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Spectral Studies on the Reaction of Chromium(VI) Compounds with Aminophosphonic Esters

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The studies on reaction of newly obtained aminophosphonic acid diethyl ester derivatives of fluorene with $Cr_2O_7^{2-}$, CrO_4^{2-}, CrO_3Cl^- and CrO_3 have been investigated using electronic, infrared, *Raman* and NMR spectral methods. It has been found that the resulting compounds are of the type $(AH)_2Cr_2O_7$, where A stands for the organic part of the molecule. The organic cation and solvent effects on the electronic states of pseudotetrahedrally arranged Cr(VI) anions are discussed.

[Keywords: Aminophosphonic ester compounds; Chromium(VI) compounds; Vibrational structure analysis]

Spektroskopische Untersuchungen über Reaktionen von Chrom(VI)-Verbindungen mit Aminophosphonsäure-Estern

Es wurden Elektronen-, Ultrarot-, *Raman*- und NMR-spektroskopische Untersuchungen beschrieben, die an neuen Verbindungen durchgeführt wurden, welche als Reaktionsprodukte von $Cr_2O_7^{2-}$, CrO_4^{2-}, CrO_3Cl^- und CrO_3 mit Aminophosphonsäurediethylesterderivaten von Fluorene synthetisiert worden waren. Es wurde festgestellt, daß diese Verbindungen mit einer allgemeinen Formel $(AH)_2Cr_2O_7$ beschrieben können werden, in der A den organischen Teil der Verbindungen bedeutet. Der Einfluß des organischen Kations wie auch der von Lösungsmitteln auf die Elektronenzustände des pseudotetraedrischen Cr(VI)-Anions wurde gleichfalls untersucht.

Introduction

In recent years there has been observed a growing interest in vibrational fine structure which is sometimes noticed in the electronic spectra of inorganic compounds[1–3]. The information obtained from

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analysis of the structure is primarily concerned with the change of position and shape of the potential energy curve during excitation. In most cases the single crystals at cryogenic temperatures have been studied; under these conditions the spectra are best resolved. The electronic spectra of chromium(VI) oxy- and haloxy compounds in organic solvents exhibit well resolved vibrational fine structure[4–9].

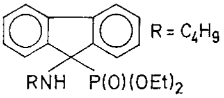

Fig. 1. The aminophosphonic esters used

The aim of this paper is a detailed spectroscopic analysis of dichromate ion in the form of the salts with large organic cations. As cations we choose recently synthetised[10] diethyl esters of *n*- and *sec*-butylamino-fluorenephosphonic acid shown in Fig. 1. The use of this cation provides information on the effect of a large organic molecule on the vibronic states of inorganic anion.

Materials and Methods

The syntheses of $(AH)_2Cr_2O_7$, where $A = 9$-*N*-*n* (*sec*)-butylaminofluorenephosphonic acid diethyl ester $(C_{21}H_{31}O_3NP)_2Cr_2O_7$ was done in the following way: 25 ml of 1:1 (HCl:H_2O) solution of *n*- or *sec*-butyl ester prepared according to the procedure described in ref.[10] have been mixed upon stirring with 25 ml of concentrated 1:1 (acetone:water) solution of chromium compounds (K_2CrO_4, $KCrO_3Cl$, $K_2Cr_2O_7$, CrO_3). The precipitate has been washed several times with water and finally with *n*-hexane and dried in a desiccator over phosphorous pentoxide. Satisfactory elemental analyses were obtained in all cases. Anal: calcd. for $(C_{21}H_{30}O_3NPH)_2Cr_2O_7$, Cr 10.78; C 52.31; H 6.015; P 6.42; N 2.90. Found: Cr 10.28; C 51.87; H 6.26; P 6.38; N 2.72. The deuterated analogs were prepared by stirring the suspension of $(AH)_2Cr_2O_7$ in D_2O for several days and drying over P_2O_5. We were not able to isolate similar compounds with related ligands, i.e. 9-aminofluorenophosphonic acid-9 and 9-*N*-phenylaminofluorenephosphonic acid-9 (see the text).

