

COMPLEXES OF TRIMETHYLPHOSPHINE AND DIMETHYLPHENYLPHOSPHINE WITH Co(II) AND Ni(II) ON HECTORITE AND ON ZEOLITES X AND Y

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Abstract—The gas-phase adsorption of trimethylphosphine onto hectorite, exchanged with Co(II) and Ni(II), gives trigonal complexes of the type $[M(O)_3(PMe_3)]^{2+}$ ($M = Co, Ni$). Ten Dq values of PMe_3 are 2.1 and 2.4 times larger than those of the structural oxygens or solvent molecules. The same complexes form between dimethylphenylphosphine and Ni(II) on hectorite and on synthetic zeolite Y. Co(II) forms pseudotetrahedral complexes with dimethylphenylphosphine ligands. These surface-immobilized transition-metal complexes interact strongly with NO and $CH\equiv CH$ and to a lesser extent with CO and $CH_2=CH_2$, giving new types of complexes.

Key Words—Adsorption, Cobalt, Dimethylphenylphosphine, Hectorite, Nickel, Trimethylphosphine, Zeolite Y.

INTRODUCTION

Transition-metal amine complexes intercalated in smectite-type minerals have been extensively studied (Schoonheydt, 1981). The studies on phosphine complexes have been restricted to cationic rhodium complexes in attempts to produce heterogenized homogeneous catalysts (Pinnavaia *et al.*, 1975, 1979; Raythatha and Pinnavaia, 1981; Pinnavaia and Welty, 1975; Quayle and Pinnavaia, 1979; Mazzei *et al.*, 1980). Trimethylphosphine (PMe_3) forms well-defined complexes with Co(II) and Ni(II) in the supercages of faujasite-type zeolites. The type of complexes depends on the transition metal ion and on the type of zeolite. For example, in Y-type zeolites the low-spin, trigonal bipyramidal complex $Ni(PMe_3)_5^{2+}$ forms, as well as a similar, low-spin complex with Co(II). These low-spin complexes cannot be synthesized in X-type zeolites; however, both zeolites contain pseudo-tetrahedral complexes which could only be identified unambiguously for Ni(II) as $[Ni(O)_3(PMe_3)]^{2+}$ (O_l = lattice oxygen) (Schoonheydt *et al.*, 1980a, 1980b, 1981).

In the present paper another variable, the type of surface, is introduced into the complexation of surface-immobilized transition metal ions by means of a comparison of the complexation of Co(II) and Ni(II) with dimethylphenylphosphine ($PMe_2\phi$) in zeolites and on clays.

EXPERIMENTAL

Materials

The $<2\text{-}\mu\text{m}$ fraction of hectorite SHCa-1 (Source Clays Repository of The Clay Minerals Society) was used throughout the experiments. Suspensions (2% by

weight) were exchanged with 0.005 mole/dm³ $CoCl_2$ or $NiCl_2$ solutions in dialysis membranes. After a Cl^- -free washing, the samples were freeze-dried and stored as such. Synthetic zeolites X and Y loaded with Co(II) and Ni(II) were prepared as previously described (Schoonheydt *et al.*, 1980a, 1981).

The exchangeable cation content of the samples was determined by atomic absorption spectrometry (Table 1). The numbers in Table 1 were calculated on a dry weight basis. The dry weight of the zeolites was obtained by calcination at 850°C until constant weight. The dry weight of the clays is obtained after calcination at 110°C until constant weight. Dimethylphenylphosphine ($PMe_2\phi$) and trimethylphosphine (PMe_3) were obtained from Strem Chemicals Inc. and purified before use as described by Schoonheydt *et al.* 1980a). The gases nitric oxide (NO), carbon monoxide (CO), ethylene ($CH_2=CH_2$), and acetylene ($CH\equiv CH$) were obtained from L'Air Liquide. They were high purity gases (99.999% by volume) and used without modification.

