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Equilibria in Pseudotetrahedral Co^{II}-halide-phosphine Systems

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Pseudotetrahedral $[CoX_2P_2]$ and $[CoX_3P]^-$ complexes ($X = Cl, Br, I$; P = tertiary phosphine) undergo practically complete solvolytic displacement of phosphine in coordinating solvents such as acetonitrile, where phosphine-containing species can be formed only partially even in the presence of large excess of ligand. $[CoX_2P_2]$ and $[CoX_3P]^-$ are more stable in non-coordinating solvents like dichloromethane, but limited solubility and solvent-ligand interactions still make accurate measurements of the phosphorus-containing chromophores difficult. Values of equilibrium constants are reported for the reaction $[CoX_3P]^- + X^- \rightleftarrows [CoX_4]^{2-} + P$ in CH_2Cl_2; phosphines replace halides with increasing facility in the order $Cl < Br < I$; the stability order for phosphine ligands is $PBu_3 > PPh_3$.

Introduction

Mixed phosphine-halide complexes of $[Co^{II}X_3P]^-$ and $[Co^{II}X_2P_2]$ type ($X = Cl, Br, I$; P = tertiary phosphine) are often quoted as representative examples of pseudotetrahedral cobalt(II) complexes,[1,2,3,4] and investigated as a convenient subject for the discussion of the electronic structure of tetrahedrally or pseudotetrahedrally coordinated cobalt(II).[3,4,5,6] Indeed such complexes, while stable in solid, are much less so in solution, where they may undergo easily oxidation of the phosphine ligands to phosphine oxides, or solvolytic displacement of coordinated phosphine, or displacement of phosphine under formation of coordination polymers.[7] Therefore, spectral data from solutions are often suspect of not being actually and completely due to $[CoX_2P_2]$ or $[CoX_3P]^-$ chromophores; unfortunately, the problem of the stability of such species in solution has received until now only scarce, scattered, and non quantitative attention. In the present paper we investigate the conditions of stability of such species in solutions and the nature of their substitution equilibria; quantitative evaluation of such equilibria was possible, owing to several experimental difficulties, only for the $[CoX_3P]^- + X^- \rightleftarrows [CoX_4]^{2-} + P$ systems in CH_2Cl_2.

We examined the behaviour of the Co^{II}-halide-phosphine systems in two kinds of solvents, of good and of poor coordinating ability, where solvolysis effects could be expected to be important and negligible respectively. As a representative of the former type we chose acetonitrile, for which previous data on formation equilibria of simple cobalt(II) halide complexes are available,[8] and for the latter type dichloromethane, which is widely used as a polar noncoordinating solvent, although it has the disadvantage of a rather limited liquid range and, in the present case, of reacting slowly with phosphines in a quaternization reaction which forms Cl^- and interferes with the investigated equilibria. The ligands were either triphenyl- or tri-n-butylphosphine, *i.e.* two phosphines of strongly different basicity.

The results described in detail below show that in a coordinating solvent such as acetonitrile, competition of the solvent molecules displaces easily and completely phosphine from both $[CoX_2P_2]$ and $[CoX_3P]^-$ species; phosphine-containing species can be formed in solution only partially and only in the presence of very large excess of phosphine. In non-coordinating solvents such as CH_2Cl_2, the behaviour is simpler and the phosphine complexes are more stable, since no solvolysis reactions occur; successive equilibria $[CoX_4]^{2-} \rightleftarrows [CoX_3P]^- \rightleftarrows [CoX_2P_2]$ are established, and quantitative data obtained for the first substitution of a halide X^- through phosphine allow an assessment of the relative affinity of different halides and different phosphines towards Co^{II} in its pseudotetrahedral complexes.

Experimental Section

Compounds. Investigated complexes include $[CoX_2P_2]$ and $R[CoX_3P]$ with $R^+ = (C_2H_5)_4N^+ = TEA$, $X^- = Cl^-$, Br^- or I^-, and P = triphenylphosphine or tributylphosphine. All six triphenylphosphine complexes were already known, and we repeated literature preparations.[1,2] $[CoI_2(PPh_3)_2]$ was isolated as the brown modification, while literature reports mention two solid state modifications, a green and a brown one, with equal magnetic moments and solution spectra.[9] With tributylphosphine, $[CoX_2(PBu_3)_2]$ com-

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(1) F. A. Cotton, O. D. Faut, D. M. L. Goodgame, and R. H. Holm, *J. Am. Chem. Soc.*, *83*, 1780 (1961).
(2) Advances in Inorganic Chemistry and Radiochemistry, 6, (1964) p. 19, Academic Press, New York.
(3) D M. L. Goodgame and M. Goodgame, *Inorg. Chem.*, *4*, 139 (1965).
(4) F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and A. Sacco, *J. Am. Chem. Soc.*, *83*, 4157 (1961).
(5) B. B. Wayland and R. S. Drago, *J. Am. Chem. Soc.*, *88*, 4597 (1966).
(6) G. Garton, D. E. Henn, H. M. Powell, and L. M. Venanzi, *J. Chem. Soc.*, 3625 (1963).
(7) M. Aresta, M Rossi, and A. Sacco, *Inorg. Chim. Acta*, *3*, 227 (1968).
(8) L. Sestili and C. Furlani, *J. Inorg. Nucl. Chem.*, *32*, 1997 (1970).
(9) K. Issleib and B. Mitscherling, *Z. Anorg. Allegm. Chem.*, *304*, 73 (1960).

