

INTERACTION OF TRIALKYL PHOSPHITES WITH MONTMORILLONITES

G. DIOS CANCELA, E. ROMERO TABOADA, F. J. HUERTAS,
A. HERNÁNDEZ LAGUNA, AND F. SÁNCHEZ RASERO

Estación Experimental del Zaidín, Consejo Superior de Investigaciones Científicas
Profesor Albareda, 1, 18008 Granada, Spain

Abstract—Complexes formed between montmorillonite, saturated in Li^+ , Na^+ , Mg^{2+} , Ca^{2+} , Co^{2+} , Fe^{3+} , Cu^{2+} and Zn^{2+} , and trimethyl phosphites (TMP) and triethyl phosphites (TEP) were studied. In all of the cases, phosphites penetrate into the interlayer space of the montmorillonite and produce solvates whose basal spacing varies depending on the characteristics of the exchangeable cation. All the complexes with low basal spacing (Li^+ , Na^+ , Mg^{2+} , Co^{2+} and Zn^{2+}) are stable in vacuum, whereas those with high basal spacing, formed by the Ca^{2+} sample with TMP, and Ca^{2+} and Fe^{3+} samples with TEP are transformed into low basal spacing complexes in vacuum. The complexes with high basal spacing (Cu^{2+} sample with TMP and TEP) are stable in vacuum.

The TMP and TEP complexes stable in vacuum with low spacing are thermally destroyed in one or two stages with two loss maxima, as a result of partial burning of phosphite molecules. Those with high spacing (Cu^{2+}) are destroyed in two stages; the first is probably the result of the transformation process from high to low spacing, as a consequence of the structural reorganization of the molecules which remain in the interlayer space, and the second, could be associated with the destruction of low spacing complexes.

The IR spectra show that the molecule and the cation are linked by the P of the phosphite, which produces a reinforcement of the other bonds in the molecule, caused by an inductive effect. The phosphite intercalation is accompanied by a partial isomerization of phosphite to phosphonate.

The heat of adsorption of phosphites shows that the molecule-cation bond is ion-dipole. In the Cu sample with trimethyl phosphite, this bond seems to be reinforced by retrodonation of electrons from copper to ligand. Finally, the possible disposition of phosphite molecules in the interlayer space is considered. For this purpose, ab initio calculations have been performed on the different conformers of the TMP molecule at 6-31G* and 6-31+G* basis sets.

Key Words—Ab initio Calculations, Complexes, Formation Mechanism, Montmorillonite, Stability, Trialkyl Phosphites.

INTRODUCTION

One characteristic of the clay minerals is their capacity to form interlayered complexes with organic compounds, which have distinctive basal spacings. The preparation and study of such complexes is of interest, not only for their applications in distinguishing and diagnosing minerals in mixtures, but also for their practical applications for industry and agriculture.

The study of interlayer complexes of saturated smectites with cations with semifilled d orbitals and polar molecules, such as phosphines and phosphites, has become very important. These solvates have great relevance to the hydrogenation and isomerization processes, because they minimize many of the technical and economic barriers which are associated with the use of such catalyzers in homogeneous dissolution (Farzaneh and Pinnavaia 1983; Pinnavaia and Welty 1975; Pinnavaia et al. 1976, 1979; Quayle and Pinnavaia 1979; Raythatha and Pinnavaia 1981, 1983).

The aim of this present work is to investigate the complexes formed between trialkyl phosphites (Trimethyl, TMP, and Triethyl, TEP) and montmorillonite saturated with cations with noble gas structures (al-

kalines and alkaline earths) and transition element cations, in order to discover their capacity for retention of organic liquids, their thermal stability and their stability under vacuum conditions, as well as the mechanism for the formation of the complexes as revealed by infrared spectrometry and calorimetry. This research can provide data of interest on: the influence of the exchangeable cation and the molecular dimension and basicity of the ligand with respect to the stability and the stoichiometry of the complexes, the magnitude of the swelling, the disposition of the ligand molecules, the type of cation coordination involved, and the determination of the group or groups which participate in the metal-ligand bonding. All of these questions are of great interest because they can be applied in catalytical processes.

MATERIALS AND METHODS

Samples

Wyoming montmorillonite with the following characteristics, SWy-1, <2 μm fraction, 752 m^2/g of surface area, 112 meq/100 g of cation exchange capacity, when dried at 120°C, and 4.07 esu/ cm^2 of charge density, was used in this study.

Organic Compounds

Trimethyl and triethyl phosphite were used to form the complexes. The TMP (analytical grade) was supplied by Sigma and the TEP was supplied by Fluka with a purity of 99%. The TMP dipolar moment was 1.82 D and the TEP dipolar moment was 1.81 D.

Homoionic Sample Preparation

The Li^+ , Na^+ , Mg^{2+} , Ca^{2+} , Co^{2+} , Fe^{3+} , Cu^{2+} and Zn^{2+} homoionic samples were prepared by treating 10 g of montmorillonite with 50 ml of 1 N solutions of chloride of the corresponding cation. The treatment was repeated five times and afterward, the samples were washed each time with a water:methanol (60:40) mixture, until the washing solution gave a negative Cl^- result using an AgNO_3 solution. Then, samples were oven-dried at 60°C and ground until the powder could be passed through a 0.030 mm sieve.

Preparation of the Complexes

The samples, previously treated at 120°C for 24 h, were put into capillary tubes of Lindeman glass and phosphites were allowed to wet the samples by imbibition, at room temperature for 48 h. Then the capillary tubes were closed by flames and were analyzed by X-ray diffraction (XRD).

Additionally, approximately 0.5 g of every sample was dried at 120°C for 24 h and was later wetted with an excess of phosphite. The crucibles containing the samples were placed in a desiccator of high vacuum (10^{-4} mm Hg) with CaCl_2 , during the 48 h. Afterwards, the complexes were desorbed in a vacuum of 10^{-2} mm Hg until constant weight was achieved. In each case, the quantity of retained phosphite was determined.

Techniques Used to Study the Complexes

X-RAY DIFFRACTION. Complexes formed in Lindeman glass were analyzed by XRD with a Philips PW-1750 diffractometer, using a Deby-Scherrer camera of 114.7 mm with a graphic register, Ni filtered and $\text{K}\alpha$ Cu radiation. The diffractograms of the stable complexes in vacuum were analyzed with the same diffractometer by means of the powder method.

THERMOGRAVIMETRIC AND DIFFERENTIAL THERMAL ANALYSIS. The TG, DTG and DTA analyses of the stable complexes in vacuum were performed in a Netsch STA-409EP, using Al_2O_3 as reference, with a heating rate of $10^\circ\text{C}/\text{minute}$ in an air atmosphere.

INFRARED SPECTRA. Infrared spectra of the stable complexes in vacuum conditions were obtained using a Zeiss IR spectrometer, from 4000 to 625 cm^{-1} . 10% of the samples were diluted in KBr disks and also a KBr disk was used as reference.

CALORIMETRY. The heat of immersion of the dried sam-

ple at 120°C under 10^{-2} mm Hg vacuum and the stable complexes in vacuum, were determined in an adsorption calorimeter LKB 2101-1221, previously calibrated by the Joule effect. All the determinations were repeated three times.

