

## Absorption Spectra and Optical Electronegativities of Cobalt(II) and Cobalt(III) Phosphine Complexes

KAI ARNE JENSEN

*Chemical Laboratory II, University of Copenhagen, Denmark*

and CHR. KLIXBÜLL JØRGENSEN

*Cyanamid European Research Institute, Cologny (Geneva), Switzerland*

The absorption spectra of  $[\text{CoX}_2(\text{R}_3\text{P})_2]$  and  $[\text{CoX}_3(\text{R}_3\text{P})_2]$  with  $\text{X} = \text{Cl}$  or  $\text{Br}$  and  $\text{R} = \text{C}_2\text{H}_5$ , are discussed with special emphasis on the "charge transfer" spectra. It is concluded that the assigning of an optical electronegativity of 2.6 to  $\text{P}(\text{C}_2\text{H}_5)_3$  accounts well for these bands.

The preparation of a series of cobalt(II) and cobalt(III) complexes of the types  $[\text{CoX}_2(\text{R}_3\text{P})_2]$  and  $[\text{CoX}_3(\text{R}_3\text{P})_2]$ , where  $\text{X} = \text{Cl}$  or  $\text{Br}$ , have recently been described<sup>1</sup>. In the following we discuss the electronic spectra of these compounds.

The tetrahedral complexes  $[\text{CoX}_2(\text{PR}_3)_2]$  have spectra (*cf.* Table 1) where the spin-allowed ligand field transition  ${}^4A_2 \rightarrow b^4T_1$  found at  $\sim 14\,000\text{ cm}^{-1}$  is split to some extent.<sup>2,3</sup> This splitting reflects partly that the spectrochemical effect of the phosphine,  $\text{PR}_3$ , is higher than that of the halogen,  $\text{X}$ , and partly that the complex has a distorted  $C_{2v}$  symmetry. For our purposes, however, the electron transfer bands at higher wavenumbers are more interesting.

The first electron transfer band of  $[\text{CoCl}_4]^{2-}$  is found at  $43\,000\text{ cm}^{-1}$ . However, from Table 1 it is seen that in our case electron transfer bands occur already in the region  $29\,000\text{--}35\,000\text{ cm}^{-1}$ . Applying<sup>4,5</sup> a spin-pairing correction of  $-6000\text{ cm}^{-1}$  and a spectrochemical correction of  $-4000\text{ cm}^{-1}$ , together with a value of  $x_{\text{opt}} = 1.9$  for  $\text{Co(II)}$  we get  $30\,000\text{--}10\,000 = 30\,000$  ( $x_{\text{opt}} - 1.9$ ) or  $x_{\text{opt}}$  of  $\text{P}(\text{C}_2\text{H}_5)_3 \sim 2.6$ . Though this value is rather uncertain, it is consistent with the electron transfer bands of comparable intensity observed<sup>6,7</sup> at  $\sim 25\,000\text{ cm}^{-1}$  for tetrahedral  $[\text{NiX}_2(\text{PR}_3)_2]$ . With a spin-pairing correction of  $-3000\text{ cm}^{-1}$ , a spectrochemical correction of  $-4000\text{ cm}^{-1}$  and with<sup>5</sup>  $x_{\text{opt}}(\text{Ni}) = 2.1$  we get here  $x_{\text{opt}}$  of  $\text{P}(\text{C}_2\text{H}_5)_3 \sim 2.7$ . The electron transfer

Table 1. Absorption band maxima for the complexes. We give wavenumbers  $\bar{\nu}$ , maximum molar extinction coefficients, and halfwidths  $\delta(-)$  towards smaller wavenumbers. Shoulders in parentheses, dubious features in double parentheses. The solvent used is pentane, except in the case of the visible spectra of the two cobalt(II) complexes where benzene was applied.

	$\bar{\nu}$ , cm <sup>-1</sup>	$\epsilon_{\max}$	$\delta(-)$ , cm <sup>-1</sup>
CoCl <sub>2</sub> (P(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>2</sub>	13 200	320	—
	(15 800)	420	—
	16 200	450	—
	((17 500))	190	—
	31 900	770	1000
	35 500	2 000	1600
	(39 700)	1 470	—
	47 000	9 500	2300
CoBr <sub>2</sub> (P(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>2</sub>	13 300	770	—
	15 200	1 190	600
	25 500	300	900
	((29 700))	2 950	—
	(33 000)	4 600	—
	35 500	5 040	—
	(44 500)?	13 000	—
CoCl <sub>3</sub> (P(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>2</sub>	47 200?	25 000	—
	18 000	6 900	1200
	(27 800)	1 960	—
	30 900	4 400	1500
	37 800	7 100	3400
	45 500	5 700	2800

bands would be expected to shift to even lower wavenumbers in Cu(II)phosphine complexes and actually an intense violet-blue colour is observed when trialkylphosphines are added to an alcoholic solution of copper(II) acetate.

