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HIGH SPIN (TETRACOORDINATE)–LOW SPIN (PENTACOORDINATE) EQUILIBRIA IN COMPLEXES OF COBALT(II) WITH TERTIARY PHOSPHINES

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INTRODUCTION

The existence of a high spin ⇄ low spin equilibrium has recently been established[1] for the compound $Co(PEt_3)_2(NCS)_2$ in solution. The high spin form has been identified as a monomeric species with a tetrahedral configuration about cobalt(II). The low spin species has been found to be dimeric in solution and it has been suggested that the cobalt atoms are probably linked by SCN bridges to give a pentacoordinate species. These results seem to indicate that tetrahedral high spin complexes of the type $Co(PR_3)_2X_2$ could easily add a fifth ligand to give 5-coordinated low spin complexes. The present work has been designed in order to provide information regarding the tendency of 4-coordinated $Co(PR_3)_2X_2$ complexes to attain 5-coordination by adding one phosphine molecule.

In contrast to the behaviour of metal ions with a d^8 configuration, cobalt(II) shows little tendency to give 5-coordinated complexes $Co(PR_3)_3X_2$ (X = halogen) in its compounds with tertiary phosphines. The only 5-coordinated complexes of this type are those with 2-phenylisophosphindoline which combines with cobalt dihalides to give compounds[2] of composition $[(C_{14}H_{13}P)_3CoX_2]$ the stability of which is probably related to the peculiar stereochemistry of the phosphine. Complexes $Co(PR_3)_3X_2$ of cobalt dihalides with tertiary phosphines of the usual type are unknown. Booth and Chatt reported that $Co(PEt_3)_2I_2$ does not react with PEt_3 and pointed out that the formation of such complexes may depend critically upon the organic phosphine[3]. In their study of the compounds formed in the reaction of PEt_3 with $CoCl_2$ and $CoBr_2$, Hatfield and Yoke did not find any evidence of 5-coordinated species[4].

To evaluate the role of the organic phosphine in determining the stability of the 5-coordinated complexes we have examined the following configurational change

$$\underset{\text{4-coordinate high spin}}{Co(PR_3)_2X_2} + PR_3 \rightleftarrows \underset{\text{5-coordinate low spin}}{Co(PR_3)_3X_2}$$

in several 4-coordinate complexes of the type $Co(PR_3)_2X_2$. We have extended our study also to the complexes with the pseudo-halides $X = SCN^-$ or NCO^- because it appeared to us that the reluctance of the halo-complexes to coordinate a third phosphine molecule could not be entirely ascribed to the organic phosphine but also to the ligand partner X. Most of the work has been carried out in solution to avoid any limitations connected with the stability of solid compounds. Dichloroethane was selected as the best solvent after it was found that a well defined equilibrium $Co(PR_3)_2(NCS)_2 + PR_3 \rightleftarrows Co(PR_3)_3(NCS)_2$ is established in this solvent. The phosphines selected for this study were PEt_3, PPr_3^n, PEt_2Ph, $PEtPh_2$, PPh_3, PCy_3. In the course of this investigation, it was possible to isolate the solid compounds $Co(PPr_3)_3(NCS)_2$ and $Co(PEt_2Ph)_3(NCS)_2$ from ethanol solutions of the reagents. In agreement with previous reports[2,3,4], our attempts to combine the tertiary phosphines with cobalt(II) halides gave only the green or blue tetrahedral complexes of the type $Co(PR_3)_2X_2$ and the 5-coordinated compounds could not be isolated. The apparent inability of cobaltous halides to form the tris(phosphine) compounds was confirmed by examining the spectra of the 4-coordinated complexes in ethylene dichloride containing the free phosphine. The spectra in the visible range showed that only tetrahedral complexes were present in solution. Similarly, we found that the compounds $Co(PCy_3)_2(NCS)_2$ and $Co(PPh_3)_2(NCS)_2$ do not possess a measurable tendency to coordinate an additional phosphine molecule.

