950 cm⁻¹ and the intense band at 936 cm⁻¹ are assigned to the vibrations of the terminal groups, in agreement with literature values for other related tungstates [18, 21]. In the 900–800 cm⁻¹ region the very strong infrared band as well as the Raman lines at 887, 871 and 828 cm⁻¹ can be attributed to the (W–O–W)_e vibrations. The next group of bands between 800 and 600 cm⁻¹ can be assigned to the

(W–O–W) remaining stretchings. It is interesting to notice that these last modes have also been observed as weak Raman lines in other polywolframates [19].

The vibrations of the OH and H₂O librations usually appear between 700 and 450 cm⁻¹. However, these bands can be overlapped with the W–O internal modes.

Below 500 cm⁻¹ it is rather difficult to assign the spectrum, although the symmetric and antisymmetric W–O₂ deformation can be assigned. Similarly, below 300 cm⁻¹ the lattice modes are located with certainty.

In relation to the water vibrations, the very strong and broad infrared band in the 3600–3100 cm⁻¹ region is assigned to the O–H stretchings. Similarly, the appearance of four intense infrared bands at 1655, 1640, 1625 and 1615 cm⁻¹ in the bending region suggests the presence of different types of

TABLE Vibrational spectrum (in cm⁻¹) of Na₁₀(H₂W₁₂O₄₂)·26H₂O. The infrared data for the anhydrous phase are also included

Na ₁₀ (H ₂ W ₁₂ O ₄₂)·26H ₂ O		Na ₁₀ (H ₂ W ₁₂ O ₄₂)	Assignment
Raman	Infrared	Infrared	
	3100–3600 vs (br)		
2960 vw			ν O–H + H-bonding
2930 vw			
	2340 w		Combinations
	2310 w		
	2070 w		
	1950 vw		
	1900 vw		
	1655 sh		δ H ₂ O
	1640 s		
	1625 s		
	1615 s		
967 vs	950 sh	958 sh	ν (W–O) _t
950 vs			
930 s	936 s	941 s	ν (W–O ₂) _t
887 sh	890 sh	897 sh	ν (W–O–W) _e
871 s	872 vs	883 vs	
828 s	838 vs	841 vs	
	807 sh		
		788 s	ν (W–O–W) _c ν (W–O–W) _{e,c}
762 w (br)	743 sh	749 sh	
	709 vs (br)	703 vs (br)	
686 m	675 sh		Lib. H ₂ O, OH
639 w	660 sh?	656 sh	
577 w	630 sh?	623 sh	
	600 sh?		
504 m	530 sh	577 w	
484 w (br)	498 m	487 m	
	480 sh?		
445 vw			δ W–O ₂
424 vw	438 w		
	405 sh	409 w	
374 sh	396 w	382 w	
	374 m	359 sh	
354 m	340 s	341 m	Lattice modes
	325 w		
316 m	310 sh	312 w	
255 s	265 s		
233 s	235 m		ν Na–O?
	210 w		
108 vw			
106 m			

vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad.

water molecules of various hydrogen bond strengths in the lattice.

Table I gives the position and assignment of the $\text{Na}_{10}(\text{H}_2\text{W}_{12}\text{O}_{42}) \cdot 26\text{H}_2\text{O}$ bands.

In order to understand the nature of the H-bond, a sample of the analysed compound was heated to 600 °C. There was a gradual evolution of the hydration water, which was later completed at 200 °C, thus leading to a weight loss of 13%, in agreement with the theoretical value. The corresponding infrared spectrum did not show appreciable form changes between 1200 and 200 cm^{-1} . However, a slight and expected shift of the stretchings to higher frequencies was clearly observed. This is due to a breaking of the H-bond between the O-terminal atoms with the water molecules, producing a reinforcement of the W–O_t bonds. This sample was not crystalline as shown by X-ray diffraction.

When the sample was heated up to 300 °C the two internal H-atoms were removed. The infrared spectrum then showed important changes and the X-ray diffraction pattern revealed the incipient formation of Na_2WO_4 spinel phase. Starting from 500 °C, a mixture of $\text{Na}_2\text{W}_2\text{O}_7$ with a small proportion of WO_3 and Na_2WO_4 was revealed by X-ray diffraction and infrared spectroscopy [23]. This thermal behaviour points out the position of the librational modes of H_2O , which are located between 400 and 600 cm^{-1} , because the infrared spectrum of the sample heated at 200 °C showed the clearest variations in this region.

In conclusion, the $\text{Na}_{10}(\text{H}_2\text{W}_{12}\text{O}_{42}) \cdot 26\text{H}_2\text{O}$ vibrational behaviour supports the suspected distortion of the WO_6 octahedra in the anion. Similarly, different water molecules with various hydrogen bond strengths are present in the compound. On the other hand, the polyhedral skeleton maintains its identity up to approximately 250 °C.

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