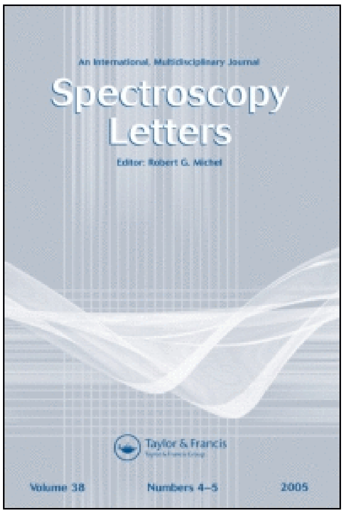

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

The Vibrational Spectra of a Series of Simple Phosphorus/Chromium Polyoxoanions

Enrique J. Baran[a]; Carmen I. Cabello[a]
[a] Facultad de Ciencias Exactas, Universidad Nacional de La Plata, La Plata, Argentina

To cite this Article Baran, Enrique J. and Cabello, Carmen I.(1986) 'The Vibrational Spectra of a Series of Simple Phosphorus/Chromium Polyoxoanions', Spectroscopy Letters, 19: 9, 981 — 991
To link to this Article: DOI: 10.1080/00387018608069303
URL: http://dx.doi.org/10.1080/00387018608069303

SPECTROSCOPY LETTERS, 19(9), 981-991 (1986)

THE VIBRATIONAL SPECTRA OF A SERIES OF SIMPLE PHOSPHORUS/CHROMIUM POLYOXOANIONS

Key words: polyoxoanions, IR spectra, Raman spectra, vibrational assignment.

Enrique J.Baran and Carmen I.Cabello
Facultad de Ciencias Exactas,Universidad
Nacional de La Plata, 1900-La Plata,Argentina

ABSTRACT

The infrared and Raman spectra of polycrystalline samples of $K_2HPCr_2O_{10}$, $Na_3PCr_3O_{13}.3H_2O$, $K_3PCr_4O_{16}$ and $(NH_4)_3PCr_4O_{16}$ were recorded and discussed. A general vibrational assignment for the internal vibrations of these species is proposed.

The structural characteristics of an interesting series of simple polyoxoanions of the $PCr_nO_{3n+4}^{3-}$ type have been determined recently[1-7]. These species are essentially built from a central PO_4-tetrahedron which share a different number of corners with CrO_4-tetrahedra.

As part of our present studies on different physico-chemical properties of polyoxoanions, we have investigated the vibrational spectra of crystalline species containing the following anions: $HPCr_2O_{10}^{2-}$, $PCr_3O_{13}^{3-}$ and $PCr_4O_{16}^{3-}$.

As the three species have some common structural features, their vibrational spectra can be analyzed

0038-7010/86/1909-0981$3.50/0

and compared in terms of these common building elements, i.e., terminal CrO_3 and PO groups and POCr bridges.

The interatomic distances in the above mentioned units are also very similar in all the anions and the Cr-O distances are similar to those found in the normal (triclinic) form of $K_2Cr_2O_7$ [8].

RESULTS AND DISCUSSION

1.$K_2HPCr_2O_{10}$

The structure of $K_2HPCr_2O_{10}$ has not been refined (cf.[2]), but it is assumed, that the general features were very similar to those found in the corresponding barium salt[1]. The central PO_4-tetrahedron presents one P-O bond which is somewhat shorter than the other three (1.48 to 1.55 Å). This implies, that one of the two terminal P-O bonds (the longer one) retains the proton, generating a PO(OH)-moiety. But, as it shall be discussed later, the hydrogen atom takes part in the formation of strong hydrogen bonds and it cannot therefore be clearly localized over one of the terminal P-O bonds.

The IR spectrum of this compound is shown in Fig.1. The Raman spectrum is rather simple and shows a more reduced number of lines. The spectral data, together with the proposed assignments are presented in Table 1.

A spectral pattern characteristic for strongly hydrogen bonded systems with the typical A,B,C band arrangement[9,10] can be observed in the high frequency region. This spectral pattern clearly points to an important delocalization of the proton between the two terminal oxygen atoms and probably to the PO_2-units of neighbouring anions.