Reactions of $Co(PEt_3)_2(NCS)_2$ with PEt_3

Several attempts to obtain the 5-coordinate compound $Co(PEt_3)_3(NCS)_2$ in the solid state were unsuccessful. Only the low spin species $Co(PEt_3)_2(NCS)_2$ could be isolated from ethanol even in the presence of a large excess of phosphine. However, magnetic spectral and molecular weight data give a clear evidence that in dichloroethane a 5-coordinated compound is formed by adding phosphine to the 4-coordinated complex.

As shown in Table I, the magnetic moment of $Co(PEt_3)_2(NCS)_2$ is 2.2 *B.M.* in the solid state; the magnetic moment is 3.4 *B.M.* in dichloroethane solution. This change is due to the presence of the tetrahedral form (about 4.4 *B.M.*) according to the following equilibrium:

$$\underset{\text{tetrahedral high spin}}{2[Co(PEt_3)_2(NCS)_2]} \rightleftarrows \underset{\text{low spin}}{[Co(PEt_3)_2(NCS)_2]_2}$$

The value of the magnetic moment is reduced to 2.05 *B.M.* at the same temperature in the presence of excess phosphine, showing that the high spin tetrahedral species is no longer present in solution. Cryoscopic measurements in $C_2H_4Cl_2$ at about -32.5 °C are in agreement with the formation of the compound $Co(PEt_3)_3(NCS)_2$ (see Table 2). The spectra of $Co(PEt_3)_2(NCS)_2$ in the same sol-

TABLE I

ANALYTICAL DATA AND PHYSICAL PROPERTIES FOR SOME COMPLEXES OF CoX_2 AND TRISUBSTITUTED PHOSPHINES

Compound[a]	*M.p.* (°C)[b]	*Color*	μ_{eff} *B.M.* (25 °C)	*% C*		*% H*		*% Co*		*% N*	
				Calcd.	*Found*	*Calcd.*	*Found*	*Calcd.*	*Found*	*Calcd.*	*Found*
$Co(PEt_3)_2(NCO)_2$	77–80 (dec.)	Blue	4.60	44.3	43.6	7.96	7.86	15.5	15.8	7.38	7.48
$Co(PEt_3)_2(NCS)_2$[e]	98–100 (dec)	Brown-red	2.20, 3.40[c], 2.05[d]	40.9	40.4	7.36	7.36	14.3	14.3	6.81	6.76
$Co(PPr^n_3)_3(NCS)_2$[e]	91–93 (dec.)	Green-brown	2.05	53.1	52.5	9.68	9.62	8.99	9.08	4.27	4.64
$Co(PPhEt_2)_2Br_2$	79–80	Green	4.50	43.6	43.4	5.49	5.40	10.7	10.6		
$Co(PPhEt_2)_2Cl_2$	71–73	Blue	4.50	51.9	51.2	6.54	6.49	12.7	12.8		
$Co(PPhEt_2)_3(NCS)_2$[e]	92–94 (dec.)	Brown	1.90	57.0	55.7	6.73	6.73	8.74	8.75	4.16	4.16
$Co(PPh_2Et)_2Br_2$	191–193	Green	4.50	51.9	51.7	4.67	4.66	9.10	9.05		
$Co(PPh_2Et)_2Cl_2$	177–178	Blue	4.50	60.2	60.1	5.40	5.53	10.5	10.6		
$Co(PPh_2Et)_2(NCS)_2$[e]	150–152	Green	4.40	59.7	59.8	5.01	5.02	9.76	9.73	4.64	4.67

[a] Abbreviations: Et, ethyl; Pr^n, n-propyl; Ph, phenyl.

[b] All melting points are uncorrected.

[c] 0.45 *M* in CH_2Cl_2.

[d] 0.25 *M* in CH_2Cl_2 solution of PEt_3 (1 *M*).