DETERMINATION OF THE PHOSPHITE STRUCTURES. The most stable structure of the phosphites was determined by means of the RHF ab initio calculations. These were performed with the Monstergauss program at 6-31G* and 6-31+G* levels (Peterson and Poirier 1978). The minima of the potential energy surface (PES) were located using the analytical gradient of the RHF wave functions. The minimal structures of the conformers and isomers of phosphites were obtained by means of Davidon's optimally conditioned methods (Davidon and Nazareth 1975). The calculations were carried out up to average gradients less than or equal to 5×10^{-4} mdyne or mdyne $\text{\AA}/\text{radian}$. No geometrical restrictions whatsoever were imposed in the optimization procedure. All conformers were calculated in vacuum.

RESULTS AND DISCUSSION

The results of the diffraction study of the complexes are shown in Table 1. Complexes of the Li^+ , Na^+ , Mg^{2+} , Co^{2+} , Fe^{3+} and Zn^{2+} samples become stable after being treated with excess of TMP in a Lindeman glass capillary tube. The basal spacings ranged from 1.58 to 1.60 nm. However, Ca^{2+} and Cu^{2+} samples produced complexes with a basal spacing of 1.96 nm. If the complexes are desorbed in vacuum until constant weight, the solvates stabilize with a basal spacing of 1.58 nm, with the exception of the Cu^{2+} sample, which shows a basal spacing of 1.84 nm.

When TEP is used, the complexes, formed in an excess of the polar liquid, exhibit basal spacings of 1.68 nm, except for Ca^{2+} , Fe^{3+} and Cu^{2+} , which gave basal spacing values of 2.00 nm. Desorption in a vacuum does not essentially modify the low basal spacing complexes. However, it decomposes the 2.00 nm complex of the Ca^{2+} sample, which changes to 1.68 nm and it partially decomposes the Fe^{3+} complex, whereas the Cu^{2+} complex remains unalterable at 2.00 nm.

Consequently, it may be concluded that the trimethyl and triethyl phosphites can penetrate into the interlayer space of the montmorillonite at room temperature, to produce stable complexes in vacuum with a ligand/cation ratio, dependent on the cation valence. Such a ratio varies between 1 to 1.5 molecules/cation for samples saturated with monovalent cations, is 3 for divalent cations and ranges from 4 to 4.5 for Fe^{3+} and Cu^{2+} .

Mg^{2+} and Cu^{2+} samples, taken as representative of the stable complex in vacuum of low and high spacing respectively, were thermally analyzed in order to test

Table 1. $d(001)$ spacing in nm of the montmorillonite complexes with excess of TMP and TEP, of the desorbed complexes in vacuum until constant weight, and retained quantity of phosphite in g of phosphite/g of sample of the stable complexes in vacuum and number of phosphite molecules per exchangeable cation.

Cation	TMP				TEP			
	$d(001)$ spacing in nm (a)	$d(001)$ spacing in nm (b)	g phosphite/g sample	moles/cation	$d(001)$ spacing in nm (a)	$d(001)$ spacing in nm (b)	g phosphite/g sample	moles/cation
Li ⁺	1.58	1.58	0.2436	1.75	1.68	1.67	0.2893	1.55
Na ⁺	1.60	1.58	0.1830	1.30	1.68	1.67	0.2160	1.16
Mg ²⁺	1.60	1.58	0.1821	2.60	1.68	1.68	0.2068	2.20
Ca ²⁺	1.96	1.58	0.2398	3.45	2.00	1.68	0.2500	2.07
Fe ³⁺	1.58	1.58	0.2134	4.60	2.00	(1.67–1.93)	0.2660	4.30
Co ²⁺	1.58	1.58	0.1990	2.86	1.68	1.68	0.2246	2.40
Cu ²⁺	1.96	1.84	0.2962	4.26	2.00	2.00	0.2988	3.20
Zn ²⁺	1.60	1.58	0.2300	3.31	1.68	1.68	0.2300	2.50

(a) Spacing of the complexes with excess of TMP and TEP.

(b) Spacing of the stable complexes in vacuum.

thermal stability. The TG, DTG and DTA curves of both complexes are shown in Figure 1.

The DTG of the Mg²⁺ complex with TMP displays two weight loss maxima, at 203 and 275°C, which are accompanied by two weak endothermic effects in the DTA curve. These effects could be due to the destruction of the 1.58 nm complex, as a consequence of the

loss of the methyl groups of the TMP, while part of the interlayered phosphite remains as Mg phosphite. This is demonstrated by the presence of phosphorus in the samples after finishing the mentioned effects at 275°C. The exothermic effect at 572°C can be associated with either the burning of the remaining carbon in the sample after the destruction of the complex or

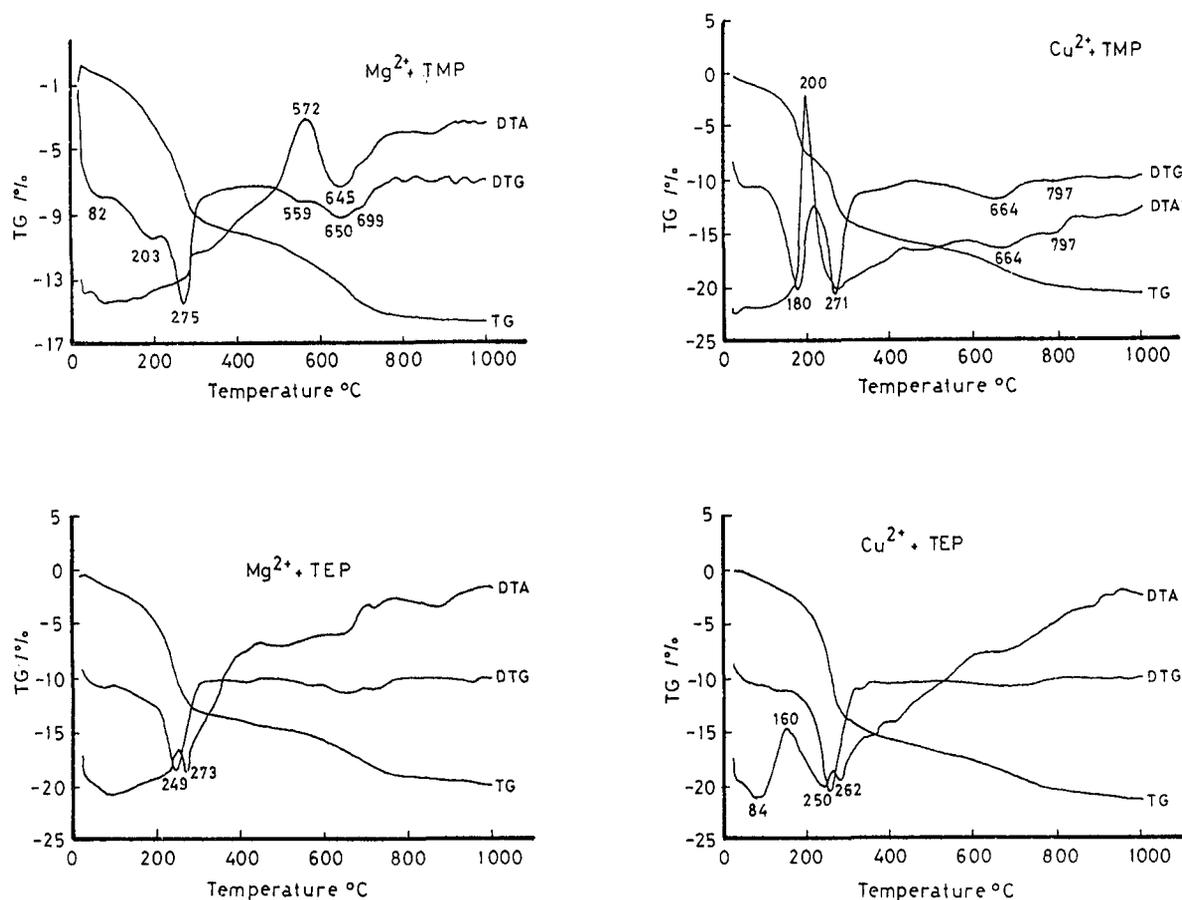


Figure 1. DTA, TG and DTG curves of the Mg²⁺ and Cu²⁺-montmorillonite complexes with TMP and TEP.