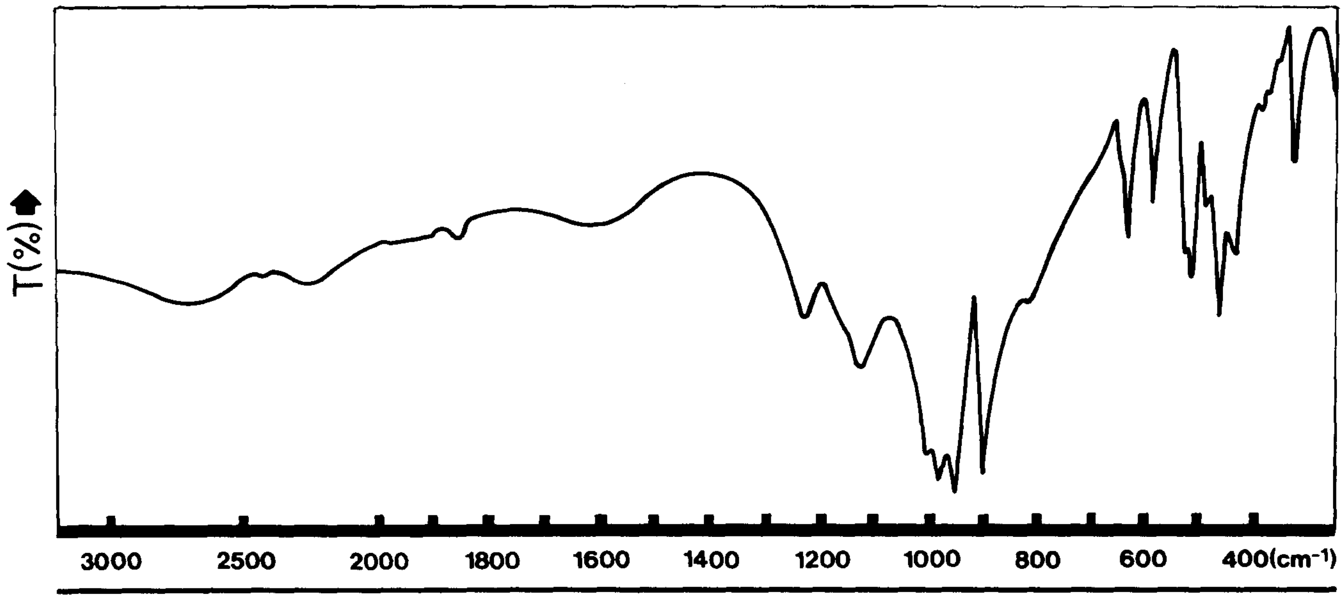

Fig.1. Infrared Spectrum of $K_2HPCr_2O_{10}$

TABLE 1
Assignment of the Vibrational Spectrum of $K_2HPCr_2O_{10}$
(values in cm^{-1})

IR	Raman*	Assignment
~2700		ν(OH) band A
~2440		2δ(OH) ?
2280		ν(OH) band B
~1858		?
1632		ν(OH) band C
1233		δ(OH) in plane
1129	---	ν(PO)
1008	997 sh	$\nu_{as}(CrO_3)$
982	983 w	
951	964 s	
901	916 vs	$\nu_s(CrO_3)$
818	---	δ(OH) out of plane(?)
630	650	ν_{as}(POCr)
585	---	δ(PO(OH))
527 sh	---	
515	---	
485	---	ν_s(POCr)
460	---	
433	437 vw	$\delta(CrO_3)$
388	390 w	
371	374 m	
357	365 s	
325	330 vw	$\rho(CrO_3O')$ (?)

*) The Raman spectrum was recorded between 1200 and 200 cm^{-1}; vs: very strong; s: strong; m: medium; w: weak; vw: very weak; sh: shoulder.

The existence of strong hydrogen bonds between neighbouring groups is also supported by the thermal behaviour of $K_2HPCr_2O_{10}$[11], because an intramolecularly generated H_2O molecule is released in the first degradation step.

Only the terminal P-O stretching can be seen from the phosphorus-oxygen vibrations, whereas the band assignable to the P-OH stretching and expected to lie around 900 cm^{-1} (cf.[12-14]) is probably overlapped by the stronger CrO_3-bands.