[e] The infrared spectra in the ranges 2000–2150 cm^{-1} and 690–860 cm^{-1} show that the NCS group is attached through the nitrogen atom.

vent at various temperatures in the presence of phosphine are shown in Fig. 1. Most of the absorption at the higher temperatures in the 500–800 mμ region derives from the presence of tetrahedral species as shown by the shape and intensity of the absorption bands. On decreasing the temperature, the relative intensity of the absorption attributed to the tetrahedral species decreases. Finally, at the lowest temperature of Fig. 1 the contribution to the absorption of the tetrahedral bands becomes negligible and the spectrum is similar to that of solutions containing large amounts of phosphine (see Fig. 2). Furthermore, in the experimental conditions of

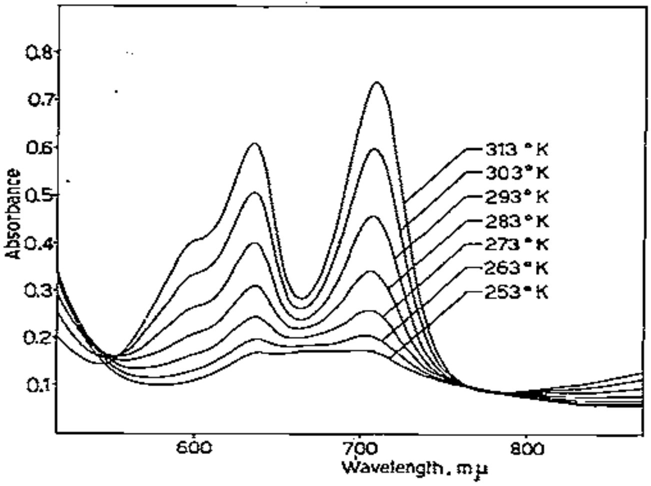

Fig. 1. Visible spectra of $Co(PEt_3)_2(NCS)_2$, 9.6 · 10^{-3} *M* in $C_2H_4Cl_2$ solution of PEt_3 (10^{-2} *M*). Temperature range 253–313 °K. Cell thickness 0.1 cm.

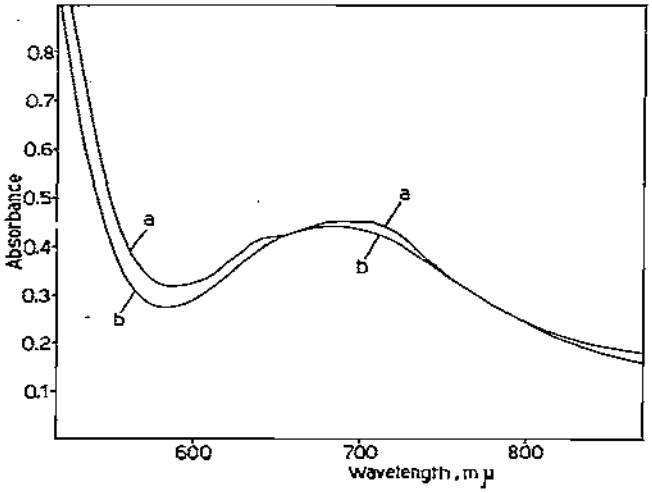

Fig. 2. Visible spectra of $Co(PEt_3)_2(NCS)_2$, 2.64 · 10^{-2} *M* in $C_2H_4Cl_2$ solution of PEt_3 (2 *M*). (a) temperature 301 °K; (b) temperature 250 °K. Cell thickness 0.1 cm.

Fig. 2 the spectra at +28° are substantially identical with those at −23°. Considering the concentrations used for the spectra of Fig. 1 and 2 and those of the molecular weight determination, one can conclude that the single chemical species absorbing in Fig. 2 and that of the lowest temperature in Fig. 1 is the 5-coordinated compound $Co(PEt_3)_3(NCS)_2$.