the oxidation of phosphite to phosphate. The endothermic effect at 645°C can be attributed to a loss of water corresponding to the structural hydroxyls. The solvate of the Cu²⁺ sample with TMP also exhibits two maxima of weight loss rate, at 180 and 271°C, the first accompanied by a strong exothermic effect and the second by an endothermic effect. After being treated at 180°C, the diffractogram shows a basal spacing of 1.58 nm, which is similar to the one displayed by the other complexes. It appears that the 1.84 nm complex of the Cu²⁺ sample is destroyed in two stages. The first relates to the loss of TMP molecules, which are responsible for the 1.84 nm spacing, and the remaining molecules acquire a similar disposition as the TMP molecules in low spacing complexes. The second exothermic effect could be the result of a reorganization of the remaining interlayered TMP molecules giving rise to a more stable disposition. The second endothermic effect may be the result of the destruction of the 1.58 nm complex.

The DTG pattern of the Mg²⁺ complex sample with TEP shows a maximum of weight loss at 249°C, accompanied by a small exothermic effect at 225°C and another endothermic effect at 273°C. The first effect may be due to a partial oxidation of phosphite molecules and the second to the total destruction of the 1.68 nm complex. The DTG curve of the Cu²⁺ complex sample with TEP displays a slight weight loss at low temperatures, with an associated exothermic effect at 160°C in the DTA curve. As with the TMP complex, this could be attributed to the loss of the molecules responsible for the 2.00 nm complex. This would give rise to a 1.68 nm and a reorganization of the remaining TEP molecules in a more stable disposition. The endothermic effects at 250 and 262°C could be associated with the destruction of 1.68 nm complex.

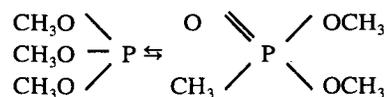
In order to understand how the phosphite molecules and the interlayered exchangeable cations are linked, infrared spectra of the stable complexes under high vacuum were performed. As in previous cases, Mg²⁺ was chosen as representative of the low-spacing solvates and Cu²⁺ was chosen as representative of high-spacing solvates. The spectra of both complexes and TMP and TEP liquids are shown in Figures 2 and 3.

The IR spectrum of TMP displays a series of bands that according to Thomas (1974), can be assigned to stretching vibration of the following groups: the bands at 2990, 2950, 2910 and 2840 cm⁻¹ to the C-H stretching in CH₃ groups; the bands at 1178 and 1010 cm⁻¹ can be assigned to stretching vibration of the P-(O-C) and C-(P-O) bonds, respectively.

In the samples of Mg²⁺ and Cu²⁺ complexes with TMP, the C-H vibration bands appear to shift to high wave numbers (2910, 2960, 2930 and 2850 cm⁻¹ for Mg²⁺ complex and 3018, 2962, 2932 and 2858 cm⁻¹ for Cu²⁺). Furthermore, the vibration band of the P-(O-C) bond of TMP shifts to 1180 for the Mg²⁺ and

1185 cm⁻¹ for the Cu²⁺ complexes. It appears that the P-Me bond reinforces the rest of the bonds in the molecule. There is no clear explanation for this, although in the case of the Cu²⁺ complex there could be a retrodonation of electrons from the cation (d⁸) to the ligand and a reinforcement of the covalent character of the bonds. However, this retrodonation would not be possible in the case of the Mg²⁺ complex, because this cation has noble gas structure lacking electrons to be retrodonated. The reinforcement of C-H and P-(O-C) bonds can only be due to an inductive effect on account of the shift of p electrons to the metal, thus increasing the polar character of such bonds. An intermediate situation between both effects could cause such shifts.

Another remarkable finding, occurring with the Mg²⁺ and Cu²⁺ complexes with TMP, is the appearance of two bands at 1312 and 1230 cm⁻¹ for Mg²⁺ and two weak shoulders at these wave numbers for Cu²⁺. According to Thomas (1974), such vibrations can be assigned to P-CH₃ and P=O, respectively. Consequently, the intercalation of TMP in the interlayer space partially produces an isomerization of phosphite to phosphonate.



Such an isomerization seems to be higher in the Mg²⁺ sample than in the Cu²⁺ sample, in inverse ratio to the strength of the P-M bond.

The IR spectrum of TEP liquid also shows the bands which could be assigned to C-H vibration of the groups, CH₃ and CH₂, at 2988, 2970, 2900 and 2880 cm⁻¹. Also a band at 1160 cm⁻¹ may be assigned to C-O(P) vibration (Thomas 1974) and another band at 1025 cm⁻¹ to P-O(C) vibration. In the complexes, these bands shift to higher wave numbers, although to a lesser extent than in the case of the TMP complexes. The reason should be attributed to the same effects which were observed for the TMP case. As well as these bands, other bands appear at 1248 cm⁻¹ in Mg²⁺ and at 1222 cm⁻¹ in Cu²⁺, which could be assigned to a stretching vibration of the P=O. Also in the case of complexes with TEP the intercalation produces a partial isomerization of phosphite to phosphonate.

The adsorption heats of the different samples in TMP and TEP were determined in order to find out the strength of the molecule-cation bond, using the following expression:

$$q_a = \frac{Q_{i0} - Q_i}{x} \quad [1]$$

where Q_{i0} is the heat of immersion (cal/g) of the sample dried at 120°C under a 10⁻² mm Hg vacuum, Q_i is the heat of immersion (cal/g) of the stable complexes in vacuum, and x is the quantity of retained phos-

