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Variable Temperature Electronic Spectra of the Two Low Spin Five-coordinate Cobalt(I) Complexes $[Co^I(CO)_2\{P(C_6H_5)(OC_2H_5)_2\}_3][B(C_6H_5)_4]$ and $Co^II(CO)_2\{P(C_6H_5)(OC_2H_5)_2\}_2$

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Solution and solid state electronic spectral measurements at 295, 77 and 7° K, have been carried out on the low spin five-coordinate $[CO^I(CO)_2\{P(C_6H_5)(OC_2H_5)_2\}_3][B(C_6H_5)_4]$ *(I) and* $Co^II(CO)_2\{P(C_6H_5)(OC_2H_5)_2\}_2$ *(II). The presence of two moderately intense ligand field bands at respectively 27.4* ($\varepsilon_{EPA} = 420$) *and 30.5 kK* ($\varepsilon_{EPA} = 980$) *for (I) and 22.6* ($\varepsilon_{EPA} = 650$) *and 26.0 kK* ($\varepsilon_{EPA} = 1700$) *for (II) is consistent with a trigonal bipyramidal geometry of* C_{2v} *symmetry for both complexes. Allowed* $I \rightarrow Co(I)$ *charge transfer bands are observed at 29.0 kK and 34.5 kK for (II), whereas an allowed* $P(C_6H_5)(OC_2H_5)_2 \rightarrow Co(I)$ *is found at 39.6 kK for (I) and 40.0 kK for (II).*

Introduction

Although a lot of work has yet been done on the nature of the bonding in five-coordinate complexes, the problem is still of interest because the geometries of these compounds are very dependent on changes in bonding.

As electronic spectroscopy is a very sensitive tool to determine the stereochemistry of the metal in d^8 complexes, we have initiated the study of the electronic spectra of the $[Co^I(CO)_2\{P(C_6H_5)(OC_2H_5)_2\}_3][B(C_6H_5)_4]$ and $Co^II(CO)_2\{P(C_6H_5)(OC_2H_5)_2\}_2$. These compounds are among the relatively scarce number of isolated five-coordinate cobalt(I) complexes containing monodentate ligands, such as $[Co^I\{P(OR)_3\}_5]^+$ [1,2], $[Co^I(CNR)_5]^+$ [3], $[Co^I(CN)_X(CO)_Y(PR_3)_Z]^{(1-x)}$ [4] and only very few electronic spectral studies have been reported [5]. They have been first prepared by Orio *et al.* [6], who have assumed for both a *cis*-trigonal bipyramidal structure (with the carbonyl groups in equatorial positions) on the basis of the number, position and intensity of the ν(CO) stretching frequencies and variable temperature PMR spectra.

Results and Discussion

We have measured the room and low (77 and 7° K) temperature electronic spectra of both complexes in E.P.A. solution at several concentrations and in the solid state (as a thin film of vinylpolyacetate). The spectra are the same in solution and in the solid state, showing that no appreciable dissociation occurs. Nevertheless, the solutions were studied immediately after the preparation, because the $Co^II(CO)_2\{P(C_6H_5)(OC_2H_5)_2\}_2$ solutions decompose on standing. At 77° K, the resolution of the spectra is significantly improved, owing to the band narrowing and no more changes occur on lowering the temperature to 7° K.

The solid state and solution spectral data are presented in Table I. As the low energy ligand field bands lie high in energy, due to the high position of the carbo-

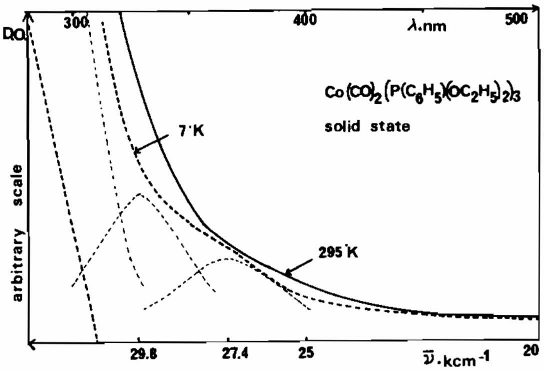


Figure 1: Solid state electronic spectrum of $Co^I(CO)_2\{P(C_6H_5)(OC_2H_5)_2\}_3^+$: ——295° K, ----7° K and the gaussian analysis of the 7° K spectrum.

TABLE I. Electronic Spectra of Complexes [ν, kK (ε)].