Reactions with PPr_3^n

A green-brown solid of composition $Co(PPr_3)_3(NCS)_2$ could be prepared by adding a small excess of phosphine to an ethanolic solution of cobaltous thiocyanate. The magnetic moment of the crystalline compound is 2.05 *B.M.* at 25 °C (Table 1). This can be compared with the same value found for solutions of $Co(PEt_3)_2(NCS)_2$ in ethylene dichloride which contain a great excess of phosphine.

The spectra of the compound in $C_2H_4Cl_2$ in the visible range are extremely similar to those of $Co(PEt_3)_3(NCS)_2$. The shape and intensity of the absorption bands clearly show that tetrahedral species are present in solution. The intensity of these bands decreases on lowering the temperature and becomes negligible at temperatures below −20°. Thus the spectral data indicate that a dissociative equilibrium occurs in solution leading to the formation of tetrahedral molecules of composition $Co(PPr_3)_2(NCS)_2$. Since the molecular weight found in freezing $C_2H_4Cl_2$ corresponds with that of $Co(PPr_3)_3(NCS)_2$ it is evident from the above observations that we are dealing with the equilibrium

$$Co(PPr_3)_3(NCS)_2 \rightleftarrows Co(PPr_3)_2(NCS)_2 + PPr_3$$

The solid 4-coordinate $Co(PPr_3)_2(NCS)_2$ could not be prepared. Usually solid products with a content higher than 2 moles of phosphine are obtained from ethanol even if one attempts the preparation in stoichiometric defect of phosphine. In order to study the possible occurrence of a dimerisation process similar to that which takes place in $C_2H_4Cl_2$ solutions of $Co(PEt_3)_2(NCS)_2$, it was necessary to prepare solutions of the 4-coordinate compound. These have been obtained by adding solid $Co(CNS)_2$ to a solution of $Co(PPr_3)_3(NCS)_2$ in $C_2H_4Cl_2$.

TABLE II

CRYOSCOPIC MOLECULAR WEIGHTS IN DICHLOROETHANE AT −32 °C

Ligand	*phosphine/$Co(CNS)_2$ (moles)*	*Molecular weight*		*Polymerisation number*[a]
		Calcd.	*Found*	
PEt_3	2	411.4	798	1.94
PEt_3	3	529.6	550	1
PPt_3^n	2	495.6	852	1.72
PPr_3^n	3	655.8	659	1
PEt_2Ph	2	507.5	675	1.33
PEt_2Ph	3	673.7	672	1

[a] Molecular weight (obsd)/molecular weight (calcd).

The heterogeneous reaction $2\,Co(PPr_3)_3(NCS)_2 + Co(CNS)_2 \rightarrow 3\,Co(PPr_3)_2(NCS)_2$ is very fast. After filtration of the unreacted $Co(CNS)_2$, a pure solution containing the 4-coordinated compound is obtained. In the solution, monomeric $Co(PPr_3)_2(NCS)_2$ is in equilibrium with dimeric species as shown by molecular weight determinations. The data in Table II indicate that $Co(PPr_3)_2(NCS)_2$ has a lesser tendency to give the dimer in respect to the ethyl derivative.

Reactions with $PPhEt_2$

In this case, it was also possible to obtain the solid 5-coordinate compound $Co(PPhEt_2)_3(NCS)_2$ from ethanol solutions of the reagents. The brown-red solid has a magnetic moment of 1.90 *B.M.* at 25 °C (Table I). The compound is monomeric in freezing dichloroethane (Table II) and the spectral patterns at different temperatures in this solvent are similar to those of the previous compounds; this indicates that the same dissociative equilibrium is established in solution. The spectra of a diluted solution in the temperature range +40° to −15° are shown in Fig. 3. The spectra in 1 molar $PPhEt_2$ solution at +20 and −20° are practically coincident and are compared in Fig. 4 with those of the solid compound. The similarity of the solid and solution spectra in the visible range shows that the two species are identical and this strongly suggests that cobalt is 5-coordinated also in the solid state. Comparison of the spectrum at −15° in Fig. 3 with the spectra of Fig. 4 shows that at low temperatures the dissociation products of $Co(PPhEt_2)_3(NCS)_2$ are present in extremely small amounts even in diluted solution. This small concentration of tetrahedral $Co(PPhEt_2)_2(NCS)_2$ is responsible for the departure of the spectrum in Fig. 3 from the apparent gaussian shape of the band attributed to $Co(PEt_2Ph)_3(NCS)_2$. The 4-coordinate compound $Co(PPhEt_2)_2(NCS)_2$ could