Dichromates of esters of *N*-*n*- and *N*-*sec*-butylaminofluorenephosphonic acid precipitated in the form of yellow-orange powders soluble in methanol, acetone and *DMSO*, insoluble in water. Concentrated solutions in organic solvents, particulary in alcohols, change the color into brown (chromium reduction). The compounds are also temperature and light sensitive.

Electronic spectra of 5×10^{-3} mol/dm^3 solutions in acetone, *DMSO* and methanol were recorded on a double-beam Hitachi 356 Spectrophotometer in 200-850 nm spectral range. The reflectance spectra were measured in lithium carbonate pellets. Infrared spectra in the range 230-3,500 cm^{-1} were measured on the sample in KBr pellets and in nujol mull using a Perkin-Elmer 621 instrument. Laser *Raman* spectra (blue line 488 nm) were performed on Jeol

RS-S_1 instrument with rotating disc. NMR spectra were measured in deuterated chloroform, acetone and *DMSO* on a Jeol 100 MHz, INM PS-160 as well as Tesla B 487 80 MHz spectrophotometers.

Results

As the spectral results for both compounds i.e. dichromates of *N*-*n*-butyl and *N*-*sec*-butyl derivatives of 9-aminofluorenephosphonic acid diethyl ester are similar we will interpret them together.

Electronic Spectra

Tables 1-3 and Fig. 2 show the data of the electronic spectra of $(AH)_2Cr_2O_7$. The data for acetone solution are limited by very short transmittance of this solvent. It is felicitous to observe that in general the electronic spectrum contains two separate absorption regions: visible and ultraviolet for anion and cation, resp. (we neglect ultraviolet anion absorption at the moment). The optical region is characteristic of two bands at ca. 22,000 and 27,500 cm^{-1}, the latter being well resolved in *DMSO* and acetone (Table 2 and 3). The ultraviolet region exhibits

Table 1. *Electronic spectra of aminophosphonic dichromates*

$(AH)_2Cr_2O_7$	$\bar{V}$ (cm^{-1}); ε
Acetone	21,980 (297); 27,470 (1,832)
DMSO	21,980 (297); 27,470 (1,674); 32,740 (838) 34,000 sh; 35,210 sh; 38,020 sh
Methanol	22,220 sh; 27,600 (487); 32,840 (3,076); 34,245 sh; 35,460 sh; 36,900 (6,250); 43,670 sh; 45,240 sh; 47,900 sh
Reflectance Spectrum	22,500; 27,400; 33,110; 36,360; 44,250
Ligand in Methanol	32,790 (342); 34,130 sh; 35,590 sh; 36,900 sh; 37,700 sh; 43,670 sh; 45,040 sh; 47,390 (33,333)

Table 2. *Spectral characteristics of the* $\bar{V}_2$ *band* ~ *27,000* cm^{-1}

	$\bar{V}_{00}$	ε_{00}	$\bar{V}_{FC}$	ε_{FC}	$\Delta\nu_{1m}$
Acetone	25,249	463	27,634	1,960	785
DMSO	25,276	444	27,540	1,650	759

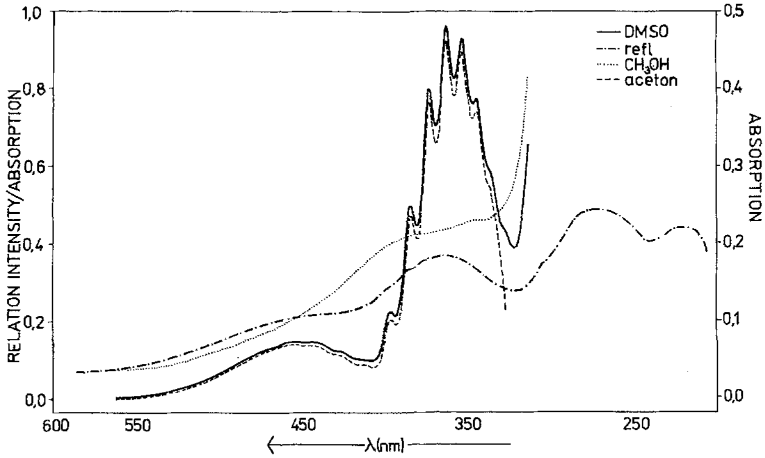

Fig. 2. Electronic spectra of $(AH)_2Cr_2O_7$; A stands for the organic part of the molecule