The fact that not one of the P-O vibrations can be seen in the Raman spectrum, which only shows bands related to the CrO_3 and POCr bridge modes, is another remarkable aspect of the spectral behaviour of this anion.

The CrO_3-vibrations, lie in a very similar range to that found for the $Cr_2O_7^{2-}$ ion (cf.for example[15-17]). The most intense Raman line clearly corresponds to one of the $\nu_s(CrO_3)$ components, which appears also very well defined in the IR spectrum.

The assignment of both POCr vibrations is not easy. We have assigned the strong IR band at 630 $cm^{-1}$to the respective antisymmetric mode, but the location of the symmetric one is more difficult because a great number of bands are observed in the lower frequency region. The proposed assignments are based on the fact that these bands were observed in all the investigated anions and they lie in very similar ranges.

The assignment of the $\delta(CrO_3)$ modes is supported by comparison with the well knwon dichromate-spectra (cf.[15-17]) and also by results of resonance-Raman experiments, which have clearly shown that these bands are related to CrO_3-modes[18].

2. $Na_3PCr_3O_{13}.3H_2O$

It is very difficult to handle this compound and to obtain well reproducible spectra, because it is highly hygroscopic.

Its IR spectrum in the region of the internal vibrations of the anion is shown in Fig.2A. The proposed band assignment is presented in Table 2.

The most intense Raman line (911 cm^{-1}) is assigned to one of the $\nu_s(CrO_3)$ components; its IR counterpart shows some splitting.

The terminal PO-stretching band appears as a very well defined IR band at 1181 cm^{-1} but, it is interesting to note that this PO vibration could not be observed in the Raman effect. This band lies at a slightly higher frequency than the similar band measured in the $HPCr_2O_{10}^{2-}$ anion although the P-O distances are practically identical[1,3]. This fact can probably be considered as another proof of the suspected partial delocalization of the proton over the two terminal PO bonds in $HPCr_2O_{10}^{2-}$.

The behaviour of the water molecules is also interesting. From the structural analysis[3], it is clear that the three molecules are not equivalent. This fact becomes also evident during the study of the thermal degradation[11]. The IR spectrum in the OH-stretching region shows three well defined bands at 3545, 3470 and 3408 cm^{-1} and a weaker one at 3240 cm^{-1}. A nicely resolved and strong doublet with components at 1637 and 1615 cm^{-1} is observed in the bending region. The weak doublet at 800-780 cm^{-1}, also seen in Fig.2A, can probably be assigned to water-librational modes.