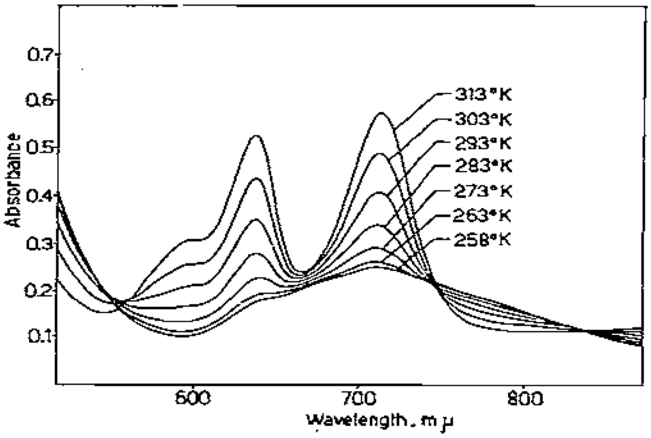

Fig. 3. Visible spectra of $Co(PPhEt_2)_3(NCS)_2$, $7.1 \cdot 10^{-3}$ *M* in $C_2H_4Cl_2$. Temperature range 258–313 °K. Cell thickness 0.1 cm.

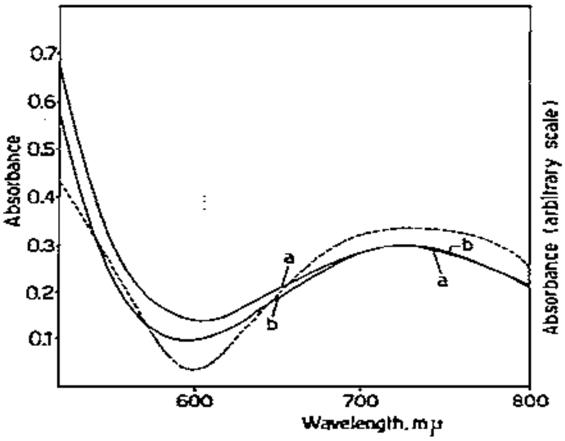

Fig. 4. Visible spectra of $Co(PPhEt_2)_3(NCS)_2$. (– – – –): reflectance spectrum, absorbance scale arbitrary. (————): spectra in $C_2H_4Cl_2$ solution. Concn. of complexes, $8.94 \cdot 10^{-3}$ *M*; concn. of $PPhEt_2$, $9.5 \cdot 10^{-1}$ *M*. (a) temperature 303 °K; (b) temperature 353 °K. Cell thickness, 0.1 cm.

not be prepared in the solid state. The compound was obtained in solution by heterogeneous reaction of solid $Co(CNS)_2$ with the 5-coordinate complex. It is slightly polymerized in freezing $C_2H_4Cl_2$ (Table II).