plexes are oily substances and could not be isolated in pure form, so spectra corresponding to these species were determined in CH_2Cl_2 solutions of known [Co] content in the presence of high excess of PBu_3, the c.n. of the phosphine never exxceeding 2 in our experimental conditions. $R[CoX_3(PBu_3)]$ complexes were prepared in analogous way as the corresponding PPh_3 complexes, from CoX_2 and TEAX in mole ratio 1:1 in ethanol with excxess PBu_3 (from 1,5:1 for X = Cl, to ~2:1 for X = Br, I). $R[CoI_3(PBu_3)]$ is more difficult to obtain in pure form, a mixture with $R_2[CoI_4]$ and $[CoI_2(PBu_3)_2]$ being formed primarily. Analytical data: $TEA[CoCl_3(PBu_3)]$ found C, 48.8; H, 9.4; N, 2.7; Co, 9.0; calcd. for $C_{20}H_{47}NPCl_3Co$: C, 48.3; H, 9.4; N, 2.8; Co, 9.3; $TEA[CoBr_3(PBu_3)]$ found: C, 39.0; H, 7.4; N, 1.9; Co, 11.2; calcd. for $C_{20}H_{47}NPBr_3Co$: C, 38.0; H, 7.4; N, 2.2; Co, 9.2.

Triphenylphosphine oxide complexes were prepared according to[10,11] and their spectra, which are remarkably different from those of like formula with phosphines, were used to check possible formation of phosphine oxides anxd their complexes by oxidation of the phosphine complexes in our experimental solutions; no detectable oxidation of this kind seemed however to take place throughout our investigations.

Solvents and solutions. Acetonitrile and dichloromethane were reagent grade solvents which we dehydrated in the usual manner and further purified by fraction distillation. Solutions were prepared either with or without supporting electrolyte (usually $TEAClO_4$, 0.02 M in CH_2Cl_2 or 0.1 M in acetonitrile) in order to ensure controlled ionic strength. While solubilities of all complexes and of anhydrous Co^{II} halides in acetonitrile are large enough, some difficulties were experienced with dichloromethane owing to insolubility of CoX_2 (except a very limited solubility of CoI_2), and small solubility of all $[CoX_2P_2]$ and $R[CoX_3P]$ complexes (seldom exceeding 10^{-3} M); the best way to prepare solutions for equilibrium determination was to dissolve weighed amounts of $R_2[CoX_4]$ into CH_2Cl_2 containing a known concentration of phosphine already dissolved. The Co content of the solutions thus prepared was checked by analysis of Co after removal of solvent and decomposition of the complex, through EDTA titration with murexide indicator.

Apparatus. Spectra were taken with a Beckman DK-1A apparatus at controlled temperature (25,0∓1°C for CH_2Cl_2 and 35.0∓0.1°C for acetonitrile) in calibrated 1 mm or 1 cm cuvettes in the spectral range 1000-500 mμ.

Experimental measurements. Spectra were measured on series of solutions containing fixed total [Co] content (usually in the range 0.5-1.10^{-3} M) and varying amounts of excess halides and/or phosphines with or without $TEAClO_4$. The observed part of the spectra was that corresponding to the tetrahedral ${}^4A_2 \rightarrow {}^4T_1$ (${}^4P$) transition, which occurs in the region between ~13 and 18 kK (770 to 550 mμ) approximately, and whose rather complex structure is particularly useful for analytical purpose. For quantitative evaluation of equilibria, the spectra of the pure species involved were determined as follows: $[CoX_n]^{(2-n)}$ in acetonitrile from ref. (8); $[CoX_4]^{2-}$ in CH_2Cl_2, from literature data,[12] confirmed by spectra run on solutions of $R_2[CoX_4]$, not affected by excess X^-; $[CoX_2P_2]$ and $[CoX_3P]^-$ in CH_2Cl_2, from solutions of the pure compounds, after checking non-occurrence of autocomplexation equilibria by non-influence of ionic strength (except for $[CoX_2(PBu_3)_2]$; see below). For a gross check of the identity of the species responsible for the limiting spectra assigned as above, occasionally also spectra of the solid compounds (reflectance with a Beckman DK-1A; or single crystal with a Shimadzu MPS-50 spectrophotometer) were measured; solution and solid spectra are never exactly coincident (as is obvious in consideration of second-sphere effects), but their similarity is sufficient definitely to support the assignment (see Table I).

Results

$[CoX_2P_2]$ when dissolved in acetonitrile (AN) produce a spectrum coincident with that of a solution of pure CoX_2 in the same solvent,[8] known to contain essentially $[CoX_2(AN)_2]$ besides a limited amount of dismutation products according to:

$$3[CoX_2(AN)_2]+2AN \rightleftarrows 2[CoX_3(AN)]^- + [Co(AN)_6]^{2+} \qquad (1)$$

