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Preparation and Proton Magnetic Resonance Spectra of Hexakis(trimethylphosphite)cobalt(III) Perchlorate

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Little attention has been paid to symmetric tervalent cobalt complexes which contain directly coordinated six phosphorus ligand atoms. Because of the strongly reducing character of tervalent phosphorus and the oxidative activity of cobalt(III), it is necessary to adjust the conditions very carefully to synthesize these $[CoP_6]$-type complexes. Several years ago, the preparation of several $Co^{III}P_6$-type complexes including trimethylphosphite was reported, but the characterization of these complexes was prevented because of their insolubility and shock-sensitivity of their perchlorates [1–3].

We have prepared these hexakis(trimethylphosphite)cobalt(III) complexes after the slightly modified procedure reported by Verkade and his coworkers [1–3]. Several characterizations were carried out including proton magnetic resonance.

Experimental

Preparation of Complexes

Cobalt (II) salts have been known to disproportionate in the presence of excess trialkyl phosphite esters. In the case that the anions have a poorly coordinating character, the following reaction occurs for trimethylphosphite:

$$2Co(II) + 11P(OCH_3)_3 \rightarrow [Co^{I}(P(OCH_3)_3)_5]^{+} + [Co^{III}(P(OCH_3)_3)_6]^{3+}$$

The recommended procedure is as follows. The precooled ethyl acetate solution of freshly recrystallized cobalt(II) perchlorate hexahydrate (3.7 g, 10 mmol) was stirred into a large excess 25 g, 200 mmol) of trimethylphosphite which was also precooled in an ice-salt bath. After the exothermic reaction ceased, the crude tervalent complex precipitated as dirty-yellow powder. The precipitate was collected by filtration and rinsed with ethanol and water. The crude complex was recrystallized rapidly from dimethylsulfoxide/water. This recrystallized complex proved to be sufficiently pure for proton magnetic resonance measurements and gave good elemental analyses, but the yellowish coloring suggested the coexistence of impurities. To obtain much purer complex, the crude complex was converted once to a water-soluble form by grinding with a suspension of strongly basic anion exchange resin (Amberlite CG-66) of fluoride form (the aqueous solution of the chloride of this complex was unstable on standing). After the resin was removed by filtration, a saturated sodium perchlorate solution was added into the filtrate. The pure perchlorate was obtained as almost colorless solids. *Anal.*: Calcd for $C_{18}H_{54}O_{30}CoCl_3P_6$ (= $[Co(P(OCH_3)_3)_6](ClO_4)_3$): C, 19.62; H, 4.94; Co, 5.34; P, 16.86%. Found: C, 19.82; H, 4.60; Co, 5.22; P, 16.85%.

The tetraphenylborate and tetrafluoroborate were obtained also as colorless solids with corresponding sodium salts as precipitants instead of sodium perchlorate, and gave good analyses.

The well-known univalent complex, pentakis(trimethylphosphite)cobalt(I) perchlorate was isolated from the mother liquor of the crude tervalent complex by dilution with a large amount of water as golden-yellow needle-like crystals.

The selection of the solvents for cobalt(II) perchlorate was very important to improve the yield of the tervalent complex. The highest yield was achieved when ethyl acetate was used as for the solvent of cobalt(II) perchlorate (45–60%). Diglyme and tetrahydrofuran yielded somewhat lower. Acetone, ethanol, acetonitrile and dioxane gave only 2–5% yields against the cobalt(II) perchlorate.

Spectral Measurements

Infrared spectra were recorded with a Hitachi EPI-G2 grating-type spectrometer as Nujol mulls. Visible and ultraviolet spectra were recorded with a Hitachi EPS-3 as an acetonitrile solution. Proton nuclear magnetic resonance (pmr) spectra were taken with JEOL-PS-100 operating at 100 MHz. The complex was dissolved in acetonitrile, and tetramethylsilane was used as an internal standard. All measurements were carried out at room temperature.

Results and Discussion

The visible and ultraviolet spectra showed a shoulder at about 350 nm, which can be assigned to the d–d transition of $3d^6$ cobalt(III) ($\log\epsilon = 2.0$). The ligand field strength in this complex is only slightly

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smaller than that in the hexacyanocobaltate(III), which is the strongest ligand among numerous tervalent cobalt complexes. The infrared spectra showed the strong ν(P–O–C) band at around 1050 cm^{-1}, but no ν(P=O) band at 1200–1300 cm^{-1}. The lack of ν(P=O) band proved that there occurred no decomposition (or rearrangement) of phosphite esters to phosphonates which occasionally occurs in the metal complex formation (*cf.* $[HgX_2 \cdot P(OR)_3]_2 \rightarrow 2XHgP(=O)(OR)_2 + 2RX$) [4–6].

