Identification of a Low-Spin Co^{2+}–Trimethylphosphine Complex in Zeolites Y

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Summary The adsorption of PMe_3 on dehydrated CoY zeolites gives a low-spin $[Co(PMe_3)_3]^{2+}$ complex, which is destroyed by room temperature evacuation

CURRENT interest in the immobilization of homogeneous catalysts on polymeric and inorganic supports[1] has prompted us to undertake a spectroscopic study of the complexes of transition metal ions and tertiary phosphines on zeolites Our aim was to identify and characterize the surface-immobilized complexes and to study their thermal stability and their interaction with small molecules Zeolites are ideally suited for this type of work because they are well-crystallized, high surface area solids whose pore system allows passage of only the smallest tertiary phosphines We report here for the first time e s r and electronic spectra of a low-spin Co^{2+}–trimethylphosphine complex, stabilized in the supercages of the zeolite Y

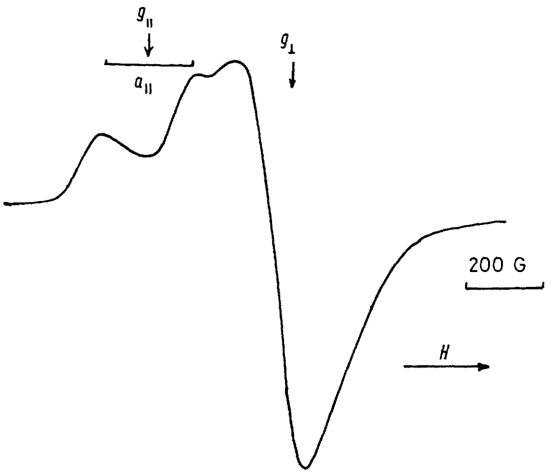


FIGURE 1 *X* Band e s r spectrum of the $Co^{2+}(PMe_3)_3$ complex in zeolite Y recorded at liquid N_2 temperature

Co^{2+} was exchanged into NaY to give the materials CoY_7, CoY_{14} and CoY_{16} [The numbers after the sample symbols are the number of Co^{2+} ions per unit cell and Y stands for $(AlO_2)_{56}(SiO_2)_{136}$] The samples were dehydrated *in vacuo* (pressure $<1\ 351 \times 10^{-2}$ Pa) at 723 K for $1\ 728 \times 10^5$ s PMe_3, prepurified by evacuation at 183 K, was adsorbed at 295 K The zeolites adsorbed 33 ± 1 PMe_3 molecules per unit cell irrespective of the Co^{2+} content and they all acquired a greyish colour An axially symmetric e s r signal was produced (Figure 1) with $g_{|} = 2\ 348 \pm 0\ 005$, $g_{\perp} = 2\ 078 \pm 0\ 005$, and $A^{P} = 0\ 0232 \pm 0\ 005\ cm^{-1}$, but no resolved Co-hyperfine lines The e s r spectrum is consistent with a low-spin Co^{2+}-complex The corresponding reflectance spectrum is shown in Figure 2 Typical bands of the phosphine complex are centered at 5700, 10,300, 17,500, and 22,100 cm^{-1} The shoulder around 15,000 cm^{-1} can be ascribed to residual, uncomplexed Co^{2+} The intensity of the 22,100 cm^{-1} band, which does not overlap with bands due to uncomplexed Co^{2+}, and the intensity of the e s r signal are both proportional to the Co^{2+}-content However, both signals disappear with evacuation at room temperature

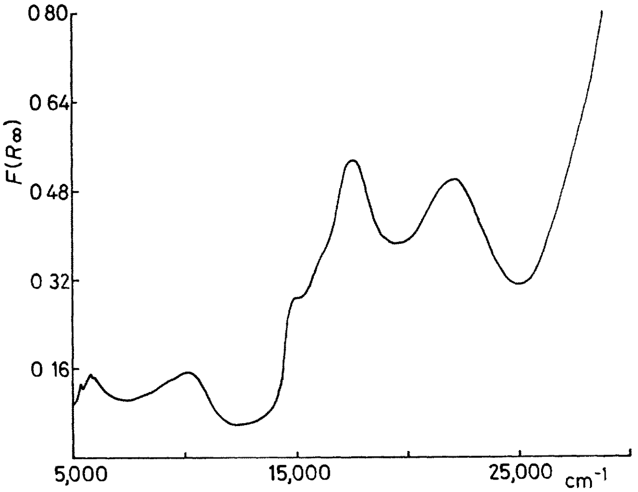


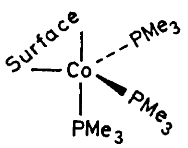
FIGURE 2 Reflectance spectrum of $[Co(PMe_3)_3]^{2+}$ on CoY_7

We suggest that the e s r signal and the reflectance spectrum are due to the low spin complex $[Co(PMe_3)_3]^{2+}$ for the following reasons Most complexes of Co^{2+} with tertiary phosphines are pseudotetrahedral $Co(PR_3)_2X_2$ complexes[2] Low-spin complexes are formed as a result either of a dimerisation process or of the equilibrium (1)

$$Co(PR_3)_2X_2 + PR_3 \rightleftharpoons Co(PR_3)_3X_2 \tag{1}$$

shifting to the right in the presence of excess of phosphine[3 4] Dimerisation is unlikely to occur in zeolites because of the low mobility of the complexes on the surface Indeed identical spectra are obtained on CoY_7 (<1 Co^{2+} per supercage) and on CoY_{16} (2 Co^{2+} per supercage) Excess of PMe_3 is present when Co^{2+} in the supercages is exposed to gaseous PMe_3 implying that an equilibrium similar to (1) is established In the presence of gaseous PMe_3 this equilibrium is completely shifted to the right and the low-spin complex is formed. Upon evacuation of excess of PMe_3 it is shifted to the left, destroying the low-spin complex. The presence of a superhyperfine structure with only one P atom, and the fact that $g_{\parallel} > g_{\perp} > 2 \cdot 0023$ lead to the conclusion that the unpaired electron formally occupies a d_{z^2} orbital, but considerable mixing between d_{z^2} and $d_{x^2-y^2}$ occurs.[4] This means that these 2 orbitals are energetically relatively close to each other which is possible if the geometry imposed by the 3 PMe_3 molecules is distorted from D_{3h} symmetry. The most likely structure is (**1**), because one PMe_3 group is co-ordinated along the z-axis which allows the closest contact between Co^{2+} and the surface.

Attempts to synthesize the complex in the supercages of zeolites X failed which illustrates the dramatic effect of surface charge density on co-ordination power of Co^{2+} in zeolites.



(1)

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