Table 3. *Vibrational analysis of the* $\overline{V}_2$ *band in DMSO and acetone (for the six most resolved peaks only); m denotes mean*

$A_1^1 \to {}^1A_1$ ($^1A \to {}^1E$)	Acetone $\overline{V}$ (cm^{-1})	Δν	ε	DMSO $\overline{V}$ (cm^{-1})	Δν	ε
ν_{00}	25,260		438	25,276		374
		781			754	
$\nu_{00} + \nu_1$	26,041		1,010	26,030		764
		831			752	
$\nu_{00} + 2\nu_1$	26,872		1,620	26,782		1,370
		762			758	
$\nu_{00} + 3\nu_1$	27,634		1,960	27,540		1,650
		749			760	
$\nu_{00} + 4\nu_1$	28,383		1,735	28,300		1,598
		806			770	
$\nu_{00} + 5\nu_1$	29,189		1,574	29,070		1,329
		ν_{1m} =	785		ν_{1m} =	758

at least two well resolved bands together with six prominent shoulders (Table 1). However, the comparison of ligand spectrum in methanolic solution with that of compound (Table 1) shows quite good similarity between them, indicating small changes of the ligand upon reaction.

Infrared and Raman Spectra

Since the ligand has been prepared for the first time quite recently[10], there are no data available for full vibrational analysis. We may only compare the results provided for other aminophosphonic acids. The cation with three square rings and two functional groups i.e. amino and phosphono sticking out of plane of aromatic fragment exhibits in the infrared and *Raman* spectra a wealth of bands. In aminophosphonic esters studied here the following characteristic absorption regions have been found: 2,500-3,500 cm^{-1} (aromatic and aliphatic C—H vibrations), 3,280 cm^{-1} (strong N—H stretching vibrations) and at 1,240 cm^{-1} (P—O stretching vibrations). In $(A\mathrm{H})_2\mathrm{Cr}_2\mathrm{O}_7$, whose spectra are much less resolved in comparison to that of pure ligand (Fig. 3), the following absorption regions may be distinguished: 2,300-3,500 cm^{-1} (C—H aromatic and NH_2^+), new bands at 1,600 cm^{-1} and the bands characteristic of anion ($\mathrm{O_3Cr—O—CrO_3}$). The deuteration of the compounds shows characteristic 1,600 cm^{-1} band shift indicating NH_2^+ presence in the compounds and confirming the formulae proposed. The additional support comes from analysis of hydrochlorides ($A \cdot \mathrm{HCl}$) spectra which exhibit 1,600 cm^{-1} band assigned to NH_2^+ grouping.