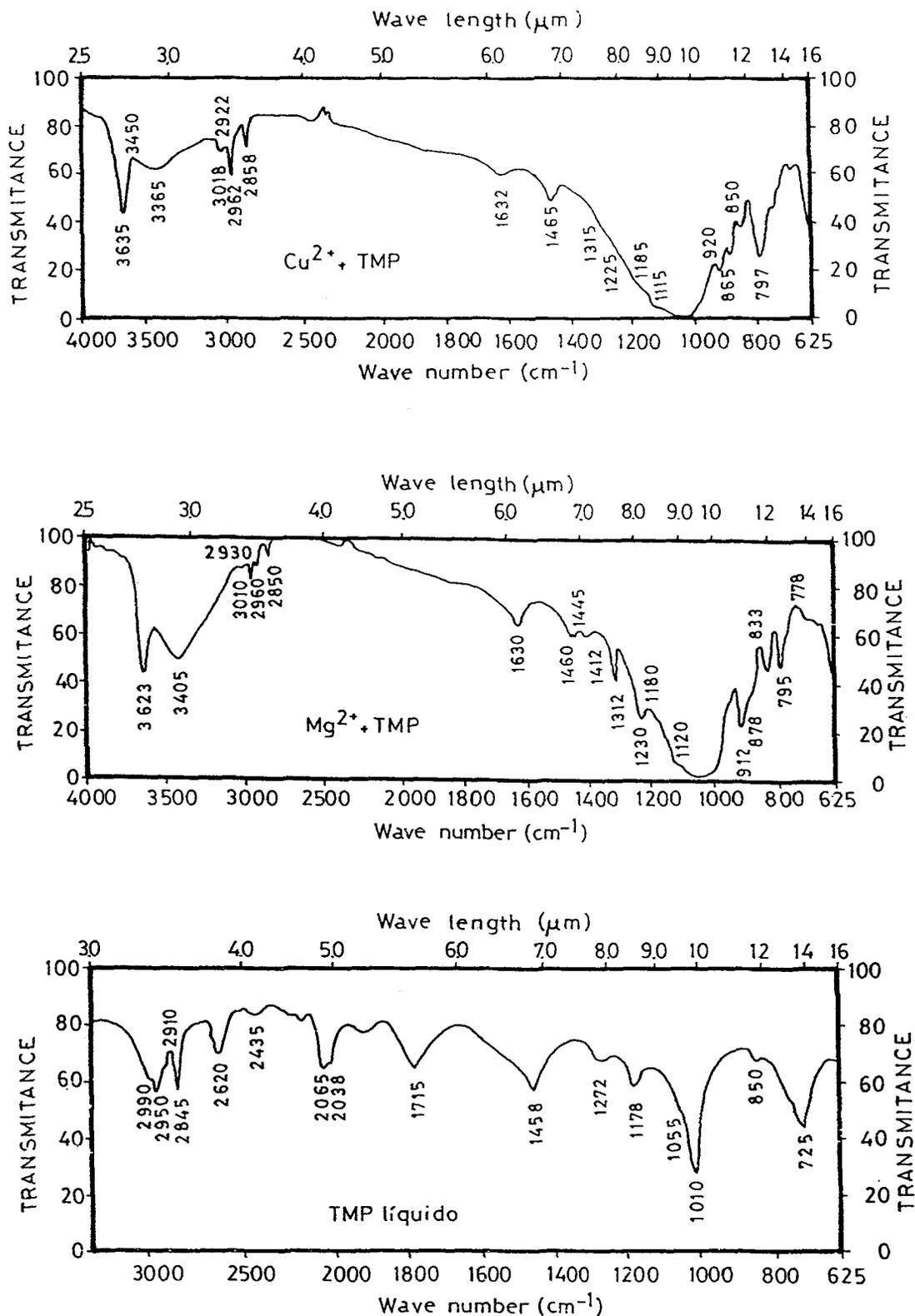


Figure 2. Infrared spectra of liquid TMP and complexes of Mg^{2+} and Cu^{2+} -montmorillonite with TMP.

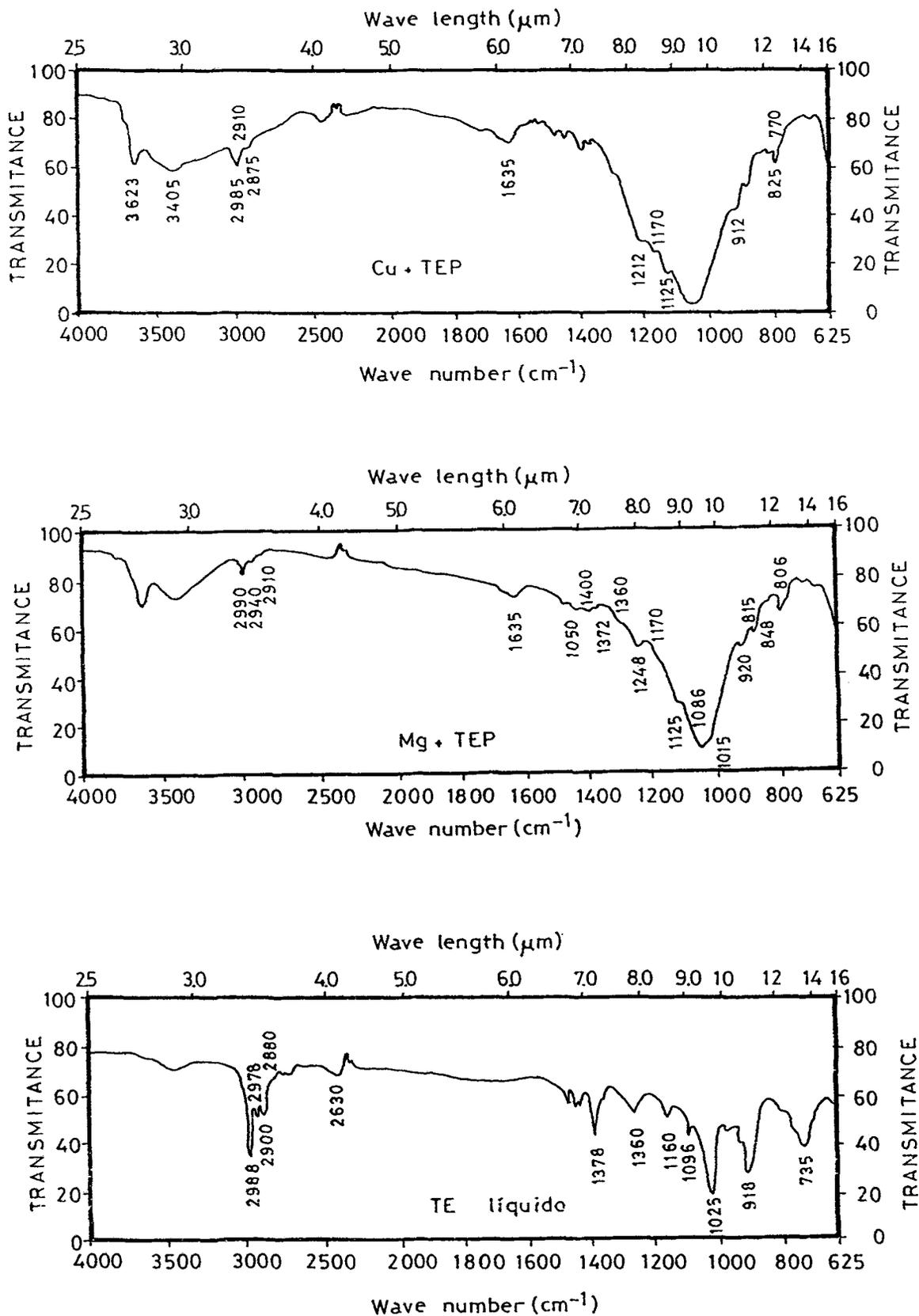


Figure 3. Infrared spectra of liquid TEP and complexes of Mg²⁺ and Cu²⁺-montmorillonite with TMP.