That is, AN displaces quantitatively PPh_3 from the complex:

$$[CoX_2P_2]+2AN \longrightarrow [CoX_2(AN)_2]+2P \qquad (2)$$

No unambiguous evidence was obtained for the possible intermediate:

$$[CoX_2P_2]+AN \longrightarrow [CoX_2P(AN)]+P \qquad (3)$$

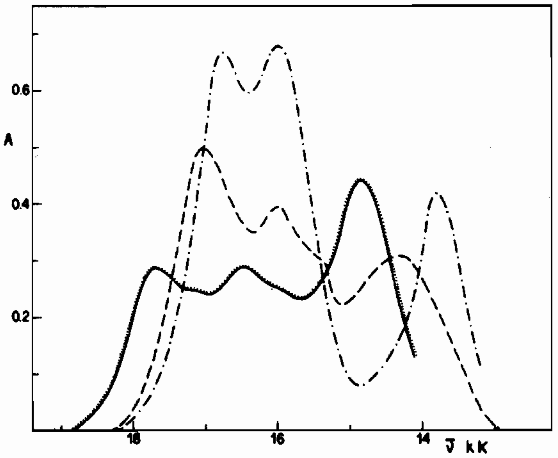

Figure 1. Absorption spectra of acetonitrile solutions containing 1.0×10^{-3} M $CoCl_2$ and varying concentrations of PPh_3 at 35,0∓0,1°C without supporting electrolyte. PPh_3: (———) 0; (.....) 2.0×10^{-3} M; (— — —) 3.0×10^{-1} M; (—·—·—): $[CoCl_2(PPh_3)_2]$ 1.0×10^{-3} M in CH_2Cl_2 at 25,0∓1°C without supporting electrolyte.

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[10] R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, *89*, 262 (1906).

[11] F. A. Cotton, R. D. Barnes, and E. Bannister, *J. Chem. Soc.*, 2199 (1960).

[12] F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Am. Chem. Soc.*, *83*, 4691 (1961).

On adding excess phosphine, the spectrum takes a form (Fig. 1, 2) suggesting presence of mixtures of $[CoX_2(AN)_2]$ and $[CoX_2P_2]$ along with $[CoX_3P]^-$ (from dismutation equilibria), with no necessary indication of existence of further species, such as $[CoX_2P(AN)]$. With larger excess of phosphine, the spectrum slowly evolves towards a form which, by comparison with the spectra of $[CoX_2P_2]$ chromophores in CH_2Cl_2 and in solid, may be taken as indicative of the latter species; it never reaches however completion, not even under the highest excess of ligand in saturated ($\sim 0.3\,M$) PPh_3 solution; anyway, formation of $[CoX_2P_2]$ under these conditions proceeds somewhat more with X = I than Br or Cl.

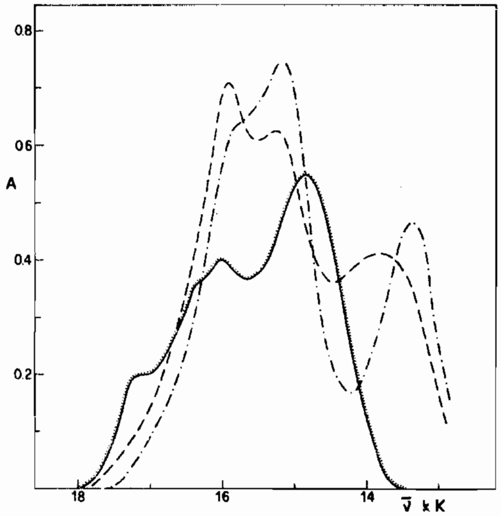

Figure 2. Absorption spectra of acetonitrile solutions containing $1.0 \times 10^{-3}\,M$ $CoBr_2$ and varying concentrations of PPh_3 at 35,0∓0,1°C without supporting electrolyte. PPh_3: (———) 0; (.....) $2.0 \times 10^{-3}\,M$; (— — —) $2.0 \times 10^{-1}\,M$; (—·—·—) $[CoBr_2(PPh_3)_2]$ $1.0 \times 10^{-3}\,M$ in CH_2Cl_2 at 25,0∓0,1°C without supporting electrolyte.

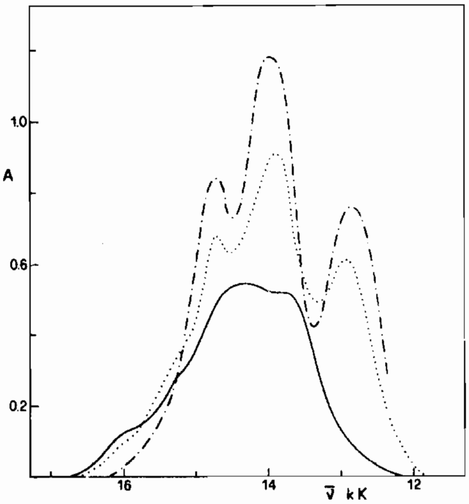

Figure 3. Absorption spectra of acetonitrile solution containing $1.0 \times 10^{-3}\,M$ CoI_2 and varying concentrations of PPh_3 at 35,0∓0,1°C without supporting electrolyte. PPh_3: (———) $2,0 \times 10^{-3}\,M$; (.....) $1.8 \times 10^{-1}\,M$; (—·—·—): $[CoI_2(PPh_3)_2]$ $1.0 \times 10^{-3}\,M$ in CH_2Cl_2 at 25,0∓0,1°C without supporting electrolyte.

Increasing ionic strength reduces formation of $[CoX_2P_2]$ and increases dismutation according to (1) since it shifts equilibrium (1) to the right (see Ref. (8)). The experimental situation is exemplified by the spectra in Figures 1, 2, 3 and 4.