It is noteworthy that  $x_{\text{opt}}$  of R<sub>3</sub>P is not lower than that of the iodide ion (2.5). However, the phosphines and arsines have only one lone-pair used for  $\sigma$ -orbital bonding in the complexes, whereas the halogen ions in addition have lone-pairs in the  $\pi$ -orbitals. The explanation is then that the optical electronegativities usually cited for the halide ligands refer to the looser bound  $\pi$ -orbitals. However, the  $\sigma$ -orbital of I<sup>-</sup> in hexahalide anions has <sup>8,9</sup>  $x_{\text{opt}} \sim 3.0$ .

A remarkable property of these cobalt(II) complexes is that they can be oxidized to five-coordinated compounds of the type [CoX<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub>]. These complexes have two unpaired spins, they are monomeric, and have probably a trigonal-bipyramidal structure. In such a chromophore the d orbitals span three levels,<sup>10</sup>

$$a_1' (2z^2 - x^2 - y^2) \quad e' (x^2 - y^2), (xy) \quad \text{and} \quad e'' (xz), (yz).$$

Let us apply <sup>11,12</sup> a qualitative LCAO—MO description. Placing the two phosphorus atoms on the z-axis,<sup>1</sup> the highest orbital  $a_1'$  is  $\sigma$ -antibonding with respect to all five ligand atoms, the  $e'$  orbitals are  $\sigma$ - and  $\pi$ -antibonding to the three halogen atoms in the plane, and the  $e''$  orbitals  $\pi$ -antibonding.

Therefore  $E(e'') < E(e') < E(a_1')$  and the ground state will have the configuration  $(e'')^4(e')^2$  possessing two unpaired spins.

The strong absorption band found at  $18\,000\text{ cm}^{-1}$  in the spectrum of  $[\text{CoCl}_3(\text{P}(\text{C}_2\text{H}_5)_3)_2]$  may be due to a ligand field transition  $e'' \rightarrow e'$  or  $e' \rightarrow a_1'$  or it may be an electron transfer band. The former possibility would normally be excluded by the high intensity of the band. However, in the trigonal bipyramidal chromophores  $[\text{PdX}(\text{As}(\text{C}_6\text{H}_4\text{AsPh}_2)_3)]^+\text{X}^-$  Savage and Venanzi<sup>13</sup> found very intense transitions ( $\epsilon \sim 7000$ ) at about  $20\,800\text{ cm}^{-1}$  with a shoulder at  $18\,700\text{ cm}^{-1}$ . They assigned these bands to an  $e' \rightarrow a_1'$  transition. The absence of a centre of inversion in  $\text{MX}_5$  complexes seems therefore to influence the intensities of the ligand field transitions more than is the case for *cis*- $\text{MX}_4\text{Y}_2$  complexes. The reason is probably that the chromophore  $\text{MX}_5$  in general has lower-lying odd states than has *cis*- $\text{MX}_4\text{Y}_2$ , and a mixing of odd and even states is therefore easier to achieve in the former than in the latter.

The lower sub-shell of octahedral cobalt(III) complexes<sup>5,14</sup> has  $x_{\text{opt}}$  between 2.3 and 2.4. A  $\sigma\text{P} \rightarrow e'$  transition makes the spin-quantum number  $S$ , associated with the electrons mainly located on the metal atom, go from  $S = 1 \rightarrow \frac{1}{2}$ . The spin pairing energy is  $D$ . On the other hand  $\sigma\text{P} \rightarrow a_1'$  makes  $S = 1 \rightarrow \frac{3}{2}$ , with a spin pairing energy of  $-2D$ .  $D \approx 7B$  is expected to be about  $3000\text{ cm}^{-1}$ . With Venanzi<sup>13</sup> we may take  $E(e') - E(e'') = 12\,000\text{ cm}^{-1}$  and  $E(a_1') - E(e'') = 30\,000\text{ cm}^{-1}$ . The transitions should then occur at

$$E(\sigma\text{P} \rightarrow e') = 30\,000 (2.6 - 2.3) + 3000 + 12\,000 = 24\,000\text{ cm}^{-1} \quad (1)$$

$$E(\sigma\text{P} \rightarrow a_1') = 30\,000 (2.6 - 2.3) - 6000 + 30\,000 = 33\,000\text{ cm}^{-1} \quad (2)$$

We then have two essentially different possibilities. Either the bands observed at  $27\,800$ ,  $30\,000$ , and  $37\,800\text{ cm}^{-1}$  (Table 1) are the electron transfer bands of eqns. (1) and (2), and the strong band at  $18\,000\text{ cm}^{-1}$  is the ligand field transition, or we have overestimated the wavenumbers in eqns. (1) and (2) slightly, and it is the transition  $\sigma\text{P} \rightarrow e'$  which occurs at  $18\,000\text{ cm}^{-1}$ .

A solution of  $[\text{CoBr}_3(\text{P}(\text{C}_2\text{H}_5)_3)_2]$  in benzene is dark blue and shows a band at  $17\,000\text{ cm}^{-1}$ . The small band shift of  $1000\text{ cm}^{-1}$  in going from the chloride complex to the bromide definitely indicates that the absorption band is not caused by electron transfer from orbitals mainly concentrated on the halide ions. However, it is in accord with both of the above assignment suggestions, and it is not possible, at present, to make a definite choice between these alternatives.

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