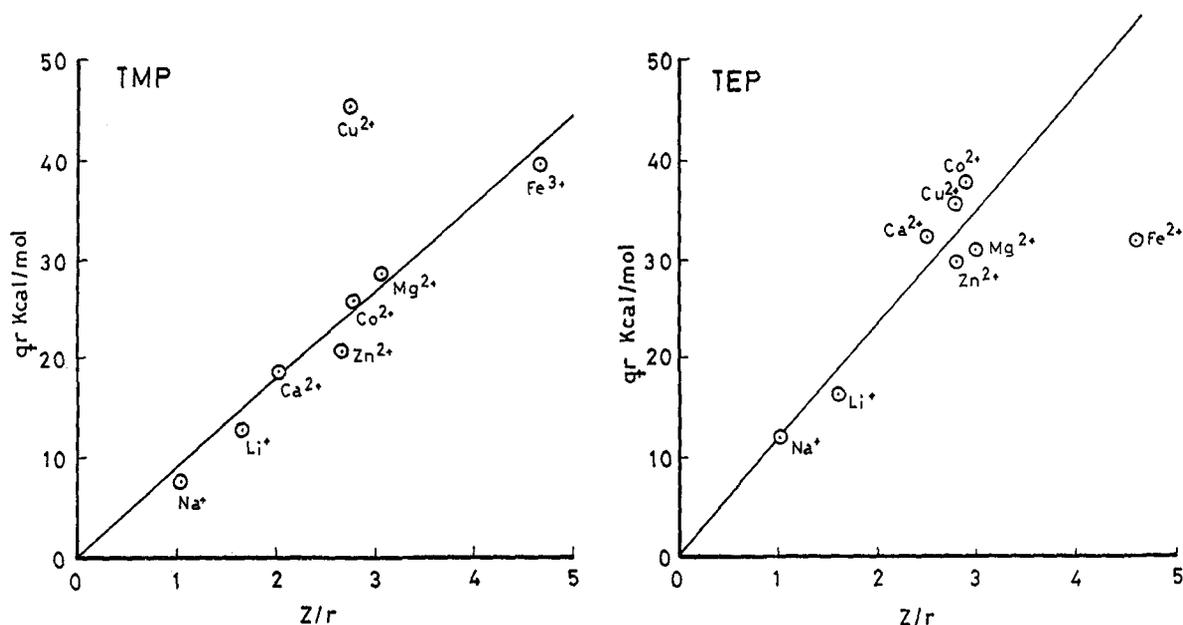


Figure 4. Total heat of adsorption (in kcal/mol) versus ionic potential (Z/r) of the exchangeable cations in the montmorillonite complexes with TMP and TEP.

phite (g of phosphite/g of sample). These heats of adsorption were corrected with the heat of interlayer swelling, from 0.96 nm in the dried sample to $d(001)$ in the corresponding solvates, using the expression proposed by Norrish (1954) and later applied by other researchers (Levy and Shainberg 1972; Van Asche et al. 1972):

$$E_{\text{exp}} = 2.39 \times 10^{-8} S \left(\frac{Ze\sigma}{2\Sigma D} - \frac{Ze\sigma'}{2\Sigma' D'} \right) \text{cal/g} \quad [2]$$

where E_{exp} is the interlayer swelling energy, S is the clay surface in cm^2/g , Z is the cation valence, e is the electron charge in esu/cm^2 , Σ and Σ' are the dielectric constants of the nonhydrated sample and the complex, respectively, in Debyes, and D is the distance between the center of the cation and D' is the distance between the center of the interlayer charge in the unhydrated

sample and the complex in cm. The center of the negative charge of the interlayer charge was assumed to be placed at 4.2 Å from the surface of the oxygen atoms (Levy and Shainberg 1972). The values of Σ and Σ' were 2.65 D (Schön and Weiss 1970). Table 2 includes the results, as well as the sum of the experimental heats of adsorption and the heats of expansion, which we call total heat of adsorption.

If the total heat of adsorption reflects the energies that were produced during the solvation of the cations and the montmorillonite surface and if this last contribution is constant for different samples in the same polar liquid, a good relationship between the magnitude of q_t and the parameter ionic potential of the exchangeable cations (Z/r) can be expected. This is because the energy produced during the cationic solvation process must be fundamentally electrostatic. In

Table 2. Immersion heats in TMP and TEP of the degasified samples at 120°C and 10^{-2} mm Hg vacuum (Q_{i0}) and of the stable complexes in vacuum (Q_i), adsorption heats (q_a), swelling heats (q_{exp}) and total heats (q_t).

Cation	TMP						TEP					
	Q_{i0} cal/g	Q_i cal/g	g phosphite/g sample	q_a kcal/mol	q_{exp} kcal/mol	q_t kcal/mol	Q_{i0} cal/g	Q_i cal/g	g phosphite/g sample	q_a kcal/mol	q_{exp} kcal/mol	q_t kcal/mol
Li ⁺	29.5 ± 0.05	12.8 ± 0.3	0.2346	8.8	3.6	12.4	27.2 ± 0.5	6.1 ± 0.1	0.2983	12.1	4.1	16.2
Na ⁺	9.6 ± 0.2	5.0 ± 0.1	0.1830	3.1	4.5	7.6	10.6 ± 0.5	2.3 ± 0.1	0.2160	6.4	5.5	11.9
Mg ²⁺	40.6 ± 0.3	11.6 ± 0.2	0.1821	19.1	9.5	29.2	25.7 ± 2.0	2.0 ± 0.1	0.2068	19.0	11.6	30.6
Ca ²⁺	37.3 ± 0.5	14.9 ± 0.3	0.2398	11.6	7.3	18.7	38.2 ± 0.8	3.3 ± 0.1	0.2500	23.2	9.6	32.8
Co ²⁺	51.0 ± 0.5	23.3 ± 0.5	0.1990	17.3	8.6	25.9	43.5 ± 0.5	8.6 ± 0.2	0.2246	27.3	10.7	38.0
Cu ²⁺	110.2 ± 4	18.0 ± 0.3	0.2962	38.6	6.9	45.5	51.6 ± 0.8	6.0 ± 1	0.2988	25.3	9.8	35.1
Fe ³⁺	94.2 ± 0.7	45.9 ± 0.8	0.2398	28.1	11.7	39.8	27.7 ± 1.0	3.1 ± 0.2	0.2660	15.3	13.9	29.2
Zn ²⁺	36.2 ± 0.2	12.0 ± 0.3	0.2300	13.0	7.5	20.5	28.9 ± 0.5	2.9 ± 0.2	0.2300	18.8	10.4	29.2