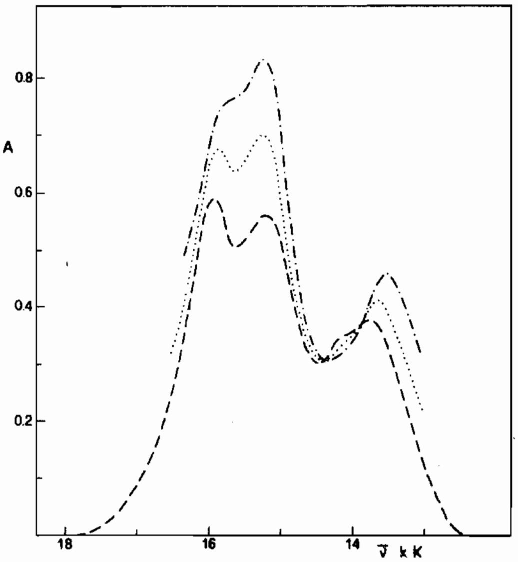

Figure 4. Spectra of acetonitrile solutions prepared from $1.0 \times 10^{-3}\,M$ $[CoBr_2(PPh_3)_2]$ and $3.0 \times 10^{-1}\,M$ PPh_3 at different ionic strength and t = 35,0∓0,1°C. (—·—·—) $\mu = 0$; (.....) $\mu = 0.01$; (— — —) $\mu = 0.1$ ($TEAClO_4$).

Also $TEA[CoX_3P]$ when dissolved in AN gives a spectrum completely coincident with that of a solution containing only Co^{2+} and X^- in ratio 1:3 as described in Ref. (8), where the predominant species is $[CoX_3(AN)]^-$, besides dismutation products according to:

$$2[CoX_3(AN)]^- \rightleftarrows [CoX_2(AN)_2] + [CoX_4]^{2-} \tag{4}$$

That is, also the displacement reaction

$$[CoX_3P]^- + AN \rightleftarrows [CoX_3(AN)]^- + P \tag{5}$$

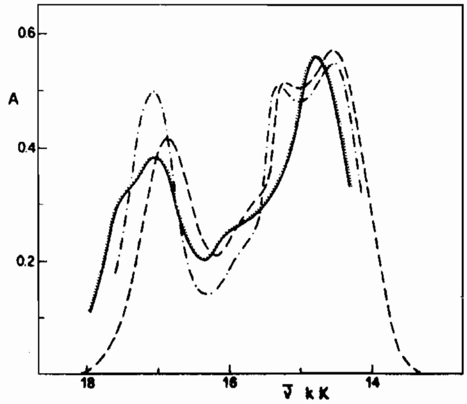

Figure 5. Spectra of acetonitrile solutions prepared from $1,0 \times 10^{-3}\,M$ $TEA[CoCl_3(PPh_3)]$ and varying concentrations of PPh_3 at 35,0°∓0,1°C. PPh_3: (———) 0; (.....) $1.0 \times 10^{-3}\,M$; (—·—:—) $3.0 \times 10^{-1}\,M$; (— — —): $TEA[CoCl_3(PPh_3)]$ $1.0 \times 10^{-3}\,M$ in CH_2Cl_2 at 25,0∓0,1°C.

Table I. Absorption spectra of Co^{II}-halide-phosphine species in dichloromethane. Shoulders in Parenthesis. Frequency in kK and (log ε)

	Maxima				Least	
$[CoCl_2(PPh_3)_2]$*	13.78 (2.6)	16.00 (2.8)	16.76 (2.8)		14.88(1.90)	16.40(2.77)
$[CoBr_2(PPh_3)_2]$**	13.44 (2.7)	15.25 (2.9)	(15.75)(2.8)		14.24(2.23)	
$[CoI_2(PPh_3)_2]$***	12.88 (2.9)	14.00 (3.0)	14.72 (2.9)		13.38(2.63)	14.50(2.86)
$R[CoCl_3PPh_3]$	16.86 (2.62)	(15.68)(2.48)	15.20 (2.71)	14.56(2.76)	16.28(2.32)	15.00(2.70)
$R[CoBr_3PPh_3]$	15.94 (2.83)	(15.08)(2.69)	(14.68)(2.77)	14.08(2.86)	15.44(2.47)	
$R[CoI_3PPh_3]$	14.48 (2.81)	14.17 (2.83)	(13.38)(2.98)	12.93(3.08)	14.38(2.78)	13.94(2.82)
$R[CoCl_3PBu_3]$	14.56 (2.77)	15.40 (2.73)	(15.80)(2.60)	16.51(2.76)	15.14(2.69)	16.00(2.54)
$R[CoBr_3PBu_3]$	14.12 (2.91)	14.92 (2.88)	14.56 (2.79)		14.48(2.81)	15.36(2.68)
$R_2[CoCl_4]$	(16.35)(2.33)	15.94 (2.62)	15.14 (2.77)	14.55(2.84)	15.60(2.53)	14.92(2.77)
$R_2[CoBr_4]$	(15.82)(2.42)	15.31 (2.76)	14.54 (2.95)	14.04(3.01)	14.99(2.59)	14.40(2.92)
$R_2[CoI_4]$	(14.40)(2.73)	(13.80)(2.87)	(13.24)(3.04)	12.90(3.13)		

* Reflectance spectrum: maxima at 13.43, 15.71, 16.43, (17.54) kK; single crystal spectrum: maxima at 13.43, 15.86, 16.50, 16.86 kK. ** Single crystal spectrum: maxima at 13.50, 15.26, 15.94, 16.66 kK. ***Single crystal spectrum: maxima at 12.90, 14.00, 14.70, 15.60, 16.40 kK.