Procedures

Before treatments with phosphine, the water of the clays was removed (1) by washing with methanol or dichloromethane (CH_2Cl_2) prior to the loading of the reflectance cell and the McBain balance with the clay samples; and (2) by loading first the reflectance cell and the McBain balance with the clay samples followed by an adsorption-evacuation process of gaseous methanol, repeated 3 times. In each experiment, the samples were evacuated at room temperature prior to the adsorption of phosphines. The reflectance cell and the McBain

Table 1. Exchangeable cation content (mmole/g).

| Sample | Na ⁺ | Co ²⁺ | Ni ²⁺ |
|--------------------|-----------------|------------------|------------------|
| Co-hectorite | 0.11 | 0.36 | |
| Ni-hectorite | 0.08 | | 0.41 |
| CoY18 ¹ | 1.45 | 1.35 | |
| CoY20 ¹ | 1.18 | 1.43 | |
| NiY18 ¹ | 1.44 | | 1.28 |
| NiY20 ¹ | 1.05 | | 1.48 |

¹ The sample symbols (Y = zeolite Y) are preceded by the symbol of the transition metal and followed by the number of transition metal ions per unit cell.

balance were connected to the same vacuum line to allow simultaneous treatments.

Dimethylphenylphosphine and trimethylphosphine were allowed to adsorb at room temperature until constant weight was reached on the McBain balance. Typical partial pressures were 267 Pa (PMe₂φ) and 2.67 × 10⁴ Pa (PMe₃). Reflectance spectra were recorded after saturation with phosphines and after evacuation of phosphines at room temperature. At this point small gaseous molecules (NO, CO, CH₂=CH₂, or CH≡CH) were allowed to adsorb until constant weight was obtained, and the spectra were recorded again.

Spectra were recorded in the 2000–200-nm range on a Cary 17 instrument with a type I reflectance unit. The standard was BaSO₄. The spectra were tape-recorded and computer-processed to obtain the Kubelka-Munk function as a function of the wavenumber. The Kubelka-Munk function is defined as:

$$F(R_{\infty}) = (1 - R_{\infty})^2 / 2R_{\infty}$$

where R_∞ is the ratio of the light intensity reflected from the sample to the light intensity reflected from the standard. Some spectra were recorded against Na-hectorite or NaX and NaY zeolite in the visible-ultraviolet region only. These spectra were plotted as such.

The pretreatment of the zeolites and the adsorption of phosphines were described by Schoonheydt *et al.* (1980a, 1981). After saturation with phosphines, the zeolites were evacuated and small gaseous molecules were allowed to adsorb as described above for the clays.

RESULTS

Adsorption of phosphines

Clays and faujasite-type zeolites adsorb PMe₂φ and PMe₃ almost instantaneously. The adsorption is accompanied by color changes which are indicative of complexation of the transition metal ions on the surface. The amounts adsorbed are reported in Table 2. The slight fluctuation in the values for the clays is due to differences in pretreatments, such as number of washings with solvent or evacuation time prior to adsorption of phosphines. These experimental details were not investigated because the spectra of the phosphine

Table 2. Adsorption of phosphines and NO, CO, C₂H₄, and C₂H₂ on hectorite and zeolite Y.

| Sample ¹ | Adsorption (molecules per transition metal ion) | | | | | |
|---------------------|---|--------------------|------|------|-------------------------------|-------------------------------|
| | PMe ₃ | PMe ₂ φ | NO | CO | C ₂ H ₄ | C ₂ H ₂ |
| Ni-hectorite | 1.83–2.28 | 3.22–3.63 | 2.28 | 0.28 | 2.95 | 1.23 |
| Co-hectorite | 2.55–3.51 | 3.73–4.33 | 0.79 | 0.27 | 2.97 | 2.23 |
| NiY18 | 2.50 ² | 1.17–1.31 | 0.89 | 1.08 | — | — |
| NiY20 | — | 1.16 | — | — | 0.49 | — |
| CoY18 | 2.35 ² | 1.14–1.34 | 0.73 | 0.72 | — | — |
| CoY20 | — | 1.16 | — | — | 0.42 | — |

¹ See footnote 1, Table 1.