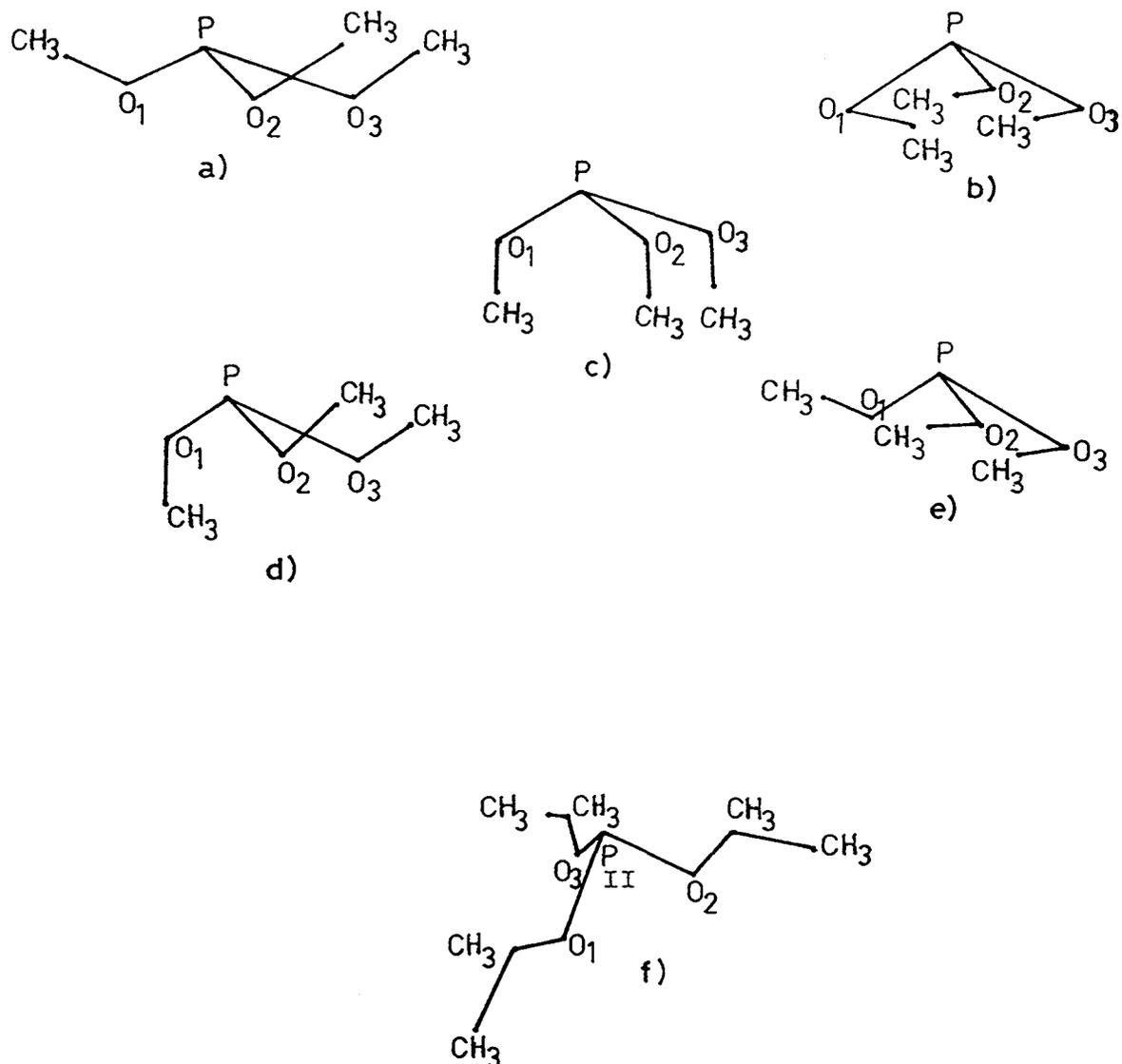


Figure 5. Conformers of the trimethyl phosphite proposed by Aroney et al. (1964) (a–d) and of the triethyl phosphite proposed by Vilkov et al. (1964) (f).

order to demonstrate this assumption, the values of q , were plotted against Z/r in Figure 4. This shows that the variation between both is approximately linear for both the TMP and TEP complexes, which demonstrates that the TMP and TEP-cation interaction is electrostatic and probably ion-dipole, as the values of the adsorption energy show.

The heat of adsorption of the Cu^{2+} samples, mainly with TMP, is higher than that which could be expected for their corresponding Z/r values. This seems to indicate that the Cu-P bond has a more covalent character than in the other samples, possibly the result of an electron retrodonation from Cu^{2+} to P, producing a reinforcement of the Cu-P bond.

Disposition of the Phosphite Molecules in the Interlayer Space

In order to obtain some information about the disposition of the phosphite molecules in the interlayer space of the montmorillonite, and to obtain knowledge of the d(001) interlayer space produced by the complex of these substances with the clay minerals, the conformations and the geometries of these molecules have to be known. These properties have been studied by Aroney et al. (1964) and Vilkov et al. (1965) in TMP, TEP and vinylphosphite. The former authors proposed five possible conformers for the TMP molecule (Figure 5a–d). From dipolar moments and Molar

Table 3. Bond lengths (in Å), bond and dihedral angles (in degrees), Total Energies (in atomic units), and dipolar moments (in Debyes) of the rotational isomers of the trimethylphosphite (Ia, Ib and Ic) and his phosphonate isomer (II) at 6-31G* basis set. Values in parentheses are 6-31+G* level.

	Ia	Ib	Ic	II
P-O ₁	1.618	1.604	1.626	1.452
P-O ₂	1.618	1.635	1.627	1.590
P-O ₃	1.618	1.621	1.626	1.592
C ₁ -O ₁	1.408	1.416	1.408	1.799 ^(a)
C ₂ -O ₂	1.408	1.408	1.407	1.412
C ₃ -O ₃	1.408	1.408	1.408	1.422
P-O ₁ -C ₁	119.8	123.9	128.0	116.0 ^(b)
P-O ₂ -C ₂	119.8	119.4	128.2	124.9
P-O ₃ -C ₃	119.8	119.8	128.1	120.9
X-P-O ₁ -C ₁	45.1 (47.2)	194.9 (183.5)	217.6 (231.7)	—
X-P-O ₂ -C ₂	32.5 (24.8)	26.1 (15.0)	222.4 (222.1)	169.6 ^(c) (173.2)
X-P-O ₃ -C ₃	69.2 (72.9)	45.4 (71.7)	217.1 (203.3)	91.0 ^(d) (90.8)
Energy	-684.16879	-684.17439	-684.16518	-684.21708
(Energy)	(-684.18124)	(-684.18573)	(-684.17552)	(-684.22730)
Dipolar moment	1.58	1.74	3.96	4.66

(a) C-P; (b) C-P = O; (c) C-O-P = O; (d) C-O₁-P-O_(i-1).

Kerr constant measurements the a conformer is proposed as the most stable. This configuration presents the three methyl groups in cis position with the lone pair of the phosphorus atom.

Vilkov et al. (1965) by means of electron diffraction, proposed a similar configuration for the TEP and vinylphosphite (Figure 5f), being the C-C bond of the alkyl or alkenyl groups in trans position with respect to the P-O bonds. All of the conformers proposed by these last authors present C_{3v} symmetry. However, they found other diffraction peaks near 0.32 nm, which could be attributed to other conformers.