is practically complete to the right-hand side. Excess phosphine causes equilibrium (5) to revert to the left; replacement of AN through phosphine appears to occur more easily in $[CoX_3(AN)]^-$ than in $[CoX_2(AN)_2]$, although still not reaching completion even in saturated phosphine solutions. Again phosphine entere more readily the iodo- than bromo-, and in turn the chloro-complexes; ionic strength has no appreciable effect here, as is expected for a reaction between species of equal total charge.[8] Also addition of excess phosphine to a solution of $[CoX_4]^{2-}$ in AN (mainly containing $[CoX_3(AN)]^-$) produces, again not completely, the same spectrum assignable by analogy to $[CoX_3P]^-$, while excess X^- stabilizes $[CoX_4]^{2-}$ so that phosphine does not replace X at all. The experimental results are exemplified for the chloro- and the bromo-systems with triphenylphosphine, in Figures 5 and 6.

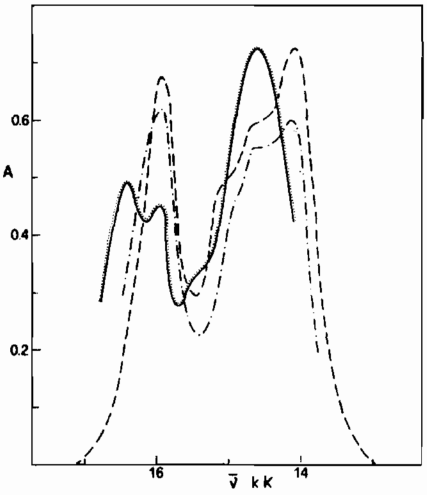

Figure 6. Spectra of acetonitrile solutions prepared from 1.0×10^{-3} *M* TEA$[CoBr_3(PPh_3)]$ and varying concentrations of PPh_3 at 35,0∓0,1°C. $[PPh_3]$: (———) 0; (.....) 1.0×10^{-3} *M*; (—·—·—) 3.0×10^{-1} *M*; (— — —): TEA$[CoBr_3(PPh_3)]$ 1.0×10^{-3} *M* in CH_2Cl_2 at 25,0∓0,1°C.

The general picture in AN solutions is thus of unfavourable competition of phosphines with the solvent for coordination to Co^{II}, so that pure phosphine-containing species cannot be formed completely. Data reported in Figures 1, 6 and described above give a sufficient qualitative account of the situation; more quantitative evaluation of the equilibria was not attempted because of complicating solvation equilibria and of lack of proper direct identification of the true spectral patterns of $[CoX_2P_2]$ and $[CoX_3P]^-$ species in AN, and also because of little practical interest in formation reactions of species which are so incomplete to be practically negligible in absence of high excess of free ligand.

In dichloromethane the situation is simpler, as anticipated, at least in some regards. Solid $[CoX_2P_2]$ and $R[CoX_3P]$ complexes dissolve undecomposed and yield spectra assignable to the pure chromophores $[CoX_2P_2]$, respectively $[CoX_3P]^-$ (Figures 7-12). Two difficulties may arise however from limited stability of solutions:

(i) solutions of $[CoX_2(PPh_3)_2]$ form on standing varying amounts of a precipitate of insoluble CoX_2 (or possibly in part of polymeric $[CoX_2(PPh_3)_x]_n$ $(x<2)$ as suggested by Sacco[7] for benzene solutions); dissolution is aided and precipitation repressed, by excess PPh_3, and both types of solutions(with and without excess phosphine, i.e. without and with pre-

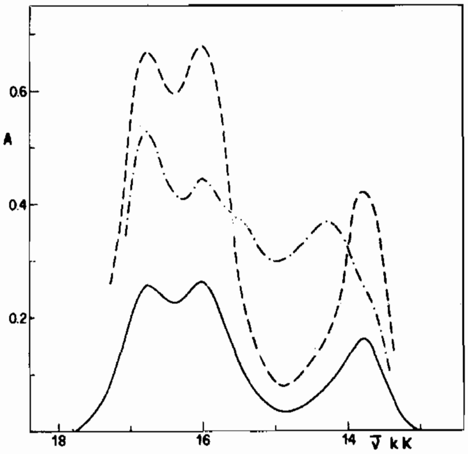

Figure 7. Spectra of $[CoCl_2(PPh_3)_2]$ in CH_2Cl_2 at 25,0∓0,1°C without TEAClO$_4$; a) (———) satd. solution ($<1.10^{-3}$ *M*) b) (— — —) 1.10^{-3} *M* with 3.0×10^{-1} *M* PPh_3, fresh solution; c) (—·—·—) same as b), aged; the spectrum corresponds to a mixture of $[CoCl_2(PPh_3)_2]$ and of $[CoCl_3(PPh_3)]^-$.

cipitate) exhibit the same spectral patterns, except of course for slightly lower intensity in the latter case. We take this for evidence that the spectrum is that of the pure [CoX_2P_2] chromophore, and that excess phosphine merely represses the tendence to precipitate CoX_2 without occupyng more than two coordination positions (see Figures 7, 8, 9 and Table I). PBu_3 complexes are more difficult to obtain in pure form, so the spectra of [$CoX_2(PBu_3)_2$] chromophores can be identified less accurately.

