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PREPARATION AND PROPERTIES OF A NOVEL COMPLEX OF THE $[Co^{III}P_6]^{3+}$-TYPE, TRIS{1,2-BIS(DIMETHYLPHOSPHINO)ETHANE}COBALT(III) PERCHLORATE

Tomoji OHISHI, Kazuo KASHIWABARA, and Junnosuke FUJITA*
Department of Chemistry, Faculty of Science, Nagoya University,
Nagoya 464

The $[Co\{(CH_3)_2PCH_2CH_2P(CH_3)_2\}_3](ClO_4)_3$ complex was prepared from *trans*-$[CoCl_2\{(CH_3)_2PCH_2CH_2P(CH_3)_2\}_2]ClO_4$ and the diphosphine ligand. The lemon yellow trisdiphosphine complex is rather unstable to air even in the solid state to turn gradually orange yellow.

Chatt and Watson$^{1)}$ prepared the zero valent chromium group metal (d^6) complexes of 1,2-bis(dimethylphosphino)ethane (dmpe), $M(dmpe)_3$(M = Cr, Mo, and W). The crystal structure of $[Cr(dmpe)_3]$ was recently determined by the X-ray diffraction method.$^{2)}$ The dmpe ligand is regarded as a good π-acceptor to stabilize a low valent metal complex.$^{1)}$ Here we report a high valent metal complex of dmpe, $[Co(dmpe)_3]^{3+}$ with the same d^6 electrons. This is the first example of the $[Co^{III}P_6]^{3+}$-type phosphine complex, although phosphite complexes of the same type have been reported.$^{3)}$

All the preparative procedures were carried out in nitrogen atmosphere. To an oxygen-free methanol solution (80 cm^3) of $CoCl_2 \cdot 6H_2O$ (150 mg, 0.63 mmol) was added dmpe (190 mg, 1.27 mmol),$^{4)}$ giving immediately a red brown solution. It was stirred for 20 min and then evaporated to dryness. The residue was dissolved in dichloromethane (100 cm^3), into which Cl_2 gas was bubbled for 10 min. The resulting green solution was evaporated to dryness, and the residue was dissolved in methanol. The solution gave a pale green precipitate upon addition of excess sodium perchlorate. Yield: 160 mg (48%). Found: C, 27.21; H, 6.17%. Calcd for $[CoCl_2(dmpe)_2]ClO_4$: C, 27.21; H, 6.09%. This complex can be assigned to the trans isomer, since the absorption spectrum in the low energy region resembles that of *trans*-$[CoCl_2(en)_2]^+$ (en = ethylenediamine). The complex is soluble in methanol and ethanol, and stable to air in solution. It is also soluble in water, but liberates the chloride ions to give an aqua complex.

To this green complex (300 mg, 0.57 mmol) in oxygen-free methanol (100 cm^3) was added dmpe (430 mg, 2.86 mmol). The solution was stirred for 10 h at room temperature, the color turning yellow slowly, and then filtered. The filtrate was mixed with excess sodium perchlorate and cooled to give a lemon yellow precipitate, which was filtered and washed with diethyl ether and methanol successively to remove excess dmpe and sodium perchlorate. Yield: 200 mg (43%). Found: C, 27.27; H, 6.08; P, 23.15%. Calcd for $[Co(dmpe)_3](ClO_4)_3$: C, 26.77; H, 5.99; P, 23.01%. The complex is soluble in dimethyl sulfoxide, but insoluble in most other solvents. It is rather unstable to air even in the solid state, changing slowly to orange yellow from lemon yellow in color. The color change is much faster in solution. The orange yellow complex is not fully characterized yet. However, it is diamagnetic and shows an infrared absorption band at 1140 cm^{-1} assignable to the P-O stretching frequency, which is not observed in the spectrum of the lemon yellow complex. The complex exposed to air gives the first absorption band at 25000 cm^{-1}. This value is between those of the lemon yellow complex (26000 cm^{-1}) and a $[CoP_4O_2]$-type complex such as $[Co(CO_3)(dmpe)_2]^+$(23500 cm^{-1}).$^{5)}$ Thus the orange yellow complex appears to be a cobalt(III) complex of the $[CoP_5O]$-type comprising dmpe and the monoxide of dmpe.

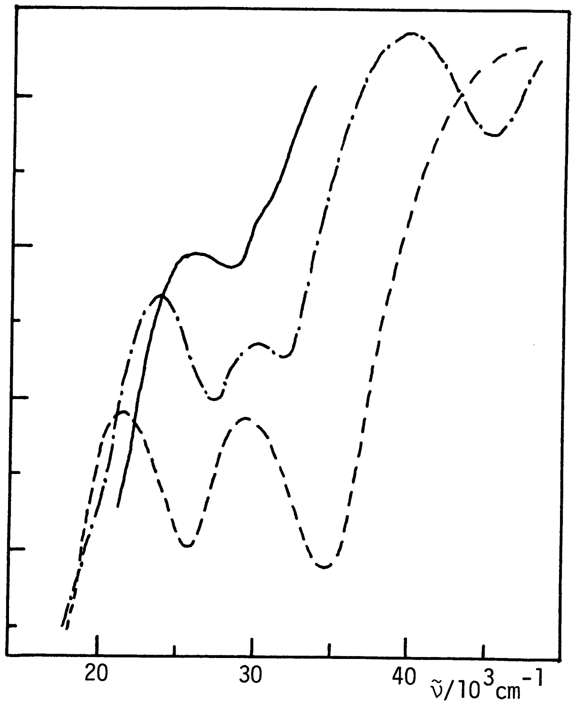

Figure Absorption spectra of $[Co(dmpe)_3]^{3+}$ in dimethyl sulfoxide (————), *fac*-$[Co(edmp)_3]^{3+}$ in water (—·—·—·—), and $[Co(en)_3]^{3+}$ in water (-------).

The lemon yellow complex in methanol containing excess halides such as KBr turns gradually green to afford *trans*-$[CoBr_2(dmpe)_2]^+$. Molecular models indicates that $[Co(dmpe)_3]^{3+}$ is like a ball surrounded by 12 methyl groups around the small Co^{3+} ion. Such a extremely crowded structure might be responsible for the lability of $[Co(dmpe)_3]^{3+}$.

The $[Co(dmpe)_3]^{3+}$ complex gives the first and second absorption bands at 26000 cm^{-1}(ε=933) and ca. 30500 cm^{-1}(shoulder), respectively. The Figure shows that the energy difference between the first and second absorption bands becomes markedly small by the coordination of a phosphine ligand, indicating strong covalent character in the Co(III)-phosphine bond.$^{6)}$ The maximum wavenumber of the first absorption band of *fac*-$[Co(edmp)_3]^{3+}$(edmp = (2-aminoethyl)dimethylphosphine) (23700 cm^{-1})$^{7)}$ is exactly the average of those of $[Co(dmpe)_3]^{3+}$ and $[Co(en)_3]^{3+}$(21400 cm^{-1}). This indicates that Yamatera's rule$^{8)}$ on the shift and splitting of d-d bands holds in cobalt(III) complexes containing a phosphine ligand.

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