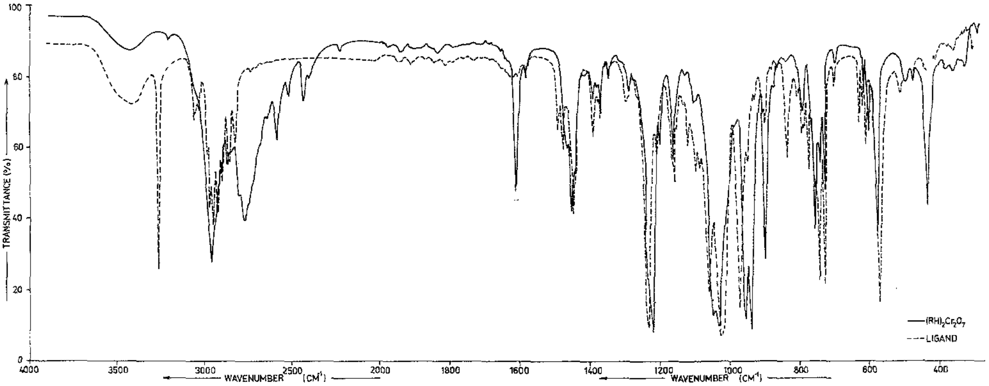

Fig. 3. Infrared Spectra of $(A\mathrm{H})_2\mathrm{Cr}_2\mathrm{O}_7$

Among chromium-oxygen vibrations the most prominent are those typical of ν_{sym} (900 cm^{-1}) and ν_{asym} (doublet at 940 cm^{-1}) Cr—O vibrations. These modes are also *Raman* active (904 and 946 cm^{-1}). Except for weaker resolution, characteristic of a salt in general, we could not observe any other changes of the band position and intensity upon reaction.

NMR Spectra

^{1}H-NMR chemical shift data taken for acetone-d_6, chloroform-d_1 and *DMSO*-d_6 solutions are as follows: Ligand [in $(CD_3)_2C=O$]: 7.8-7.0 (8 H, m, aromatic proton): 3.9-3.4 (4 H, quintet), $J_{CH-CH} = 7$ Hz; $J_{CH-O-P} = 7$ Hz; 2.9 (1 H, s, NH); 2.0-1.6 (2 H, m, —CH_2N); 1.2-0.4 (13 H, m, $CH_3CH_2CH_2$—, CH_3CH_2—O), in which may be seen 0.75, t, CH_3—CH_2—O, $J_{CH-CH} = 7$ Hz.

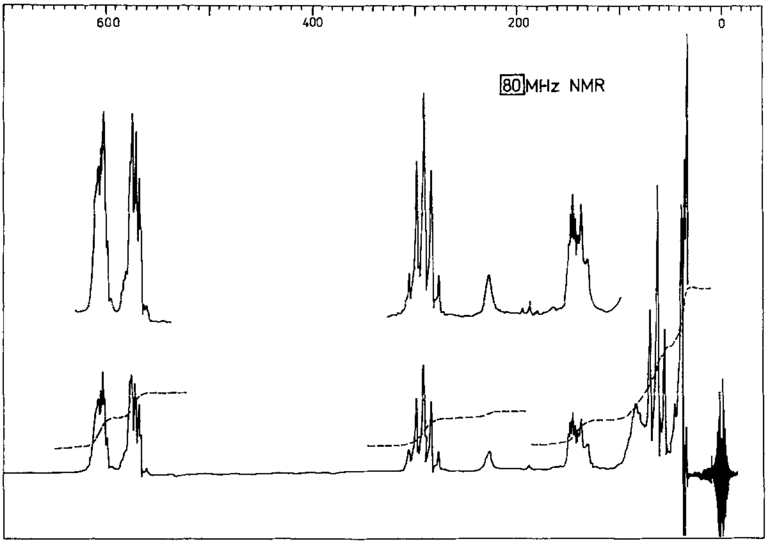

Fig. 4. Spectrum of the ligand 9-*N*-*n*-butylaminofluorenephosphonic acid diethyl ester in acetone-d_6

$(AH)_2Cr_2O_7$ in *DMSO*-d_6: 8.5-7.5 (8 H, m, aromatic proton); 4.4-3.5 (4 H, m, CH_2—O); 2.5-2.1 (2 H, m, NH—CH_2); 1.8-0.6 (13 H, m, $CH_3CH_2CH_2$—, CH_3—CH_2O, in which may be seen 1.1, t, CH_3CH_2O, $J_{CH-CH} = 7$ Hz.

Unfortunately, we could not find a suitable solvent for both the ligand and the compound, which greatly diminished the information content taken from NMR spectra.

Discussion

Spectral Characteristics of the Compounds

The theoretical calculations and experimental results show a similarity of dichromate ion to the tetrahedral chromate ion[9,12]. The two main electronic bands at ca. 22,000 cm^{-1} and 27,000 cm^{-1} correspond to the $^1A_1\,(t_1^6) \rightarrow {}^1T_1\,(t_1^5e^1)$ and $^1A_1\,(t_1^6) \rightarrow {}^1T_2\,(t_1^5e^1)$ charge transfer transitions split under $T_d \rightarrow C_{2v}$ symmetry lowering.