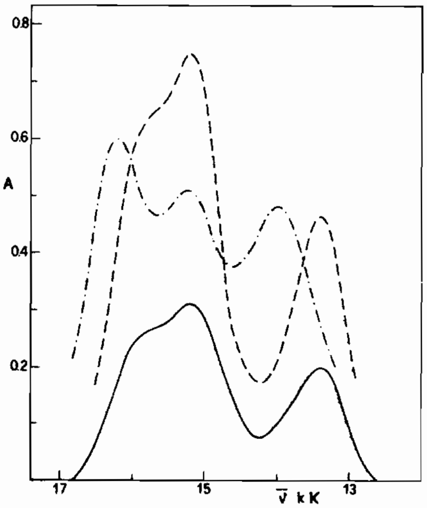

Figure 8. Spectra of [$CoBr_2(PPh_3)_2$] in CH_2Cl_2 at 25,0∓0,1°C without $TEAClO_4$. a) (———) satd. solution ($<1.10^{-3}$ *M*); b) (— — —) 1.10^{-3} *M* with 3.0×10^{-1} *M* PPh_3, fresh solution; c) (— · — · —) same as b), aged.

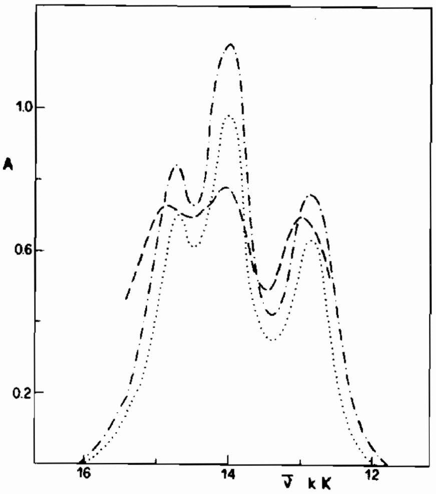

Figure 9. Spectra of [$CoI_2(PPh_3)_2$] in CH_2Cl_2 at 25,0∓0,1°C without $TEAClO_4$. a) (.....) satd. solution ($<1.10^{-3}$ *M*); b) (— · — · —) 1.10^{-3} *M* with 3.0×10^{-1} *M* PPh_3, fresh solution; c) (— — —) same as b), aged.

(ii) CH_2Cl_2 is capable of reacting with phosphine to give the quaternization reaction $PR_3+CH_2Cl_2 \rightleftarrows [P(R)_3(CH_2Cl)]^+ + Cl^-$. The reaction is slow if only coordinated phosphine is present, but becomes more rapid where free phosphine is present; PBu_3 reacts much more rapidly than PPh_3. Thus, solutions of [$CoX_2(PPh_3)_2$] with excess PPh_3 prepared as in paragraph (i) are not stable, and become decomposed more and more rapidly with increasing ionic strength, because of complexation by the Cl^- ions set free in the quaternization reaction, which is favoured in ionic medium. Also solutions prepared by [CoX_2P_2] alone without excess phosphine are unstable in the same manner, just reacting more slowly; actually, precipitation of CoX_2 leaves also in these solutions a small concentration of free phosphine in excess (see *e.g.* Fig. 10 for X = Br). Aged solutions evolve in any case after longer time towards the spectral patterns of $[CoCl_3P]^-$, since Cl^- can replace both Br^- and I^-, but is not able to displace completely the least phosphine molecule under the present experimental conditions in presence of excess phosphine. R[$CoX_3(PPh_3)$] complexes are generally more soluble and more stable than [CoX_2P_2], and their solution spectra do not change in a detectable manner either with time or with ionic strength; R[$CoX_3(PBu_3)$] are still rather unstable (although more stable than [CoX_2P_2]), and their solution spectra on standing evolve slowly towards $[CoCl_3(PBu_3)]^-$.

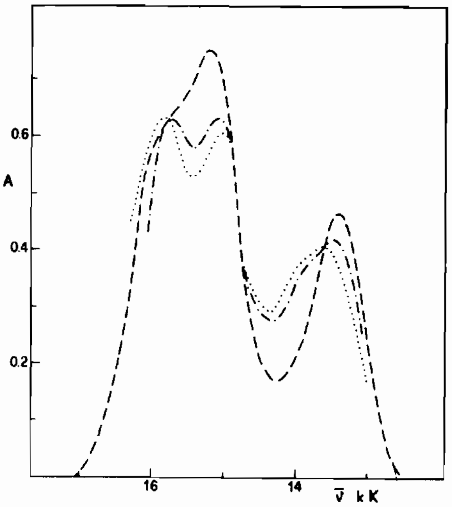

Figure 10. Spectra of 1.0×10^{-3} *M* [$CoBr_2(PPh_3)_2$] with 3.0×10^{-1} *M* PPh_3 in CH_2Cl_2 at 25,0∓0,1°C and different ionic strength. (— — —) $\mu = 0$; (— — —) $\mu = 0.01$; (.....) $\mu = 0.02$.

In summary, lack of complicating solvolysis reactions allow the behaviour of cobalt(II)-halide-phosphine systems in dichloromethane to be accounted for by only two equilibria:

$$[CoX_2P_2]+X^- \rightleftarrows [CoX_3P]^- + P \qquad (6)$$

$$[CoX_3P]^- + X^- \rightleftarrows [CoX_4]^{2-} + P \qquad (7)$$

as long as solubility is not a limiting factor, and quaternization reaction do not set free any non-negligible amount of Cl^-. But precisely these two factors invariably occur when observing equilibrium (6), excess phosphine being necessary to solubilize the complexes, and $TEAClO_4$ to ensure controlled ionic strength, and this circumstance prevents us from obtaining reasonably accurate spectrophotometric values of stability constants for (6); Fig. 11 reports as an example a series of spectra taken on solutions of $[CoI_3P^-]$ with excess P, where the spectrum actually evolves towards $[CoI_2P_2]$ but does not reach completion, and the high excess of phosphine makes the quaternization reaction intoleraly fast.