Reactions with PPh_2Et

A green crystalline product of composition $Co(PPh_2Et)_2(NCS)_2$ may be obtained by adding PPh_2Et to a solution of cobalt(II) thiocyanate in ethanol. The solid compound has a magnetic moment of 4.4 *B.M.* (Table I), typical for a number of tetrahedral complexes with general formula $Co(PR_3)_2(NCS)_2$. Attempts

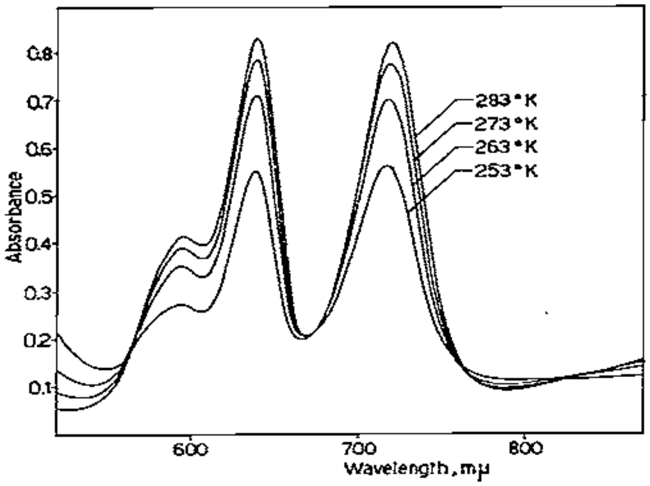

Fig. 5. Visible spectra of $Co(PPh_2Et)_3(NCS)_2$, $6.46 \cdot 10^{-3}$ *M* in $C_2H_4Cl_2$ solution of PPh_2Et ($9 \cdot 10^{-3}$ *M*). Temperature range 253–283 °K. Cell thickness 0.1 cm.

to prepare at low temperature the 5-coordinated compound gave brown-red products which were unstable and decomposed quickly at room temperature giving the green tetrahedral species. The absorption spectra of the compound in dichloroethane solution of PPh_2Et are shown in Fig. 5. In comparing the spectra in Fig. 5 with those of the previous compounds (Fig. 1 and Fig. 3) one visualizes the much smaller tendency of $Co(PPh_2Et)_2(NCS)_2$ to form complexes with a higher coordination number. As a matter of fact, the intensity at +10° of the tetrahedral bands at 635 and 715 mμ is nearly as strong as that expected for tetrahedral complexes of this type, and this indicates that a very small amount of cobalt is present as a 5-coordinate compound. The smaller tendency of the tetrahedral $Co(PPh_2Et)_2(NCS)_2$ to coordinate an additional molecule of phosphine, is paralleled by the fact that, contrary to the behaviour of the similar complexes with PEt_3, PPr_3 and $PPhEt_2$ it does not dimerize in $C_2H_4Cl_2$ solution. The compound does not dimerize appreciably at $-20°$ as shown by the similarity of the tetrahedral spectra at various temperatures.

Reactions of Co(NCO)$_2$ with PEt$_3$

A blue solid of composition $Co(PEt_3)_2(NCO)_2$ could be prepared by reacting PEt_3 with an aqueous solution of $K_2[Co(NCO)_4]$. The compound was recrystallized from ethanol. The magnetic moment of the crystalline solid is 4.60 *B.M.* (Table I). The spectra of 10^{-2} *M* solutions of the compound in $C_2H_4Cl_2$ in the presence of 1 *M* phosphine do not appreciably differ in the temperature range -20 to $+20°$ from the spectra in pure $C_2H_4Cl_2$ given in Fig. 6. This result shows that, contrary to the behaviour of $Co(PEt_3)_2(NCS)_2$, with the compound $Co(PEt_3)_2(NCO)_2$ equilibrium (1) lies far to the left.

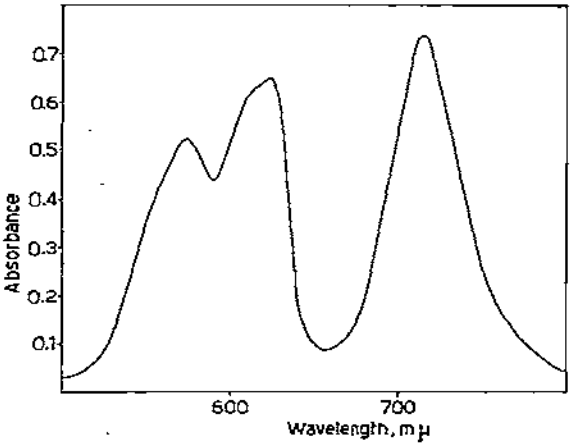

Fig. 6. Visible spectrum of $Co(PEt_3)_2(NCO)_2$, 10^{-2} *M* in $C_2H_4Cl_2$ solution. Temperature 298 °K. Cell thickness, 0.1 cm.