However, by contrast to the solid state, the spectra of dichromate ion in organic solvents show the overall similarity with those of monosubstituted chromates, CrO_3X^- [7,9]. For example, the well resolved "line" spectrum at 18,500 cm^{-1} in $Cr_2O_7^{2-}$ observed by *Teltow*[13] is not seen in organic solution spectra of $Cr_2O_7^{2-}$ and the first longwave band is observed at 22,000 cm^{-1}, exactly as in CrO_3X^- ion. We may consider thus dichromate ion in organic solvents as two CrO_3O chromophores of C_{3v} symmetry, each of them absorbing independently. Comparing ε values for $Cr_2O_7^{2-}$ and CrO_3X^- compounds[7,9] and including cation as well as ligand X effects we may state that this rough picture agrees quite well with the experiment.

The spectral correlation between dichromate and chromate is also good. The low $^1T_1$ state splits into ^1E state and $^1A_2$ state and as $^1A_1 \rightarrow {}^1A_2$ is forbidden in C_{3v} symmetry we observe only $^1A_1 \rightarrow {}^1E$ transition.

The second band system $\bar{\nu}_2$ at about 27,000 cm^{-1} appears to have prominently resolved vibrational fine structure in totally symmetric $\nu_1\,(A_1)$ quanta of 760 cm^{-1} and 780 cm^{-1} in *DMSO* and acetone solutions, resp. (Table 3, Fig. 2).

The diminishing of the ground state ν_1 quantum (A_1) value by $\sim 16\%$ is in line with the value of other oxo- and mono-substituted chromium(VI) compounds in solution as well as in the crystalline state. In general, the best information on vibronic states is usually obtained from diluted crystal oriented in one of the cristallographic directions in polarized line and at cryogenic temperature. However, the results of this paper and other recent papers[7,9] show that organic aprotic solvents which are known to coordinate mainly cation are also good "matrices" for studying electronic-vibrational features. Methanol, similarly to formamide and water, disturbs the structure by hydrogen bonding $CrO_3 \ldots HOCH_3$. This may change the full C_{3v} symmetry around the chromium ion and thus seriously affects the structure. The remainding Cr ← O CT bands have been overlapped by strong intra ligand transitions.

Considering the results of the electronic spectra we must state, that different species i.e. (CrO_3A) [I], $(CrO_3OH)^-$ [II] and $(Cr_2O_7^{2-})$ [III], could be undistinguishable, and even elemental analysis can not yield a unique results. All these compounds could be isolated in experimental conditions provided in this paper. As the variation of L in the CrO_3L^{n-} group is known to cause only a small shift on CT band position and intensity of the spectra[6] we may expect to deal with similar spectra for all three compounds, just as it has been observed. The choosing of the proper formula is of importance, since CrO_3L^{n-} type of compounds are known to be the first step of oxidation of organic compounds by chromate ion[6], where L denotes organic or inorganic *Lewis* base.

A detailed analysis of the infrared spectra shows one prominent band at ~ 1,600 cm^{-1} absent in the spectra of the ligand. This band is characteristic of NH_2^+ groups, shifting upon deuteration, as expected and thus eliminating formula [I]. Similarly, the absence of strong and broad OH stretching vibration in the region of ~ 3,200 cm^{-1} eliminates the presence of hydrochromate ion, formally written as CrO_3OH^- [II].

Formula [III] provides the presence of the bands characteristic of the $Cr_2O_7^{2-}$ ion and we were able to observe them in the spectra. The original assignment of *Stammreich*[11] has been done by dividing the IR dichromate bands into those arising from modes of the CrO_3 group and those of the Cr—O—Cr bridge. The bands at 770 (as), 560 (sym) and 220 cm^{-1} (bending) were assigned to the bridge. In our spectrum we have been able to see the band at 770 cm^{-1} only. All left bands are overlapped by strong ligand transition. The stretching bands at 965 and 902 cm^{-1} (the position of the bands depends slightly upon the cation) and rocking and bending at 365 cm^{-1} all typical of a CrO_3 group can be easily seen in the spectra. The *Raman* spectra, although also very complicated by the ligand transition, show 904 and 946 cm^{-1} bands very prominently.