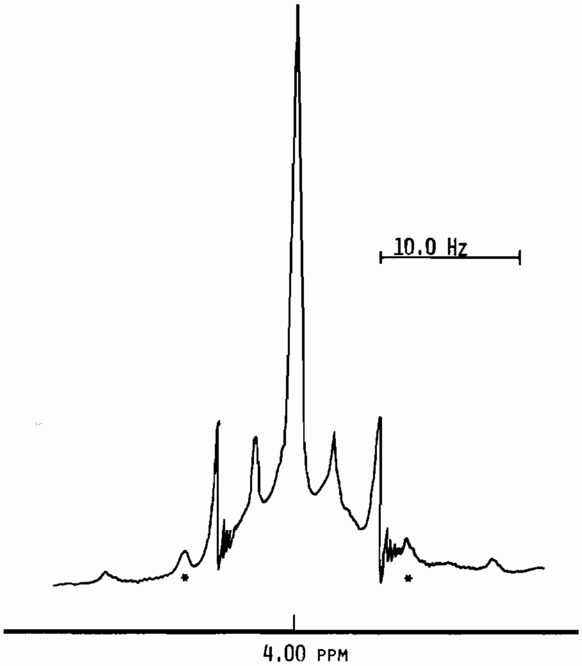

Figure 1. Proton nmr spectra of hexakis(trimethylphosphite)-cobalt(III) perchlorate in acetonitrile solution (100 MHz, room temp.) The starred peaks are spinning sidebands.

The typical pmr spectrum of this $[Co(P(OCH_3)_3)_6]^{3+}$ complex is shown in Fig. 1. The symmetric multiplet is 4.00 ppm downfield from tetramethylsilane. No other protons can be observed in the ordinary region (0–10 ppm). This multiplet can be analyzed as follows.

The spin system of this complex cation $[Co(P(OCH_3)_3)_6]^{3+}$ is very complicated. There are one cobalt-59 ($I = 7/2$), six phosphorus-31 ($I = 1/2$), and fifty-four protons. From the feature of the spectrum of Fig. 1, the scalar coupling constants between central cobalt-59 and protons, (${}^4J$(Co–P–O–C–H)), and between four *cis*-phosphorus-31 nuclei and protons, (${}^5J$(P–Co–P–O–C–H) (*cis*) can be assumed to be negligibly small. If the former coupling constant were moderately large, octets of nearly equal intensities should appear due to the scalar coupling with cobalt-59. The lack of quintets whose relative intensities are 1:4:6:4:1 also proved that the ${}^5J$(P–Co–P–O–C–H) (*cis*) is almost zero. From the above-mentioned spectral characteristics, the spin system can be so simplified as $X'_9A'AX_9$, where A and A′ refer to phosphorus-31 nuclei which coordinate to the central cobalt in *trans*-position, and X and X′ to methyl protons, respectively. Namely, only two phosphite groups should be considered which are *trans*-coordinated to each other.

After Harris [7], the spectra of the X part in the $X'_nA'AX_n$ system (where J(A–X) = J(A′–X′), and J(A–X′) = J(A′–X)) consist of (i) a pair of intense doublets, whose intensity Z(0) is the sum of J(A–X) and J(A–X′), (ii) n pairs of inner doublets, and (iii) n pairs of outer doublets. The separation S and intensity Z for each doublet are calculated in the following equation (the intensity of the weakest doublet was taken as 1). The calculation of X and Z values are much simplified by applying the following parameters:

$$N = {}^3J(P\text{–}O\text{–}C\text{–}H) + {}^5J(P\text{–}Co\text{–}P\text{–}O\text{–}C\text{–}H)\,(\textit{trans})$$
$$L = {}^3J(P\text{–}O\text{–}C\text{–}H) - {}^5J(P\text{–}Co\text{–}P\text{–}O\text{–}C\text{–}H)\,(\textit{trans})$$
$$J = {}^2J(P\text{–}Co\text{–}P)\,(\textit{trans})$$
$$g = [x(x-1)L^2 + J^2]/([x^2L^2 + J^2]\cdot[(x-1)^2L^2 + J^2])^{1/2}$$

In our case, x is from 1 to 9 and n is equal to 9.

(i) The intense Doublet

$$S(0) = N$$
$$Z(0) = 2^{2n-1} = 2^{17}$$

(ii) The Inner Doublets

$$S_i(x) = (x^2L^2 + J^2)^{1/2} - [(x-1)^2L^2 + J^2]^{1/2}$$
$$Z_i(x) = (2n)^{-1}(1+g)\sum_{r=x}^{n} r\cdot{}_nC_r\cdot{}_nC_{r-x}$$

(iii) The Outer Doublets

$$S_o(x) = (x^2L^2 + J^2)^{1/2} + [(x-1)^2L^2 + J^2]^{1/2}$$
$$Z_o(x) = (2n)^{-1}(1-g)\sum_{r=x}^{n} r\cdot{}_nC_r\cdot{}_nC_{n-r}$$

The separation of the most intense lines in the X part of $X'_nA'AX_n$ multiplets is given by N. Using the above arguments, this implies that when an intense singlet is observed for the pmr spectra as in our case, J(A–X) seems nearly equal to –J(A–X′), that is, the two phosphorus–proton coupling constants, ${}^3J$(P–O–C–H) and ${}^5J$(P–Co–P–O–C–H) (*trans*), are equal in magnitude and opposite in sign. The shape of these multiplet spectra is strongly dependent on the L and J values. The three coupling constants can be obtained from the best-fit values of L and J as ${}^3J$(P–O–C–H) = 6.25 Hz, ${}^5J$(P–Co–P–O–C–H) (*trans*) = –6.25 Hz (or *vice versa*), and the absolute value of ${}^2J$(P–Co–P) (*trans*) is 10.5 Hz. The last coupling constant is probably negative [8]. The simulated spectrum is shown in Fig. 2 with the above parameters.