² These numbers are measured on NiY17 and CoY14. (See Schoonheydt *et al.*, 1980a, 1981.)

complexes were not affected by them. The corresponding d(001) spacings are in the range 13.80–15.60 Å, independent of the type of cation, the type of phosphine, and the pretreatment. The PMe₃:M(II) ratios of the clays and zeolites are equal, but the PMe₂φ:M(II) ratios are much lower in the zeolites than in the clays.

Reflectance spectra of Ni(II)-phosphine-clays

Ni-hectorite turns brown immediately upon adsorption of PMe₂φ or PMe₃. The reflectance spectra of the phosphine complexes (Figure 1) are very similar and independent of the phosphine loading; partial saturation or evacuation of phosphines after saturation give the same spectra. The bands of the PMe₃ complex are at slightly higher frequencies than those of the PMe₂φ complex, indicating that the former is a somewhat stronger ligand. The main band has its maximum intensity at 8200 cm⁻¹ (PMe₂φ) or at 8400 cm⁻¹ (PMe₃). For both materials, the weak, sharp bands on the low frequency tail are CH-overtone stretching vibrations. In the visible regions, a broad shoulder at 20,900 cm⁻¹ for PMe₂φ and 22,500 cm⁻¹ for PMe₃ was noted with a low-frequency tail and a band at 24,900 cm⁻¹ for PMe₂φ (26,500 cm⁻¹ for PMe₃ and much sharper). All of these bands fall in the range expected for d-d transitions of Ni(II). In the ultraviolet region, well-resolved bands were only obtained when the spectra were recorded against Na-hectorite (see insert of Figure 1). The bands at 33,300 cm⁻¹ (300 nm) for PMe₂φ and 36,500 cm⁻¹ (275 nm) for PMe₃ are P → Ni(II) charge-transfer transitions. The supplementary band at 38,500 cm⁻¹ (260 nm) for PMe₂φ is the π → π* transition of the phenyl ring.

Reflectance spectra of Co(II)-phosphine clays

Upon adsorption of PMe₂φ or PMe₃, Co-hectorite becomes green. The reflectance spectra (Figure 2) are independent of the phosphine loading, i.e., 50% saturation, saturation, and evacuation of a phosphine-saturated Co-hectorite give the same spectra. The spectrum of Co-hectorite PMe₂φ is typical for pseudotetrahedral, high-spin Co(II) complexes. It contains

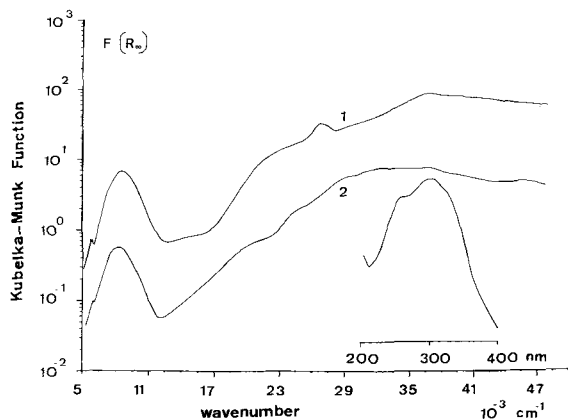


Figure 1. Plot of $F(R_{\infty})$ against wavenumber for (1) Ni-hectorite + PMe_3 ; (2) Ni-hectorite + $\text{PMe}_2\phi$. Spectrum (2) is shifted downwards by one order of magnitude of $F(R_{\infty})$. The insert is part of the spectrum of Ni-hectorite + $\text{PMe}_2\phi$ recorded with Na-hectorite as a reference.

3 sets of d-d bands: a weak band at 5700 cm^{-1} superposed on C-H overtones; a triplet in the near infrared region ($7625\text{--}8900\text{--}9950\text{ cm}^{-1}$) and a triplet in the visible region ($15,275\text{--}15,800\text{--}16,850\text{ cm}^{-1}$). All of these bands are d-d transitions of tetrahedral Co(II). In the UV range the shoulder around $25,000\text{ cm}^{-1}$ is probably due to the clay, the $31,750\text{ cm}^{-1}$ band is the $\text{P} \rightarrow \text{Ni(II)}$ charge transfer, and the $37,000\text{ cm}^{-1}$ band is the $\pi \rightarrow \pi^*$ of phenyl.