The NMR data demonstrates that the main fragments of ligand did not change upon reaction i.e. the aromatic ring, *n*-butyl group situated by nitrogen atom, as well as ester groups by phosphorus atom are present in salt. The chemical shift changes are caused only by solvent changing. Thus we may state that although under the conditions of the experiment [acidic (HCl-water) solution] we may have dealt with various equilibria between $Cr_2O_7^{2-}$, CrO_3Cl^-, CrO_3OH^- and CrO_4^{2-} ions, with the less probable chromate ion, the IR and *Raman* spectra show the isolation of $Cr_2O_7^{2-}$ organic salts. The experiment favoured also the protonation of ligand—*conditio sine qua non*—to obtain $(AH)_2Cr_2O_7$. Thus, the formula shown in Fig. 5 fully satisfies the results.

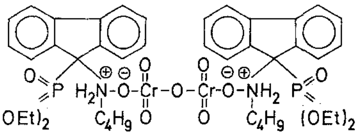

Fig. 5. The general formula of the compounds obtained

Vibrational Analysis of the $Cr_2O_7^{2-}$*-Ion*

To analyse quantitatively the vibrational structure which sometimes appears in the electronic spectra one must determine the overlap integral between the ground and excited vibrational states. In the *Franck-Condon* (*FC*) approximation the square of the transition dipole moment for a single vibronic allowed transition *Gg-Ee* (the transition probability) can be expressed as follows

$$|<Gg|\vec{\mu}|Ee>|^2 = |<G|\vec{\mu}|E>|^{\circ} <g|e>^{\circ} \tag{1}$$

It depends only upon the pure electronic transition $<G|\vec{\mu}|E>^{\circ}$ and the overlap integral $<g|e>^2$ called the *Franck-Condon* factor. $\vec{\mu}$ is here the electronic moment operator, *Gg* and *Ee*—the wavefunction of the ground and excited vibronic state, resp. In the absorption of dichromate ion $Cr_2O_7^{-2}$ single quantum progression in 770 cm^{-1} (a_1) mode—the symmetric stretching mode of Cr—O in CrO_3 chromophore, has been observed. If only this coordinate is considered and it is assumed that its force constant $k_{Cr—O}$ is the same for both states, the relative displacement ($\xi'—\xi''$) of the potential surfaces may be calculated[14]. As evident from the energy distribution (Fig. 2) for $Cr_2O_7^{-2}$ ion, this displacement is not expected to be large, and appears to be similar for all Cr(VI) compounds containing CrO_3 grouping[5–9]. The intensity I_n of each vibrational progression quantum n is given by a *Poisson* distribution:

$$I_n / I_0 = S^n / n! \tag{2}$$

where I_0 and I_n are intensities of the origin and n band, resp., S is FC factor, which may be obtained from the ratio I_1/I_n, since n is equal to zero. Under the assumption, that the upper potential surface is harmonic, S may be defined as follows[15]:

$$S = \frac{E_\alpha}{\hbar \omega_\alpha} = \frac{1/2\, k_\alpha}{\hbar \omega_\alpha} (Q_o^{\alpha})^2 \tag{3}$$

where E_α is the wave-number associated with (Q_o^{α}) distortion along a_{1g} having ω_α as its frequency (cm^{-1}). The force constant calculation for $Cr_2O_7^{-2}$ ion has given k_α(Cr—O) = 6.33 mdyn/Å (0.633 kN/m). Using the experimental $S = 2.2$ we can calculate (Q_o^{α}) to be 0.102 Å (10.2 pm). Under the above assumption the FC factor is related simply to the change of Cr—O bond length upon excitation.