$[Co^I(CO)_2\{P(C_6H_5)(OC_2H_5)_2\}_3][B(C_6H_5)_4]$

Assignment	E.P.A.		Solid		
	295°K	77°K	295°K	77°K	7°K
$^1A_1 \rightarrow {}^1A_1$	27.8 sh (500)	27.4 sh (420)	27.8 sh	27.4 sh	27.2 sh
$^1A_1 \rightarrow {}^1B_1$		30.5 sh (980)		29.8 sh	30.5 sh
Charge Transfer					
P→Co	39.6 (22300)		38.5	38.0	

$Co^II(CO)_2\{P(C_6H_5)(OC_2H_5)_2\}_2$

Assignment	E.P.A.		Solid		
	295°K	77°K	295°K	77°K	7°K
$^1A_1 \rightarrow {}^1A_1$	22.5 (300)	22.6 (650)	22.2	22.2	22.7
$^1A_1 \rightarrow {}^1B_1$	26.3 sh (1700)	26.0 sh (1700)	26.0 sh	25.6 sh	26.7 sh
I→Co	29.0 (3000) 34.5 (4200)	29.1 (4100)	29.0	29.0	29.4
P→Co	40.0 (>22000)		39.2	39.2	

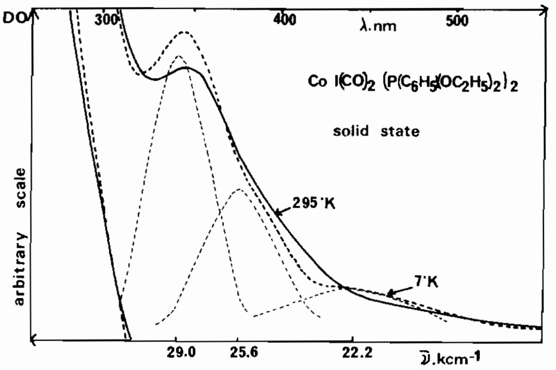
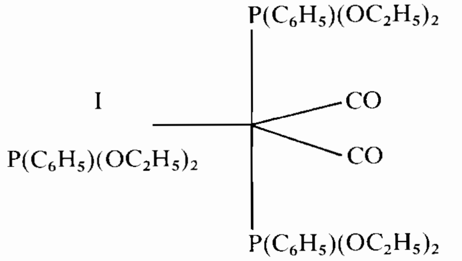


Figure 2: Solid state electronic spectrum of $Co^II(CO)_2\{P(C_6H_5)(OC_2H_5)_2\}_2$: ——295° K, ----7° K and the gaussian analysis of the 7° K spectrum.

nyl and the phosphonite groups in the spectrochemical series, a gaussian analysis was necessary to elucidate the energies and the extinction coefficients of these bands. The solid state spectrum of both complexes and their gaussian analyses are shown in figures 1 and 2.

If following the infrared and NMR results of Orio *et al.*[6], we assume for both complexes a *cis*-trigonal bipyramidal geometry of C_{2v} symmetry,



we should expect in the ligand-field part of the electronic spectra a three-band system, as for the isoelectronic Ni(II) complex $Ni^{II}I_2\{P(OCH_3)_3\}_3$[7]. These bands should correspond to the symmetry allowed $^1A_1 \rightarrow {}^1A_1$ $(a_1d_{x^2-y^2} \rightarrow a_1d_{z^2})$, $^1A_1 \rightarrow {}^1B_1$ $(b_1d_{xy} \rightarrow a_1d_{z^2})$ and $^1A_1 \rightarrow {}^1B_2(b_2d_{xz} \rightarrow a_1d_{z^2})$ transitions.

We observe for both compounds two bands resolved at 77° K in EPA at 27,4 kK (ε = 420) and 30.5 kK (ε = 980) for $[Co^I(CO)_2\{P(C_6H_5)(OC_2H_5)_2\}_3]^+$ and 22.2 kK (ε = 650) and 25.6 kK (ε = 1700) for $Co^II(CO)_2\{P(C_6H_5)(OC_2H_5)_2\}_2$ the energies and extinction coefficients of which are nicely consistent with the two expected $^1A_1 \rightarrow {}^1A_1$ and $^1A_1 \rightarrow {}^1B_1$ ligand field transitions. These bands lie in the same region as those found for the $^1A_1 \rightarrow E$ transition in the trigonal bipyramidal (D_{3h} symmetry) $[Co^I\{P(OCH_3)_3\}_5]^+$ (26.2 kK, ε = 1000) and isoelectronic $Ni^{II}\{P(OCH_3)_3\}_5^{++}$ (24.8 kK, ε = 2500)[1]. Another argument which confirms our attribution is the shift of these bands to the lower energies when one phosphonite group is replaced by one iodide group. The $^1A_1 \rightarrow {}^1B_2$ transition, known to be less intense[8], does not appear on the spectra, certainly buried under the more intense, fully allowed charge transfer transitions which are present for the same energy.