In order to gain a better insight of the molecular

structure of these molecules, ab initio calculations have been performed. In Table 3 the main bond distances, bond and dihedral angles and total energies for different conformers of the TMP (Ia-Ic) and one isomer (dimethyl-methylphosphonate) (II) are presented. In the calculations, the lone pair of the phosphorous atom is assumed with a dummy atom (X) linked to the phosphorus atom. The conformational angles are measured by the XPO_iC_i angle, with the X as the "simulated lone pair" (SLP). Ia conformer shows the three methyl groups roughly in cis configuration with the SLP and the other two in cis configuration with the SLP; and Ic shows the three methyl groups in trans

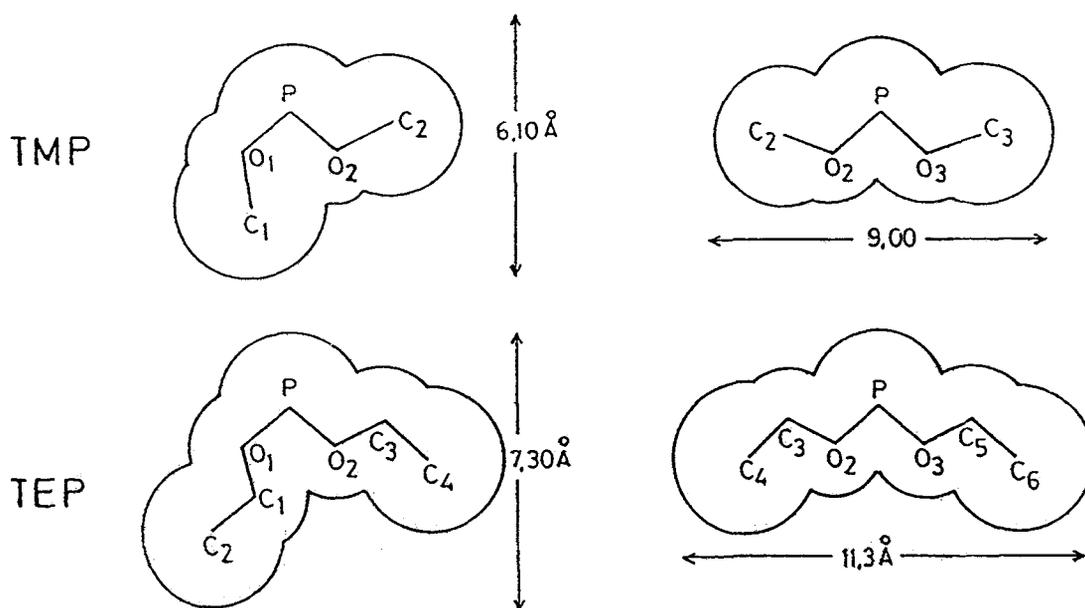


Figure 6. Scaled projection of the TMP and TEP molecules corresponding to the most stable conformers (Ib).

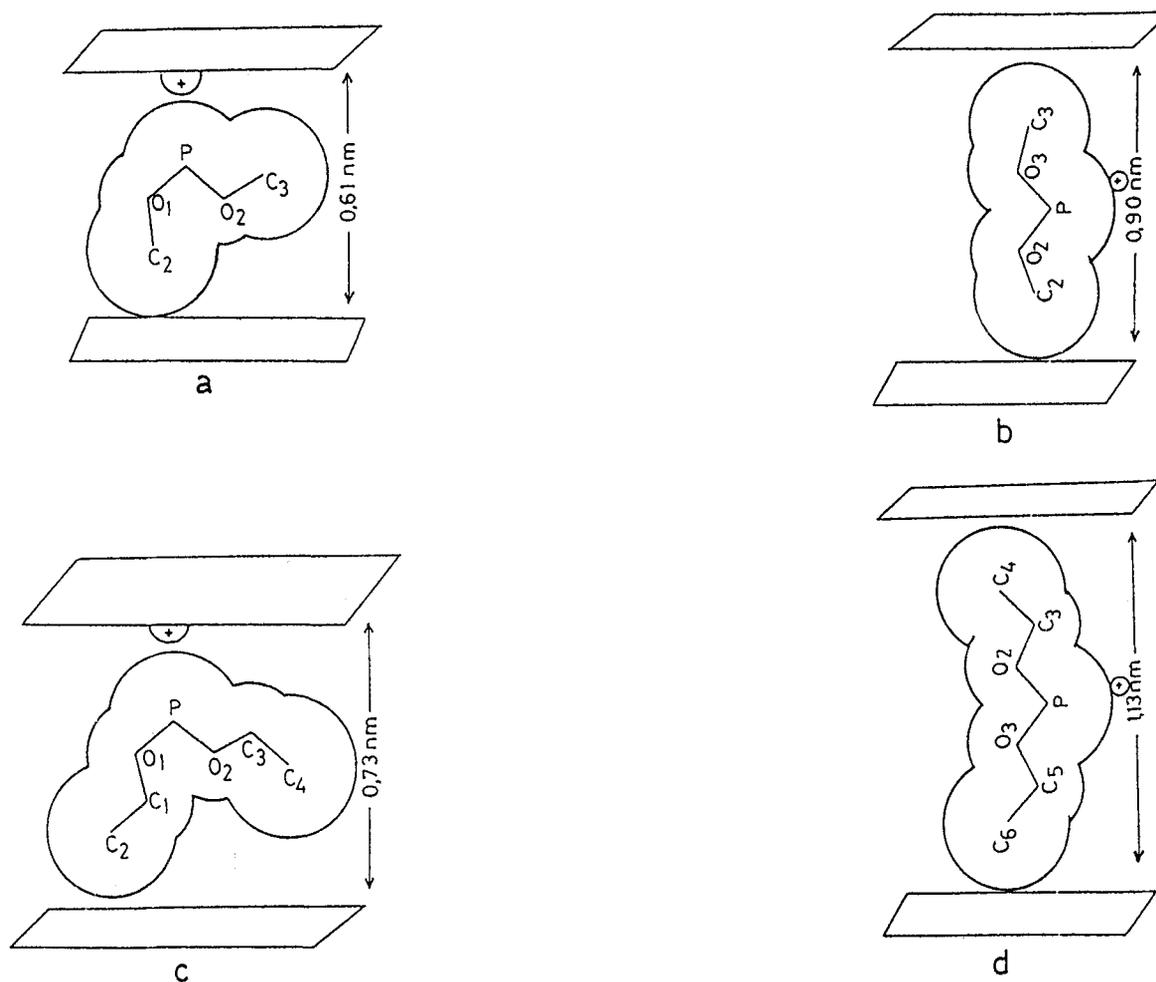


Figure 7. Disposition of the TMP or TEP molecules in the montmorillonite interlayer in the low (a, c) and high (b, d) spacing complexes.

configuration with the SLP. These three critical points approximately correspond to the a, d and c structures, respectively, found by Aroney et al. (Figure 5). According to the total energies obtained, Ib is the most stable conformer of TMP. However, this is not consistent with the results found by Aroney et al. (1964) for TMP and Vilkov et al. (1965) for TEP and vinylphosphite. Nonetheless, we have found the Ia (a in Aroney's notation) conformer is 3.5 kcal/mol at 6-31G* and 2.8 kcal/mol at 6-31+G* basis sets higher than the conformers Ib. Finally, the Ic rotational isomer is 5.8 kcal/mol higher than the most stable conformers, showing the methyl groups roughly in *trans* configuration with the SLP. It should be noticed that the a conformer proposed by Aroney et al. (1964) (Figure 1) and Vilkov et al. (1965) (Figure 1f) for TMP and TEP molecules, with the three methyl groups in *cis* with respect to the lone pair, is very improbable in metallic cationic complexes because the methyl groups would block the phosphorus lone pair, obstructing to

a great extent, the coordination of the alkyl phosphites with metallic cations.