Regarding the isolated compounds it is worth mentioning, that among four related ligands studied in this paper [i.e. diethyl esters of (a) 9-aminofluorenephosphonic acid-9; (b) and (c) 9-*N*-*n*(*sec*)-butylaminofluorenephosphonic acid-9 and (d) 9-*N*-phenylaminofluorenephosphonic acid-9] only (b) and (c) yielded precipitates with chromium(VI) compounds. At least two facts may contribute to the explanation of this observation: (i) during the preparation of (a), (b), (c), and (d) the crystallization processes are easiest for (b) and (c); (ii) the strong interaction of the electron pair at the nitrogen atom with the electrons of aromatic ring connected with nitrogen drastically decreases the basicity of (d) and this diminishes cation—anion electrostatic interaction. On the other hand, at almost equal basicity of (a), (b), and (c), a more favourable steric factor in (a) should facilitate the $(AH)_2Cr_2O_7$ isolation, in disagreement with the results of this paper. Perhaps factor (i) dominates, and we observe precipitation of *N*-*n*- and *N*-*sec*-butyl derivatives.

The information on large organic cation—inorganic anion interaction from solid state electronic and infrared spectra demonstrate that this effect is rather weak and, with good approximation, we are dealing with two independent electronic arrangements. However, to study this problem in detail an analysis of bands as well as variety of instrumental methods are necessary.

Conclusion

1. The reactions of organic molecules: 9-*N*-*n*(*sec*)-butylaminofluorenephosphonic acid diethyl ester (denoted by *A*) with chromium compounds: CrO_3, CrO_4^{-2}, CrO_3Cl^{-1} and $Cr_2O_7^{-2}$ lead to $(AH)_2Cr_2O_7$.
2. The spectral studies in a wide energy range show relative independence of electronic-vibrational levels of cation and anion.
3. A solvent effect on the vibrational fine structure has been observed. Similary to other hydrogen bond forming solvents methanol disturbs the vibronic states of the dichromate ion.
4. The vibrational analysis of $Cr_2O_7^{-2}$ in organic aprotic solvents shows lengthening of the chromium—oxygen bond upon excitation. The value of 10.2 pm (0.102 Å) is in agreement with results of other cases known from literature.

Acknowledgments

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References

[1] *C. D. Flint*, Coord. Chem. Rev. **14**, 47 (1974).

[2] *P. J. Stephens*, in: Electronic States of Inorganic Compounds (*P. Day*, ed.), Vol. **20**. Dordrecht (Neth.): Reidel. 1975.

[3] *C. D. Flint*, in: Adv. Infrared and Raman Spectroscopy (*R. J. H. Clark* and *R. E. Herter*, eds.), Vol. **2**, p. 53. Leyden. 1976.

[4] *E. Diemann*, *E. Ahlborn* and *A. Müller*, Z. Anorg. Allgem. Chem. **390**, 217 (1972).

[5] *P. J. Aymonino*, *H. Schultze*, and *A. Müller*, Z. Naturforsch. **24 b**, 1508 (1969).

[6] *D. C. McCain*, J. Phys. Chem. **79**, 1102 (1975).

[7] *A. Bartecki* and *M. Cieślak-Golonka*, Rocz. Chem. **51**, 1325 (1977).

[8] *M. Cieślak-Golonka* and *A. Bartecki*, Bull. Pol. Acad. Sci. **26**, 53 (1978).

[9] *A. Bartecki*, *L. Liberacka*, and *M. Cieślak-Golonka*, Pol. J. Chem. **52**, 247 (1978).

[10] *J. S. Wieczorek* and *R. Gancarz*, Rocz. Chem. **50**, 2171 (1976).

[11] *H. Stammreich*, *D. Bassi*, *O. Sala*, and *H. C. Siebert*, Spectrochim. Acta **13**, 1972 (1958).

[12] *B. Nissen*, *L. Natkaniec*, and *B. Jezowska-Trzebiatowska*, Bull. Pol. Acad. Sci. **25**, 203 (1977).

[13] *J. Teltow*, Z. Phys. Chem. **B 43**, 198 (1939).

[14] *C. J. Ballhausen*, Theoret. Chim. Acta **1**, 285 (1963).

[15] *E. I. Solomon* and *C. J. Ballhausen*, Mol. Phys. **29**, 279 (1975).

[16] *R. Mattes*, Z. Anorg. Allgem. Chem. **382**, 163 (1971).