The spectrum of Co-hectorite + PMe_3 is quite different and contains a band at 5900 cm^{-1} with superposition of CH overtones but no triplets in the NIR and visible regions. Instead, a band at $10,600\text{ cm}^{-1}$ (with a shoulder around 8800 cm^{-1}), a band at $14,200\text{ cm}^{-1}$, and one at $23,000\text{ cm}^{-1}$ were noted. A broad charge transfer band at $38,500\text{ cm}^{-1}$ was noted in the UV range.

Reflectance spectra of Co(II) and Ni(II) with $\text{PMe}_2\phi$ on faujasite-type zeolites

On Y-type zeolites, $\text{PMe}_2\phi$ interacts with Co(II) and Ni(II) to form complexes with the same spectra as for hectorite. The various bands are, however, better resolved (Figure 3); thus, on a Y-type zeolite with 18 Ni^{2+} per unit cell (NiY18) the characteristic bands are at 8400 cm^{-1} , $19,400\text{ cm}^{-1}$ with low frequency tailing, $26,300\text{ cm}^{-1}$, $32,200\text{ cm}^{-1}$, and $37,100\text{ cm}^{-1}$. For CoY, saturated with $\text{PMe}_2\phi$, in addition to the weak band at 5500 cm^{-1} , a triplet in the NIR region ($7900\text{--}8500\text{--}10,000\text{ cm}^{-1}$), a quadruplet in the visible ($14,700\text{--}15,500\text{--}16,900\text{--}17,700\text{ cm}^{-1}$), and bands at $22,550\text{ cm}^{-1}$, $27,200\text{ cm}^{-1}$, $30,500\text{ cm}^{-1}$, and $38,000\text{ cm}^{-1}$ were noted. The last is mainly the $\pi \rightarrow \pi^*$ band of the phenylring. Faujasite-type zeolites must be carefully saturated to obtain these spectra. Incomplete saturation leads to

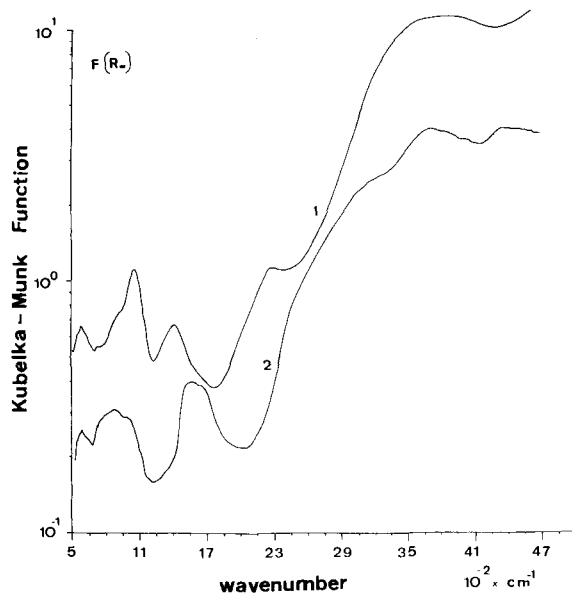


Figure 2. Plot of $F(R_{\infty})$ against wavenumber of (1) Co-hectorite + PMe_3 ; (2) Co-hectorite + $\text{PMe}_2\phi$.

a complex spectrum of phosphine complexes and uncomplexed transition metal ions. The 5500 cm^{-1} band and the $17,700\text{ cm}^{-1}$ band of $\text{CoY} + \text{PMe}_2\phi$ may partially be due to uncomplexed Co(II). This problem is especially pronounced with X-type zeolites; after saturation with $\text{PMe}_2\phi$, both CoX and NiX show reflectance spectra dominated by bands of the structural Co(II) and Ni(II). New bands due to phosphine complexes are not or almost not visible.