The equilibria in solution

The molar conductance of 10^{-2} *M* solutions of the complexes in $C_2H_4Cl_2$ was in the range 0.1–0.4 ohm^{-1}, that of a 10^{-2} *M* solution of $(AsPh_4)_2Co(NCS)_4$ was 16.5 ohm^{-1}. Adding small amounts of phosphine caused a marked reduction in the molar conductances. The low conductivity values, which could arise from slight solvolysis in the dilute solutions, rules out the occurrence of equilibria leading to the formation of ionic cobalt(II) complexes. The following equilibria were considered to be likely to occur in the investigated solutions:

$$Co(PR_3)_2(NCS)_2 + PR_3 \rightleftarrows Co(PR_3)_3(NCS)_2 \tag{1}$$

$$2Co(PR_3)_2(NCS)_2 \rightleftarrows [Co(PR_3)_2(NCS)_2]_2 \tag{2}$$

$$Co(PR_3)_2(NCS)_2 + 2PR_3 \rightleftarrows Co(PR_3)_4(NCS)_2 \tag{3}$$

Whereas the evidence presented here leaves little doubt about the simultaneous occurrence of equilibrium (1) and (2), it is important to show, for the purpose of the present investigation, that equilibrium (3) is of negligible importance compared with equilibrium (1). No evidence for the formation of six-coordinated species was found even in solutions of high phosphine content. The absence of appreciable amounts of 6-coordinated species is established on the basis of several lines of reasoning.

First, in solutions with mole ratio $PR_3 : Co(NCS)_2 = 3$ the spectra in dichloroethane at low temperatures show that there are no tetrahedral molecules in solution. If 6-coordinated compounds were present, 4-coordinated tetrahedral molecules would also be detected in solution owing to the choice of the mole ratio of the reagents.

Secondly, the extinction coefficient of the spectra performed with a large excess of phosphine in order to force the reaction to go to the 6-coordinated compound, is the same as those of solutions containing an equal number of moles of phosphine and of 4-coordinated compound. Moreover, these spectra do not show important changes as the temperature decreases from +20 to −20 °C showing that only one chemical species is present in solution.

Finally, we already mentioned the fact that the depression of the freezing temperature of $C_2H_4Cl_2$ containing phosphine and cobaltous thiocyanate in the ratio 3:1, is in accordance with a monomeric 5-coordinate compound.