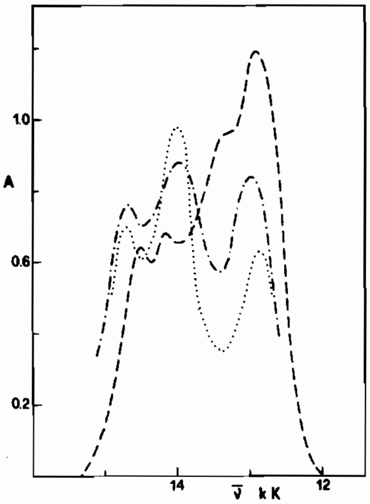

Figure 11. Spectra of cobalt-iodide-phosphine complexes in CH_2Cl_2 at 25,0∓0,1°C without $TEAClO_4$: (— — —) TEA-$[CoI_3(PPh_3)]$ 1.0×10^{-3} *M*; (—:—:—) same, plus 5.0×10^{-1} *M* PPh_3; (.....) $[CoI_2(PPh_3)_2]$ 1.0×10^{-3} *M*.

Therefore we concentrated upon equilibrium (7), which is more tractable and can be actually followed with good reproducibility and accuracy for the PPh_3 complexes (and somewhat less so for PBu_3 complexes, quaternization of ligand set free at equilibrium being faster), by measuring spectra of solutions containing fixed concentrations of $[CoX_3P]^-$ and increasing concentrations of X^-, or of solutions prepared from $R_2[CoX_4]$ plus a small constant excess of phosphine and increasing amounts of X^-, always in the presence of 0.02 *M* $TEAClO_4$. Values of equilibrium constants obtained by numerical evaluation of the spectra of such simple systems (Figures 12 and 13) are reported in Table II. It will be noted that, for the reasons noted above, the accuracy is better for PPh_3 complexes.

Table II. Constants of the equilibrium $[CoX_3P]^- + X^- \rightleftarrows [CoX_4]^{2-} + P$ (X=Cl, Br, I; P=PPh_3, PBu_3) in dichloromethane at 25.0±0.1°C and $\mu=0.02$ ($TEAClO_4$)

	P=PPh_3	P=PBu_3
K$[CoCl_4]^{2-}$	$(1.7\pm0.1)10^2$	$(7.4\pm0.1)10^{-1}$
K$[CoBr_4]^{2-}$	$(2.2\pm0.2)10^1$	$(1.3\pm0.2)10^{-1}$
K$[CoI_4]^{2-}$	$(8.7\pm0.2)10^{-1}$	$(7.6\pm2)10^{-3}$

Discussion

The solution behaviour of mixed cobalt(II)-halide-phosphine complexes, described above in detail, offers