Interaction with small molecules

When excess $\text{PMe}_2\phi$ is removed by evacuation at room temperature, all of the samples readily adsorb small molecules such as NO, CO, $\text{CH}_2=\text{CH}_2$, and $\text{CH}\equiv\text{CH}$ (Table 2). NO and $\text{CH}\equiv\text{CH}$ strongly interact with the phosphine complexes on the surface and new spectra are produced (Figure 4). For NO the most prominent feature is a 2-band system with maxima around $18,000$ and $21,000\text{ cm}^{-1}$. Acetylene produces a broad band in the visible region. No spectral changes occur upon adsorption of ethylene, and only minor spectral changes are produced upon adsorption of CO. These observations were made on the clays and on the zeolites. The small molecules were, however, not allowed to adsorb on PMe_3 -clays or zeolites. In the preliminary IR spectra of NO and CO on CoY18 and NiY18 after loading with $\text{PMe}_2\phi$, several bands were observed of NO and CO coordinated to different types of Co(II)- and Ni(II)-species. These bands are indicative of the presence of different types of complexes. On clays, CO and NO bands were too weak for a systematic investigation.

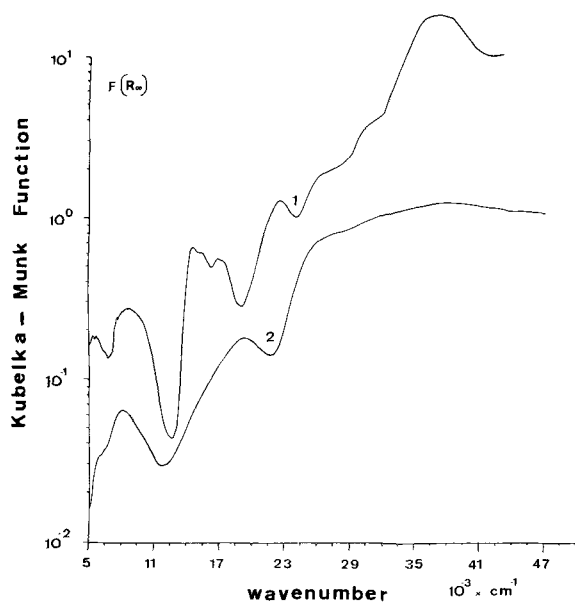


Figure 3. Plot of $F(R_{\infty})$ against wavenumber for (1) CoY18 + $\text{PMe}_2\phi$; (2) NiY18 + $\text{PMe}_2\phi$.

DISCUSSION

The maximum numbers of PMe_3 and $\text{PMe}_2\phi$ molecules that can be adsorbed in the supercages of zeolites are in the ratio 2PMe_3 to $1\text{PMe}_2\phi$ (Table 2), in agreement with a space-filling model, based on bond distances (CRC, 1971–1972). The surface areas per molecule for the models of PMe_3 and $\text{PMe}_2\phi$ are estimated to be 0.22 nm^2 and 0.47 nm^2 , respectively. The adsorbed amount of $\text{PMe}_2\phi$ in the interlamellar space of hectorite ($800 \text{ m}^2/\text{g}$) suggests exactly monolayer coverage. This is not true for PMe_3 , and we can offer no explanation for this difference. The measured spacings are close to those of the methanol-clays prior to adsorption of phosphines (1.41 \AA) and can therefore not be used to learn something about the orientation of the phosphine complexes with respect to the clay surface. Expansion above the monolayer, however, is excluded.

Analysis of the spectra

For Ni(II), the three-dimensional packing in the supercages of faujasite-type zeolites and the bidimensional packing in the interlamellar space of hectorite lead to identical reflectance spectra and, most probably, to identical complexes. For Ni-zeolites, the spectra obtained with PMe_3 were interpreted by Schoonheydt *et al.* (1980a) in terms of a pseudotetrahedral complex $[\text{NiO})_3(\text{PMe}_3)]^{2+}$ with the PMe_3 ligand, a 2.1- to 2.3-times stronger ligand than the structural oxygens. A similar ligand-field analysis of the present spectra gives the results summarized in Table 3. The physical meaning of the tabulated parameters is given in Appendix