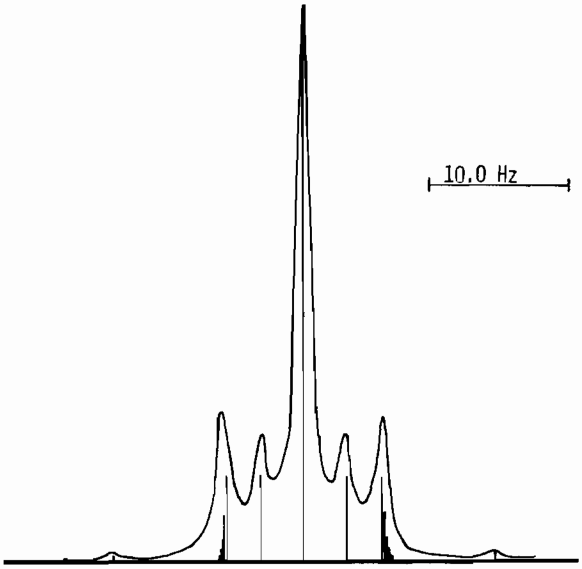

Figure 2. Calculated proton nmr spectrum of hexakis(trimethylphosphite)cobalt(III) complex as $X'_9A'AX_9$ spin system with the following parameters: ^3J(P–O–C–H) = 6.25 Hz, ^5J(P–Co–P–O–C–H) (*trans*) = –6.25 Hz, ^2J(P–Co–P) (*trans*) = 10.5 Hz.

The algebraic cancellation of ^3J(P–O–C–H) and ^5J(P–Co–P–O–C–H) (*trans*) is interesting but there are cases to be compared with. The only one example is the carbon-13 nmr spectra of phosphite complexes which have been studied by Verstuyft, Nelson and Cary [9] for several d^8 complexes, who concluded that such algebraic cancellation of coupling constants in $[A_2]X$ spin systems containing two phosphorus nuclei is fairly common. The lack of similar cancellation data in proton nmr might be attributed to the complexity of the spectra and the difficulty of the preparation of these *trans*-bis(phosphite) complexes.

The decrease of ^3J(P–O–C–H) on complex formation of phosphite can be attributed to the change of s-character of the phosphorus atoms and the change of conformation of trimethylphosphite molecules. In a free molecule, the most stable conformation of trimethylphosphite seems to be an umbrella-like one considering the repulsion of three bulky methyl groups. In the hexakis-complex, however, the much crowded geometry surrounding the relatively small cobalt(III) ions might cause a change of conformation to a bell-like one, which is somewhat similar to that in "cage phosphites" such as $P(OCH_2)_3CCH_3$ which have much smaller ^3J(P–O–C–H) values. For *trans*-bis(phosphite) complexes such as *trans*-$Mo(CO)_4[P(OCH_3)_3]_2$, which have much looser structure (or smaller steric hindrances) than the hexakis(phosphite) complexes, only a slight change of ^3J(P–O–C–H) values has been reported on complex formation [10].

The relatively large ^2J(P–Co–P) (*trans*) value (probably negative) shows the existence of *trans*-interaction in this $3d^6$-type complex as well as in many d^8 complex. This seems to be consistent with the large ^5J(P–Co–P–O–C–H) (*trans*) value. For the first transition metal complexes, the ^2J(P–M–P) (*trans*) values of ^5J(P–M–O–C–H) (*trans*) values have been only scarcely reported except several Cr(0) complexes [11]. The decreasing trend of this "virtual coupling constant" is obvious as $5d^6$ complexes > $4d^6$ complexes > $3d^6$ complexes, which is parallel to the nd^8-type complexes. This "virtual coupling" and the long range interaction (^5J) can be attributed to the fact that a common P_σ orbital of metals is shared between the two *trans*-coordinated phosphorus nuclei, whereas this is not the case in the *cis*-phosphorus nuclei [10].

From the acetonitrile solution of this hexakis(trimethylphosphite)cobalt(III) perchlorate stored for several days, a small amount of transparent plate-like colorless crystals was deposited. The proton nmr spectra of these crystals in acetonitrile solution were very complicated, but their similarity to those of the carbonylpentakis(trimethylphosphite)molybdenum(0) suggests that pentakis(trimethylphosphite)-cobalt(III) complexes were formed by decomposition or ligand exchange in acetonitrile. Further investigation on these complexes is in progress.

Acknowledgments

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