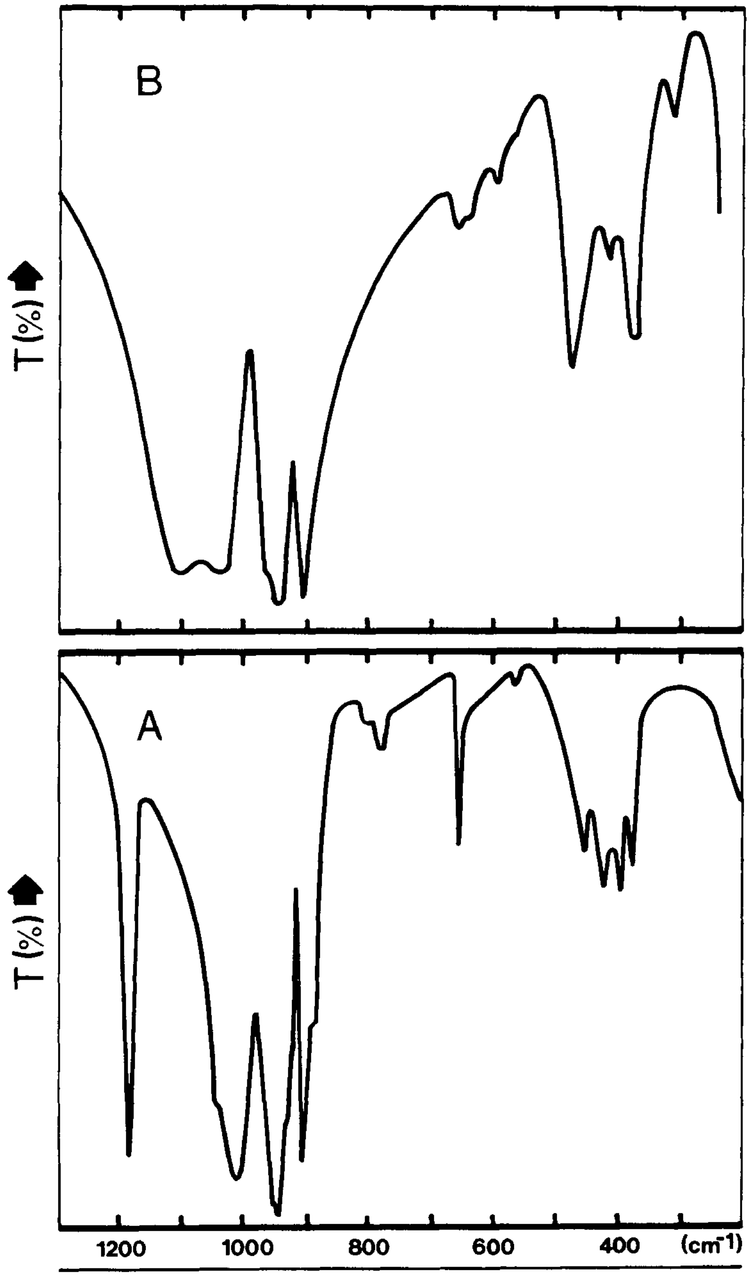

Fig.2.IR Spectra of $Na_3PCr_3O_{13}.3H_2O$ (A) and $K_3PCr_4O_{16}$(B)

TABLE 2

Assignment of the Internal Vibrations of $PCr_3O_{13}^{3-}$ and $PCr_4O_{16}^{3-}$ (K^+ and NH_4^+ salts). Values in cm^{-1}.

$Na_3PCr_3O_{13}\cdot 3H_2O$		$K_3PCr_4O_{16}$	$(NH_4)_3PCr_4O_{16}$		Assignment
IR	Raman	IR	IR	Raman	
1181	--	--	--	--	$\nu(PO)$
1050 sh		1104	1100		
1020		1042	1030		
952 sh		962 sh			
948	955 s	948	940	946 m	$\nu_{as}(CrO_3)$
932 sh					
905 sh					
902	911 vs	905	900	916 vs	$\nu_s(CrO_3)$
890 sh		882 sh			
650		657,637sh	655,635sh		$\nu_{as}(POCr)$
565		592	600		(?)
455		475	472		$\nu_s(POCr)$
422		415	410	381 s	$\delta(CrO_3)$
395					
378	374 s	375	372		
-	-	311	312	-	$\rho(CrO_3O')$

vs: very strong; s: strong; m: medium; sh: shoulder

3.$K_3PCr_4O_{16}$

The IR spectrum of this compound, shown in Fig.2B, is relatively simple. It was very difficult to obtain good quality Raman spectra of this coapound. These spectra show always only one, medium intensity line, located at 917 cm^{-1}.

In the CrO_3-stretching region the IR spectrum shows a strong and broad doublet and a strong band assignable to the ν_{as}-mode and another, well defined band, with a weak shoulder on the low frequency side, corresponding to the symmetric vibration.

The weak intensity of the 657/637 cm^{-1} doublet, assignable to the antisymmetric POCr bridge-vibration, is very interesting in this compound. This weakness is probably originated by the higher symmetry around the central phosphorus atom in this case, when compared with that of the other anions discussed before.

The proposed assignment, is included in Table 2.

4. $(NH_4)_3PCr_4O_{16}$

The IR spectrum of the ammonium salt is totally similar, although it has a less defined band structure, than that of the just discussed potassium compound. The proposed assignment is also shown in Table 2.

For the fundamental NH_4^+ modes, the following IR bands were found: in the N-H stretching region, ν_3 appears as a very broad not well structured band centered around 3180 cm^{-1}. A weak band at ca. 3045 cm^{-1} can be assigned to the symmetric stretching mode ν_1, although it could also be originated by the $\nu_2 + \nu_4$ combinational mode. The antisymmetric bending ν_4 is seen as a very strong bant at 1408 cm^{-1} and the corresponding symmetric vibration, ν_2, as a weak and not well defined one at ca. 1645 cm^{-1}. The spectrum shows also two additional weak bands at 2825 and 1852 cm^{-1}, which can be assigned to $2\nu_4$ and to a combination mode $\nu_4 + \nu_6$ respectively, being ν_6 a torsional oscillation of the NH_4^+-group[19].