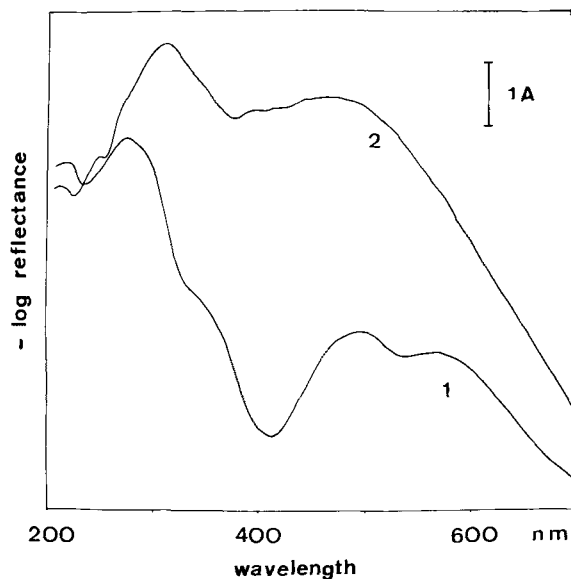


Figure 4. Diffuse reflectance spectra with Na-hectorite as reference: (1) Ni-hectorite + $\text{PMe}_2\phi$ + NO; (2) Ni-hectorite + $\text{PMe}_2\phi$ + C_2H_2 .

1. It follows from the $10 Dq^p$ values in Table 3 that PMe_3 is a slightly stronger ligand than $\text{PMe}_2\phi$ because it is a stronger base (Henderson and Streuli, 1960). Also, on the basis of the $10 Dq$ values the phosphines are stronger ligands than the other atoms in the coordination sphere by a factor of 2.16–2.32. For hectorite, solvent molecules are present in the interlamellar space, and the O_T -ligands may be structural oxygens and solvent molecules. It follows from this analysis that one phosphine molecule is coordinated per Ni(II) in Ni-hectorite. As with the zeolites, chemisorption of phosphine molecules on structural oxygens accounts for the fact that the adsorbed amount of phosphine exceeds 1 phosphine per Ni(II).

The situation is more complicated for Co(II) because the formation of the complexes depends on the type of support and the type of phosphine. With $\text{PMe}_2\phi$, tetrahedral-like complexes form on hectorite and on

Table 3. Ligand field parameters of complexes of Ni(II) with PMe_3 , and $\text{PMe}_2\phi$.

| Variable | Ni-hectorite + PMe_3 | Ni-hectorite + $\text{PMe}_2\phi$ | NiY + $\text{PMe}_2\phi$ |
|-------------------------------------|-------------------------------|-----------------------------------|--------------------------|
| G_4^o/B | 5–6 | 6–6.5 | 6–7 |
| $B \text{ (cm}^{-1}\text{)}$ | 985–792 | 735–668 | 751–627 |
| | 0.95–0.76 | 0.71–0.64 | 0.72–0.60 |
| $G_4^o \text{ (cm}^{-1}\text{)}$ | 4925–4752 | 4410–4342 | 4506–4389 |
| $G_4^p \text{ (cm}^{-1}\text{)}$ | 11,032–10,644 | 9878–9726 | 10,093–9831 |
| $10 D_4^o \text{ (cm}^{-1}\text{)}$ | 3648–3520 | 3267–3216 | 3338–3251 |
| $10 D_4^p \text{ (cm}^{-1}\text{)}$ | 8172–7884 | 7317–7204 | 7476–7282 |

Table 4. Comparison of experimental and theoretical d-d spectra of $\text{Co}(\text{O})_3(\text{PMe}_3)^{2+}$.

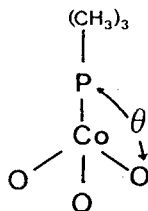
| Experimental | Band positions/ cm^{-1} | | Assignment | |
|--------------|----------------------------------|------------------|--|---|
| | (a) | (b) | | |
| 5500–5900 | 5500 | 5900 | ${}^4\text{A}_2, {}^4\text{A}_1, {}^4\text{A}_2$ | $\text{B} = 783\text{--}840 \text{ cm}^{-1}$ |
| 10,600 | 8910 | 9590 | ${}^4\text{A}_2, {}^4\text{E}$ | $\text{G}_4^{\text{O}} = 3133\text{--}3359 \text{ cm}^{-1}$ |
| 14,200 | $14,770 \pm 300$ | $15,800 \pm 300$ | ${}^4\text{A}_2, {}^4\text{E}$ | $\text{G}_4^{\text{P}} = 7025\text{--}8062 \text{ cm}^{-1}$ |
| 23,000 | 22,330 | 23,950 | ${}^4\text{A}_2, {}^4\text{A}_2$ | |

For the definition of the parameters, Appendix 1.