The bands at 29.0 kK and 34.5 kK are probably $p\pi I \rightarrow d\sigma^*$ and $p\sigma I \rightarrow d\sigma^*$ charge transfer transitions respectively. For comparison $Ni^{II}I_2\{P(OCH_3)_3\}_3$ has analogous charge transfer bands at 29.4 and 35.7 kK and no band occurs in this region in the $[Ni^{II}\{P(OCH_3)_3\}_5]^{++}$ and $[Co^I\{P(OCH_3)_3\}_5]^+$ species. Consequently, the band at about 39.6 kK ($\varepsilon_{EPA} = 22300$) in $[Co^I(CO)_2\{P(C_6H_5)(OC_2H_5)_2\}_3]^+$ and 40.0 kK ($\varepsilon_{EPA} = 22000$) in $Co^I I(CO)_2\{P(C_6H_5)(OC_2H_5)_2\}_2$ are attributable to the $\sigma P\{(C_6H_5)(OC_2H_5)_2\} \rightarrow d\sigma^*$ Co^I, a result which is confirmed by the presence of a similar transition at 39.6 kK ($\varepsilon = 16000$) in $[Co^I\{P(OCH_3)_3\}_5]^+$, 40.2 kK ($\varepsilon = 16000$) in $[Ni^{II}\{P(OCH_3)_3\}_5]^{++}$ and 39.8 kK ($\varepsilon = 21000$) in $Ni^{II}I_2\{P(OCH_3)_3\}_3$.

A summary of transition assignments for both complexes is given in Table I. The entire spectra are consistent with those expected for a trigonal bipyramid of C_{2v} symmetry for both complexes, that is with the scheme proposed. This result agrees with the fact that the trigonal bipyramidal geometry seems to be the preferential structure for d^8 complexes $(ML_5)^{n+}$ or MX_2L_3 with soft central atom (Co^I, Fe^0) and soft monodentate ligands, that is when no steric nor chelating properties of the ligands are to be considered.

The occupation of the equatorial positions of the trigonal bipyramid by the two CO groups in $[Co^I(CO)_2\{P(C_6H_5)(OC_2H_5)_2\}_3]^+$ and by two CO and one iodide groups in $Co^I I(CO)_2\{P(C_6H_5)(OC_2H_5)\}_2$ is too in agreement with the expectation that more strongly bonding ligands should preferentially occupy the equatorial position because of the greater availability of metal *d* orbitals of the proper symmetry to form bonds with the ligands in equatorial position. This result agrees, too, with the observation that when two ligands are in competition in a trigonal bipyramid, the more polarizable one is preferentially in equatorial position: iodine, more polarizable than $P(OCH_3)_3$, $P(C_6H_5)(OC_2H_5)_2$, $P(CH_3)_3$, $P(C_6H_5)(CH_3)_2$, $PH(C_6H_5)_2$, is always in equatorial position in the trigonal bipyramidal $Ni^{II}I_2L_3$ complexes [7–10]. Nevertheless, other arguments (such as σ bonding) must not be neglected since the former observations cannot explain why, in the low spin five-coordinate TBP $Ni^{II}(CN)_2(PR_3)_3$, the CN groups, more polarizable and better σ bonding than the phosphine groups, are found in axial position[5,12,13].

Experimental Section

Preparation of the Compounds $[Co^I(CO)_2\{P(C_6H_5)(OC_2H_5)_2\}_3][B(C_6H_5)_4]$ *and* $Co^I I(CO)_2\{P(C_6H_5)(OC_2H_5)_2\}_2$.

The two complexes have been prepared following the procedure of Orio *et al.*[6].

Physical Measurements

Electronic spectra were measured on a CARY 14 recording spectrophotometer, using E.P.A. (a 5:5:2 mixture of diethylether, isopentane and ethanol (FLUKA *puriss.*)). Solutions in 1 cm silica cells were held in a low temperature Dewar. The spectra of solid complexes are examined using a thin film of Rhodopas (vinylacetate) as a support.

Gaussian analysis are performed on the spectra using a DUPONT Model 310 curve analyser.

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