We have also calculated the dipolar moments of these structures (Table 3). The Ib value (1.74 Debyes) gave the closest value to the experimental value (1.81 Debyes). Aroney et al. (1964) calculated the dipolar moments for the Ia, Ib and Ic configuration types (1.9 Debyes for a, 0.9 Debyes for d and 4.1 Debyes for c), they selected the Ia conformation type (a) for the TMP. However, from our calculations, it is clear that a structure like Ib must have a greater dipolar moment than Ia. In fact, the dipolar moment of Ib must be halfway between Ia and Ic.

The dimethyl-methylphosphonate is the most stable isomer (II) determined, it is 26.8 kcal/mol more stable than the most stable rotational isomers of the TMP at 6-31G* level.

The bond length and bond angle differences between the basis sets, with and without diffuse basis functions, are not important at all. However, as usual,

we found greater differences with dihedral angles, with no change in the quality of the conformation. The average value of the P-O bonds in the conformers of TMP is 1.62 Å, changing in the different rotational isomers, a little higher than those found by Vilkov et al. (1965) (1.58 ± 0.02 for TEP and 1.60 ± 0.01 Å for vinylphosphite). This bond distance is shortened to 1.59 Å in the phosphonate isomer. The C-O lengths present an average value of 1.41 Å consistent with that of 1.42 proposed by Vilkov et al. (1965) in TEP. This bond distance presents a more constant value for the different conformers than that of the P-O bond. The POC angles range from 119° in Ia to 128° in Ic, being the shorter values for the configurations Ia (the experimental value is $113 \pm 3^\circ$ by Vilkov et al. 1965).

From the preceding studies, the Ib conformer could be proposed as the most stable configuration of the TMP molecule and by extension, a similar conformer for the TEP molecule. Taking into account the geometry of these molecules in Table 3 (C-C bond length of the TEP has been extracted from Vilkov et al. 1965) and the van der Waals atomic radii, the distance from the hydrogens of the CH₃ in trans position to the P atom and the CH₃ . . . CH₃ distance of the methyl and ethyl groups in cis position with the lone pair of the phosphorous atom of Ib conformer, are shown in Figure 6.

The complexes of almost every sample with TMP showed a basal spacing of 1.58 nm with an increase over the spacing of the unhydrated sample of 0.63 nm. This shift is in agreement with the height of the molecule of TMP (0.61 nm) giving rise to the conclusion that in the complex, the molecule acquires a disposition, as in Figure 7a when it is intercalated with the P directed toward the cation placed over one of the silicate layers, and the CH₃ group below the plane formed by the oxygens of the PO₃³⁻, supported on the opposite layer.

The complex of the Cu²⁺ sample with TMP has a basal space of 1.84 nm, with a shift of 0.91 nm over that of the unhydrated sample. This shift can be explained by a disposition of the TMP molecules, as in Figure 7b with the CH₃ groups over the plane of the PO₃³⁻ oxygens, each of which are directed toward opposite layers. The theoretical shift for such complexes should be 0.91 nm, close to the experimental value.

The complexes of the different samples with TEP, with the exception of Cu²⁺ and Fe³⁺, have basal spacings of 1.68 nm, with a shift of 0.75 over the nonhydrated sample. Such an increase is in accordance with the height of the TEP molecule in Figure 6. So that the disposition of the TEP in this complex should be plotted as in Figure 7c, thus having a similarity to the TMP disposition in the 1.58 nm complexes with TMP. The Cu²⁺ sample and partially the Fe³⁺ sample gave complexes with TEP with a d(001) spacing of 2.00 nm, with a shift of 1.07 nm over the spacing in the

nonhydrated sample. Such a shift is similar to the CH₃-CH₃ distance in Figure 6. Thus, the most probable disposition of TEP in such a complex is plotted in Figure 7d.

ACKNOWLEDGMENTS

Authors are indebted to M^a Dolores Maroto and J. Rodríguez Robledo for technical assistance. Financial support for the preparation of this paper was provided by DIGICYT Grants number NAT-91,0704 and PB90-0279.

REFERENCES

- Aroney J, Chia LHL, Le Febre RJN, Jaxby JDL. 1964. Molecular polarizability, dipole moments, molar Kerr constants, and conformations of eleven phosphates and phosphites triesters as solutes in benzene. *J Chem Soc* 2948.
- Davidon WC, Nazareth L. 1975. Program OC included with MONSTERGAUSS. The algorithm is described by Davidon W.C. *Math Program* 9:1-30.
- Farzaneh F, Pinnavaia TJ. 1983. Metal complexes catalysts interlayered in smectite clay. Hydroformylation of 1-hexene with rhodium complexes ion-exchanged into hectorite. *Inorg Chem* 22:2216-2220.
- Levy R, Shainberg I. 1972. Calcium-magnesium exchange in montmorillonite and vermiculite. *Clays & Clay Miner* 20:37-46.
- Norrish K. 1954. Swelling of montmorillonite. *Diss Faraday Soc* 18:120-134.
- Peterson MR, Poirier RA. 1978. Program MONSTERGAUSS. University of Toronto, Ontario (Canada).
- Pinnavaia TJ, Raythatha R, Lee JGS, Halloran LJ, Hoffman JF. 1979. Intercalation of catalytically active metal complexes in mica-type silicates Rhodium hydrogenation catalysts. *J Am Chem Soc* 101:6891-6897.
- Pinnavaia TJ, Welty PK. 1975. Catalytic hydrogenation of 1-hexene by rhodium complexes in the intra-crystal space of a swelling layer lattice silicate. *J Am Chem Soc* 97: 3819-3820.
- Pinnavaia TJ, Welty PK, Hoffman JF. 1976. Catalytic hydrogenation of unsaturated hydrocarbons by cationic rhodium complexes and rhodium metal intercalated in smectite. *Proc Int Clay Conf Mexico*. 1975 373-381.
- Quayle WH, Pinnavaia TJ. 1979. Utilization of a cationic ligand for the intercalation of catalytically active rhodium complexes in swelling layer-lattice silicates. *Inorg Chem* 18:2840-2847.
- Raythatha R, Pinnavaia TJ. 1981. Hydrogenation of 1,3-butadiene with a rhodium-complexes-layered silicate intercalation catalyst. *J Organomet Chem* 218:115-122.
- Raythatha RH, Pinnavaia TJ. 1983. Clay intercalation catalysts interlayered with rhodium phosphine complexes. Surface effects on the hydrogenation and isomerization of 1-hexene. *J Catal* 80:47-55.
- Schön G, Weiss A. 1970. Measurements of the dielectric properties of vermiculite simple crystals and interpretation of the high frequency conductivity within the zero, 155 and 255 states of hydration. *Reunión Hispano-Belga de Minerales de la Arcilla*. Madrid. 37-44.
- Thomas LE. 1974. Interpretation of the infrared spectra of organophosphorus compounds. London:Hayden. 276p.
- Van Asche JB, Van Canwelaert FH, Uytterhoeven JB. 1972. Sorption of organic polar gases on montmorillonite. *Proc Int Clay Conf Madrid* 1972. p. 605-615.
- Vilkov LV, Akishin PA, Salove GE. 1965. Investigation electronographic of the structure of the molecules of P(OC₂H₅)₃ and P(OC₂H₃)₃ in phase gas. *Ah Struk Khim* 6:355.

(Received 18 June 1994; accepted 23 May 1995; Ms. 2519)