¹ (a) the band maximum is at 5500 cm^{-1} ; (b) the band maximum is at 5900 cm^{-1} .

CoY zeolites. The parameters were calculated from the spectra by taking the average band frequency of the triplet bands. Thus, for CoY: $\nu_1({}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_2(\text{F})) = 5500 \text{ cm}^{-1}$; $\nu_2({}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{F})) = 8800 \text{ cm}^{-1}$; and $\nu_3({}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})) = 15,700 \text{ cm}^{-1}$ with $\text{B} = 533\text{--}575 \text{ cm}^{-1}$ and $10 \text{ D}_q^{\text{tet}} = 5292\text{--}5500 \text{ cm}^{-1}$ (König, 1971). For Co-hectorite almost the same values are obtained: $\nu_1 = 5700 \text{ cm}^{-1}$; $\nu_2 = 8825 \text{ cm}^{-1}$; and $\nu_3 = 15,975 \text{ cm}^{-1}$, with $\text{B} = 513\text{--}596 \text{ cm}^{-1}$ and $10 \text{ D}_q^{\text{tet}} = 5288\text{--}5700 \text{ cm}^{-1}$. These $10 \text{ D}_q^{\text{tet}}$ values are larger than usually encountered for coordination to oxygen atoms (König, 1971; Schoonheydt *et al.*, 1980a), but similar to those found for the system $\text{CoX} + \text{PMe}_3$ (Schoonheydt *et al.*, 1981). Thus, the phosphine has a distinct influence on the spectra. Whether this is due to its coordination as $\text{PMe}_2\phi$ or the phosphine oxide $\text{OPMe}_2\phi$ or to an indirect effect on the coordination of Co^{2+} is not known. The formation of phosphine oxide is the result of a chemisorption reaction between $\text{PMe}_2\phi$ and structural oxygens. A similar reaction has been described for faujasite-type zeolites (Schoonheydt *et al.*, 1981).

The spectrum of the complexes of Co(II) with PMe_3 , on the surface of hectorite can be described in terms of a compressed tetrahedron model as shown for Ni(II) in Table 3 and for Co(II) on zeolite X (Schoonheydt *et al.*, 1981); namely,



The best fit of the spectra is obtained for $\theta = 104\text{--}106^\circ$. The ground state is ${}^4\text{A}_2$. If the experimental band maxima are assigned as shown in Table 4, the fit is reasonable. The tetrahedral splitting parameter of the structural oxygens and/or solvent molecules (G_4^{O}) and the tetrahedral splitting parameter of PMe_3 (G_4^{P}) are systematically lower than those calculated from the spectra of the Ni(II) complexes (see Table 3). The same

trend was observed for tetrahedral halogenide complexes (Lever, 1968).

Interaction with small molecules

The gravimetric and spectral data show that NO and $\text{CH}\equiv\text{CH}$ enter the coordination sphere of the phosphine complexes of Co(II) and Ni(II) on hectorite and on the zeolites. The complexity of both the reflectance and IR spectra is indicative of either a chemical reaction between these molecules and the complexes, or the presence of several types of complexes prior to adsorption of the small molecules. The present data do not allow an unambiguous interpretation.