The existence of hydrogen bonding, which restricts the free motion of the NH_4^+ groups[19,20], is suggested by the presence of the last combination band, by the position of the ν_3 and ν_4 fundamentals and the intensity of the $2\nu_4$ band. Notwithstanding, the comparison of the ammonium and potassium salts of the

$PCr_4O_{16}^{3-}$ anion (Table 2) clearly shows that, although all the CrO_3-bands are slightly displaced to lower frequencies in the former salt, the overall effect is really **negligible**.

EXPERIMENTAL

1.Syntheses of the compounds. $K_2HPCr_2O_{10}$ was obtained from $K_2Cr_2O_7$ and concentrated H_3PO_4[2] and $Na_3PCr_3O_{13}\cdot 3H_2O$ from a 3:1 mixture of CrO_3 and Na_2HPO_4[3]. From the quaternary phosphates, the $K_3PCr_4O_{16}$, was obtained from concentrated 4:1 CrO_3/K_3PO_4 solutions[6] and the respective ammonium salt from a 2:1 $(NH_4)_2Cr_2O_7/H_3PO_4$-mixture[4,5].The purity of all the compounds was checked by chemical analysis and X-ray diffractometry[2,3,4,6].

2.Spectra.The IR spectra were recorded on a Perkin Elmer 580 B spectrophotometer using the KBr-pellet technique. Raman spectra of the crystal powders sealed in glass capilars were obtained on a SPEX-Ramalog 1403-double monochromator spectrometer equipped with a SCAMP controll unit and employing the 488 nm-line of an argon-ion laser for excitation.

ACKNOWLEDGEMENTS

This work is supported by the CONICET (Programa QUINOR) and CIC-Provincia de Buenos Aires. We are also specially indebted to Mr.R.García for the measurement of the Raman spectra.

REFERENCES

1. M.T.Averbuch-Pouchot, A.Durif and J.C.Guitel, Acta Crystallogr. B33, 1431 (1977).
2. M.T.Averbuch-Pouchot, A.Durif and J.C.Guitel, Acta Crystallogr. B34, 3725 (1978).

3. M.T.Averbuch-Pouchot, A.Durif and J.C.Guitel, J.Solid State Chem. 33, 325 (1980).
4. M.T.Averbuch-Pouchot and A.Durif, J.Solid State Chem. 33, 439 (1980).
5. M.T.Averbuch-Pouchot, A.Durif and J.C.Guitel, J.Solid State Chem. 36, 381 (1981).
6. M.T.Averbuch-Pouchot, A.Durif and J.C.Guitel, J.Solid State Chem. 38, 253 (1981).
7. J.Coing-Boyat, A.Durif and J.C.Guitel, J.Solid State Chem. 30, 329 (1979).
8. J.K.Brandon and J.D.Brown, Canad.J.Chem. 46, 933 (1968).
9. D.Hadzi, Pure Appl.Chem. 11, 435 (1965).
10. E.E.Berry, Spectrochim.Acta 24A, 1727 (1968).
11. E.J.Baran and C.I.Cabello, Thermochim.Acta, in the press.
12. A.C.Chapman and L.E.Thirlwell, Spectrochim.Acta 20, 937 (1964).
13. E.E.Berry and C.B.Baddiel, Spectrochim.Acta 23A, 2089 (1967).
14. G.E.B.Y.Ahlijah and E.F.Mooney, Spectrochim.Acta 22, 547 (1966).
15. M.S.Mathur, C.A.Frenzel and E.B.Bradley, J.Mol. Struct. 2, 429 (1968).
16. R.L.Carter and C.E.Bricker, Spectr.Lett. 2, 247 (1969).
17. R.Mattes, Z.anorg.allg.Chem. 382, 163 (1971).
18. A.H.Jubert, E.J.Baran and O.Sala, J.Mol.Struct., in the press.
19. T.C.Waddington, J.Chem.Soc. 1958, 4340.
20. E.J.Baran and P.J.Aymonino, Z.anorg.allg.Chem. 354, 85 (1967).

Date Received: 04/23/86
Date Accepted: 07/21/86