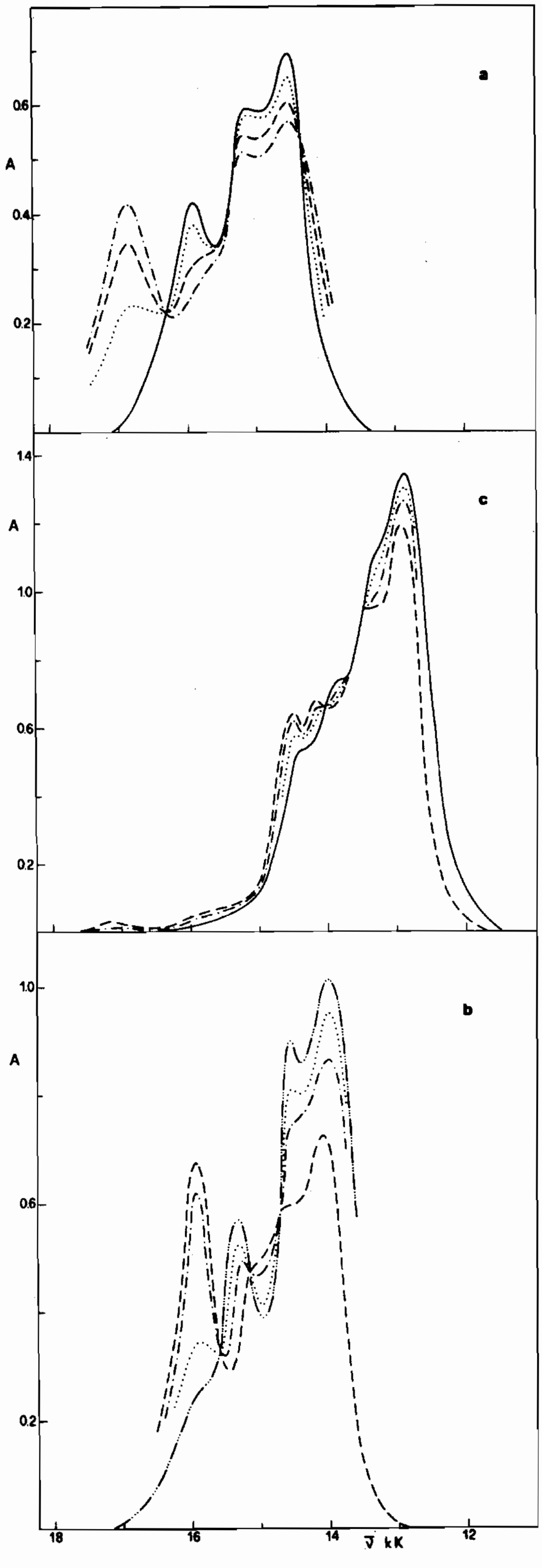

Figure 12. Absorption spectra of solution containing TEA-$[CoX_3(PPh_3)]$ and TEAX (X = Cl, Br, I) in CH_2Cl_2 at 25,0∓0,1°C and $\mu = 0.02$ ($TEAClO_4$), with fixed [Co] 1.0×10^{-3} *M* and varying $x = [X]_{tot}/[Co]_{tot}$ ratios. a) X = Cl: x = (—:—·—) 3.00; (— — —) 3.24; (.....) 3.49; (———): $R_2[CoCl_4]$ 1.0×10^{-3} *M*; b) X = Br: x = (— — —) 3.00; (—.—.—) 3.42; ((.....) 4.05; (—...—): $R_2[CoBr_4]$ 1.0×10^{-3} *M*; c) X = I: x = (— — —) 3.00; (—:—·—) 3.38; (.....) 3.96; (———): $R_2[CoI_4]$ 1.0×10^{-3} *M*.

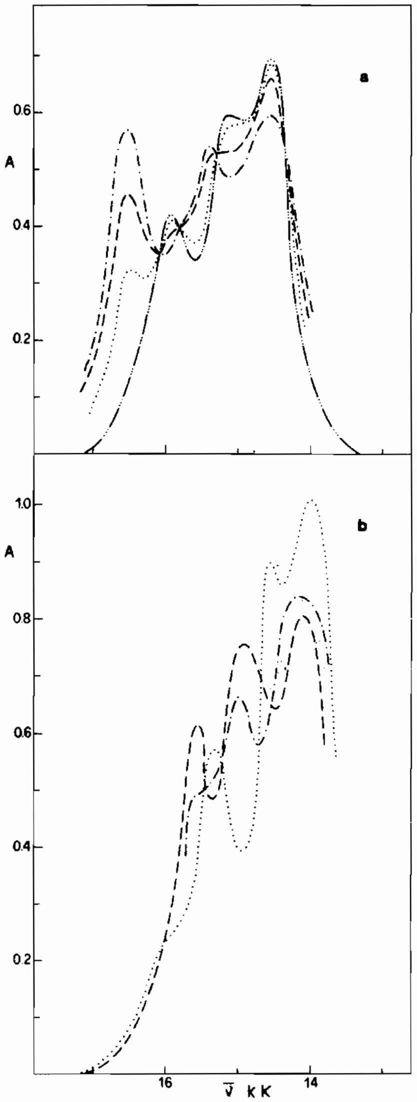

Figure 13. Absorption spectra of solutions containing TEA-$[CoX_3(PBu_3)]$ and TEAX (X = Cl, Br) in CH_2Cl_2 at 25,0∓0,1°C and $\mu = 0.02$ ($TEAClO_4$), with fixed $[Co] = 1.0 \times 10^{-3}$ *M* and varying $x = [X]_{tot}/[Co]_{tot}$ ratios. a) X = Cl: x = (— · — · —) 3.00; (— — —) 3.69; (. . . . .) 6.45; (— · · · —): $R_2[CoCl_4]$ 1.0×10^{-3} *M*; b) X = Br: x = (— — —) 3.00; (— · — · —) 8.00; (. . . . .): $R_2[CoBr_4]$ 1.0×10^{-3} *M*.

a general picture of low affinity of phosphines for Co^{II}; coordinated phosphines are completely displaced by solvolysis in coordinating solvents, and phosphine-containing species are stable only in noncoordinating solvents such as dichloromethane, which do not challenge the affinity of phosphorus to cobalt, however small it may be. Thus, the high spectrochemical position of phosphine ligands does not reflect an equally high stability of coordinate bonds, rather it contrasts with a particularly low affinity.

Quantitative data of equilibrium constants for the reaction $[CoX_3P]^- + X^- \rightleftarrows [CoX_4]^{2-} + P$ suggest a comparison between the affinity of the halides and of the two phosphines investigated here. Values of spectrophotometric constants collected in Table II indicate that replacement of a halide by a phosphine is easier for I than for Br and in turn Cl, and easier with PBu_3 than with PPh_3. This reflects the increasing affinity for Co^{II} in the order Cl > Br > I, but might also in part be a « sympathy » effect by which the soft phosphine ligand enters easily a soft environment of iodide ions, but much less so a harder environment of chlorides. The trend within the phosphines parallels the higher basicity of PBu_3, althoug the correlation is actually not so simple, basicity being a σ-effect, and stability the result of a cooperation of σ- and π-effects.

As noted above, properties truly pertaining to the actual phosphorus-containing chromophores can be observed and measured only in noncoordinating solvent, and even there the small stability of cobalt-phosphine coordination leaves us to face several difficulties which may in practice be severely limiting, and require special caution. Therefore, if the inherent properties of phosphorus-containing cobalt(II) chromophores are to be discussed, experimental data from solutions should be used with great care and criticism; solid state data, such as crystal spectra, are to be considered a far more sure and valuable source, also in consideration of the better spectral resolution that can be achieved.[13]

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[13] C. Sismo and S. Holt, *Inorg. Chem.*, 7, 2655 (1968).