CONCLUSIONS

Ni(II) coordinates more easily to the tertiary phosphines, PMe_3 and $\text{PMe}_2\phi$, than does Co(II). On the surface of faujasite-type zeolites and hectorite, trigonal complexes form with 1 phosphine molecule and 3 structural oxygens or 3 residual solvent molecules in the coordination sphere. This arrangement is also found for Co(II) and PMe_3 on hectorite. With $\text{PMe}_2\phi$, pseudotetrahedral Co(II) complexes form. On the zeolites complexation of $\text{PMe}_2\phi$ with Co(II) and Ni(II) is incomplete, especially on X-type zeolites. The complexes readily take up NO and $\text{CH}\equiv\text{CH}$ in their coordination sphere, and to a lesser extent, CO and $\text{CH}_2=\text{CH}_2$.

Our attempts towards a direct complexation of Cu(II) with phosphines on hectorite failed; the experiment lead to reduction of Cu(II) as it was previously shown for Y-type zeolites (Herman, 1979).

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Appendix 1. Definition of ligand field parameters

B is Racah's electronic repulsion parameter of the 3d-electrons of Ni(II). Its free ion value B_0 is 1041 cm^{-1} (Griffith, 1971). The ratio B/B_0 is a measure of the expansion of the 3d electron density on the ligands. It is always less than 1 because of the covalent character of the coordination bond. The parameters, $10 D_q^P$ and $10 D_q^O$, describe the extent of splitting of the 5 d-orbitals into 2 groups (dxz, dyz, dxy and dz^2, dx^2-y^2) under the action of the tetrahedral ligand field. The superscripts P and O refer respectively to phosphines and structural oxygens and/or solvent molecules. G_4^O and G_4^P have a similar meaning.

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Резюме—Адсорбция газовой фазы триметилфосфина на гекторите, обменным Co(II) и Ni(II) дает тригональные комплексы типа $[\text{M}(\text{O})_3(\text{PMe}_3)]^{2+}$ (где M = Co, Ni). Десять величин D_q для PMe_3 являются 2,1 и 2,4 раза больше, чем эти же величины для структурных атомов кислорода или молекул растворителя. Такие же комплексы формируются между диметилфенилфосфином и Ni(II) на гекторите и на синтетическом цеолите Y. Co(II) формирует псевдотетраэдрические комплексы с диметилфенилфосфиновыми лигандами. Эти поверхностно связанные комплексы переходных металлов сильно взаимодействуют с NO и $\text{CH} \neq \text{CH}$ и слабее с CO и $\text{CH}_2 = \text{CH}_2$, формируя новые типы комплексов. [E.G.]

Resümee—Die Gasphasenadsorption von Trimethylphosphin an mit Co(II) und Ni(II) ausgetauschten Hectorit ergibt trigonale Komplexe vom Typ $[\text{M}(\text{O})_3(\text{PMe}_3)]^{2+}$ (M = Co, Ni). Die 10- D_q -Werte von PMe_3 sind 2,1 und 2,4 mal größer als die der Struktur-Sauerstoffe oder der Lösungsmittelmoleküle. Die gleichen Komplexe bilden sich zwischen Dimethylphenylphosphin und Ni(II) an Hectorit und an synthetischem Zeolith Y. Co(II) bildet pseudotetraedrische Komplexe mit Dimethylphenylphosphin-Liganden. Diese Oberflächen-immobilisierten Übergangsmetallkomplexe zeigen starke Wechselwirkung mit MO und $\text{CH}=\text{CH}$ und geringere Wechselwirkung mit CO und $\text{CH}_2=\text{CH}_2$, wobei neue Komplexotypen entstehen. [U.W.]

Résumé—L'adsorption du gaz triméthylphosphine sur hectorite, échangée par Ni(II) et Co(II), mène aux complexes trigonaux du type $[\text{M}(\text{O})_3(\text{PMe}_3)]^{2+}$ (M = Co, Ni). Les valeurs de 10 D_q du ligand PMe_3 sont 2,1-2,4 fois plus larges que celles des oxygènes du réseau ou des molécules du solvant. Les mêmes complexes sont synthétisés par adsorption de diméthylphénylphosphine sur hectorite et sur la zéolithe synthétique Y, échangées par Ni(II). Le Co(II) forme des complexes pseudotétraédriques avec diméthylphénylphosphine. Tous ces complexes de surface réagissent fortement avec NO et acétylène et faiblement avec CO et éthylène.