DISCUSSION

We shall now discuss briefly the peculiar role of the NCS ion in determining the stability of the $Co(PR_3)_3X_2$ complexes. The presence of NCS ligand in the molecule seems to be necessary to attain 5-coordination in complexes with tertiary phosphines. Indeed the halocomplexes of the type $Co(PR_3)_2X_2$ do not show any tendency to coordinate a third phosphine molecule. An exception occurs in the case of 2-phenylisophosphindoline[2]. This ligand combines with cobalt halides to give compounds of composition $[(C_{14}H_{13}P)_3CoX_2]$. The ability of this unusual type of trisubstituted phosphine to form tris(phosphine) complexes with cobalt(II) halides has been attributed mainly to purely steric factors, although electronic factors have also been taken into consideration. The existence of the low spin compound[6] $Co(PHPh_2)_3Br_2$ and the fact that PCy_3 and PPh_3 show no power to form stable tris(phosphine) complexes with $Co(CNS)_2$, also support the importance of steric requirements. Indeed, if one considers the opposite inductive or conjugative effects of the two organic groups on the phosphorus atom it is difficult to see why PCy_3 should behave differently from PEt_3 and similarly to PPh_3 in its coordinative ability. The importance of steric factors is also suggested by the decrease in stability, evidenced by the spectral patterns, in going from $Co(PPhEt_2)_3(NCS)_2$ to $Co(PPh_2Et)_3(NCS)_2$. The above arguments might suggest that the large difference in the effects of halide and thiocyanate is due to the unfavourable size of the halogen atoms which imposes a serious steric harrier to the formation of tris(phosphine) complexes. However, the fact that the compound $Co(PEt_3)_2(NCO)_2$ shows little or no tendency to coordinate an additional phosphine molecule, clearly indicates that an interpretation in terms of steric factors alone is unsatisfactory. It is significant that similar behaviour is exhibited by the high spin octahedral complexes $Co(pyridine)_4X_2$. A study of the stability constants for the formation of tbe compound $Copy_4X_2$ by reaction of $Copy_2X_2$ with pyridine, shows that there is a large increase of stability in going from X = Cl, Br, I, NCO to X = NCS[5]. In both cases the peculiar influence of the NCS ion is therefore in conflict with purely steric arguments. It is clear that the effect of the NCS ion is to increase the acceptor properties of the cobalt atom by an electronic mechanism which does not operate in the case of the cyanate ion. In the case of the pyridine complexes this effect is related to a less unfavourable entropy loss on formation of $Copy_4(NCS)_2$. This smaller entropy loss has been interpreted in terms of dative π-bonding ($d\pi$–$p\pi$) in the Co–NCS bond, which renders the non-bonding metal orbitals less available for overlap with pyridine π-orbitals, raising thus the rotational freedom of the pyridine molecules[5]. This explanation may appear to be reasonable since cyanate ion should be a less effective π-acceptor than thiocyanate. However, in the case of the tris(phosphine) complexes we find it difficult to rationalize the experimental facts along the same lines of reasoning. Undoubtedly π-acceptor capacity can be one of the deciding factors, however there are other important differences between the two ions such as polarizability (or "softness") and σ-donor properties, and these may have even a greater influence. We do not think that the much larger stability of the thiocyanato complexes may be interpreted in terms of increasing rotational freedom of the phosphine molecules. We are more inclined to stress the importance of electronic factors because the nature of the bonding of thiocyanate and cyanate to the cobalt atom is substantially different owing to the large difference in electronegativity of the two groups. The cobalt–cyanate bond should have a much more ionic character and this might explain the large difference in the effects of cyanate and thiocyanate.

Further work on these compounds is in progress. The present results emphasise the fact that steric and electronic factors are both important in determining the stability of the low-spin complexes $\mathrm{Co(PR_3)_3X_2}$. The role of the ligand X in governing the coordination number appears to be of smaller importance when steric requirements are not critical. Thus, with 2-phenylisophosphindoline, 5-coordinate complexes can be formed even with X = halogen. However, when 5-coordination is difficult for steric reasons, the nature of the ligand X becomes important, and electronic factors are critical because they can supply the driving force for the formation of the 5-coordinated compound.

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REFERENCES

1 M. NICOLINI, C. PECILE AND A. TURCO, *J. Am. Chem. Soc.*, 87 (1965) 2379.
2 J. W. COLLIER AND F. G. MANN, *J. Chem. Soc.*, (1964) 1815.
3 G. BOOTH AND J. CHATT, *J. Chem. Soc.*, (1962) 2099.
4 W. E. HATFIELD AND J. T. YOKE, *Inorg. Chem.*, 1 (1962) 475.
5 H. C. A. KING, E. KÖRÖS AND S. M. NELSON, *J. Chem. Soc.*, (1963) 5449.
6 K. ISSLEIB AND E. WENSCHUH, *Z. Anorg. Allgem. Chem.*, 305 (1960) 15.