

Dithiocyanatobis(triethylphosphine)cobalt(II). High Spin–Low Spin Equilibria in Solution¹

Marino Nicolini, Cesare Pecile, and Aldo Turco²

Contribution from the Department of Chemistry, University of Padova, Italy.
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The magnetic moments and electronic and infrared spectra of the compound $\text{Co}(\text{PEt}_3)_2(\text{NCS})_2$ in solvents such as dichloromethane and dichloroethane are found to depend markedly on temperature and concentration. It is shown that this behavior is related to the existence of a monomeric (high spin) \rightleftharpoons dimeric (low spin) equilibrium. The high spin form is identified as a monomeric species with a tetrahedral configuration about cobalt(II). It is suggested that the low spin species is a dimer in which the cobalt atoms are linked by SCN bridges to give a penta-coordinate, approximately pyramidal configuration. The values of the equilibrium constants for the solution equilibria, derived from temperature dependence of magnetic susceptibilities, are presented.

Introduction

The coordination compounds of cobalt(II) of the type L_2CoX_2 (where L is $\text{P}(\text{C}_6\text{H}_{11})_3$, $\text{P}(\text{C}_6\text{H}_5)_3$, $\text{OP}(\text{C}_6\text{H}_{11})_3$, $\text{OP}(\text{C}_6\text{H}_5)_3$, and X = Cl, Br, I, NCS) have a tetrahedral structure and magnetic moments in the range 4.4–4.8 B.M.³ Also, the complexes of cobalt(II) halides with *n*-alkylphosphines are tetrahedral⁴ whereas the complex $\text{Co}(\text{PEt}_3)_2(\text{NCS})_2$ (Et = C_2H_5) has a magnetic moment indicating the presence of only one unpaired electron, as we reported recently.⁵

However, we found that in CH_2Cl_2 solutions the compound $\text{Co}(\text{PEt}_3)_2(\text{NCS})_2$ has a magnetic susceptibility larger than expected for the presence of one unpaired electron but lower than expected for a spin-free tetrahedral complex. The visible spectra in CH_2Cl_2 solutions are also drastically different from the reflection spectra of the solid compound, the major change being the appearance of absorption bands typical of tetrahedral cobalt(II) complexes. So, the magnetic and electronic spectral data show that both high spin and low spin species are present in CH_2Cl_2 solution. The existence in solution of the equilibrium diamagnetic \rightleftharpoons paramagnetic has already been established for quadri-coordinate nickel(II) complexes.⁶ A preliminary report indicates that a geometric isomerism between a square-planar (diamagnetic) and a tetrahedral (paramagnetic) form occurs in $\text{Ni}(\text{PEtPh}_2)_2\text{Br}_2$ (Ph = phenyl).⁷ For quadri-coordinate cobalt(II) complexes,

however, the existence of an equilibrium low spin \rightleftharpoons high spin has not been previously reported. One example of equilibrium spin free \rightleftharpoons spin paired in the solid state has been reported for a six-coordinate cobalt(II) compound.⁸

The present work offers evidence for the existence of a true chemical equilibrium between species of different configuration in solutions of $\text{Co}(\text{PEt}_3)_2(\text{NCS})_2$ and attempts to elucidate the nature of the species present in solution.

Experimental

Preparation of the Complexes. Some of the compounds described are very easily oxidized by air. When necessary, preparation and handling of the compounds were carried out in a nitrogen atmosphere closed system, and all solvents were distilled under nitrogen just prior to use. The infrared spectra of the phosphine complexes were examined to ensure that the products did not contain derivatives of phosphine oxides as an impurity. None of these complexes showed bands attributable to P–O vibrations.

The following complexes were known compounds and were prepared by the methods reported in the literature. Analytical data, physical properties, and the symbols used are reported in Table I. Methods of preparation for $\text{Co}(\text{PEt}_3)_2\text{Cl}_2$, $\text{Co}(\text{PCy}_3)_2\text{Br}_2$, $\text{Co}(\text{OPCy}_3)_2\text{Br}_2$, and $\text{Co}(\text{Diars})_2(\text{CNS})_2$ may be found in ref. 9–12, respectively.

The other complexes used in this investigation (Table I) were prepared by essentially the same method. This involved mixing an alcoholic solution of CoX_2 , where X is Cl^- , Br^- , or SCN^- , with an alcoholic solution of a stoichiometric amount of ligand L, where L is phosphine or phosphine oxide, to give the products $[\text{L}_2\text{CoX}_2]$. The amounts used were of the order of 5 mmoles of CoX_2 dissolved in 50 ml. of absolute ethanol and 10 mmoles of the ligand L dissolved in 25 ml. of absolute ethanol. Both reactant solutions were mixed at room temperature, and usually the products precipitated immediately upon mixing or after stirring for a few minutes. The mixture was set aside to cool at 0°, and the solid product was filtered, washed with ice-cold ethanol and petroleum ether (b.p. 30–50°), and dried *in vacuo* over P_2O_5 . Minor variations in this method are given as footnotes to Table I.

Dithiocyanatobis(triethylphosphine)cobalt(II). Triethylphosphine (1.7 ml., 1.35 g., 11.4 mmoles) was added to a solution of cobalt(II) thiocyanate (1.0 g., 5.7

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(2) Istituti Chimica Generale e Chimica Fisica, Università di Padova, Italy.

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Table I. Analytical Data and Physical Properties for $\text{Co}(\text{PR}_3)_2\text{X}_2$ Complexes

Compound ^a	Yield, %	M. p., °C. ^b	Color	μ_{eff} , B.M. (25°)	% C		% H		% Co		% other	
					Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$\text{Co}(\text{PEt}_3)_2\text{Cl}_2$	Not det.	102	Blue	4.45	39.4	39.6	8.26	8.39			Cl 19.35	19.6
$\text{Co}(\text{PEt}_3)_2(\text{NCS})_2^c$	50	98–100 (dec.)	Brown-red	2.20 3.40 ^d	40.9	40.4	7.36	7.36	14.3	14.3	N 6.81	6.76
$\text{Co}(\text{PCy}_3)_2\text{Br}_2$	52	199 ^e	Blue	4.50	55.5	54.2	8.53	8.50	7.56	7.60		
$\text{Co}(\text{PCy}_3)_2\text{Cl}_2$	52	198 ^e	Blue	4.45	62.9	61.3	9.63	9.45	8.53	8.50		
$\text{Co}(\text{PCy}_3)_2(\text{NCS})_2^f$	44	179 ^e	Green	4.40 4.40 ^g	62.0	60.4	9.04	8.83	8.01	8.00	N 3.81	3.87
$\text{Co}(\text{OPCy}_3)_2\text{Br}_2$	50	204 ^e	Blue	4.75	53.3	53.5	8.20	7.82	7.27	7.15		
$\text{Co}(\text{OPCy}_3)_2\text{Cl}_2$	40	209 ^e	Blue	4.70	59.8	59.3	9.20	9.08	8.17	8.12		
$\text{Co}(\text{OPCy}_3)_2(\text{NCS})_2$	60	189	Blue	4.50	59.4	59.8	8.66	8.86	7.67	7.58	N 3.65 P 8.07	3.7 8.05
$\text{Co}(\text{Diars})_2(\text{CNS})_2$	Not det.		Light brown	2.30	35.3	34.7	4.31	4.30				

^a Abbreviations: Et, ethyl; Cy, cyclohexyl; Diars, *o*-phenylenebisdimethylarsine. ^b All melting points are uncorrected. ^c Molecular weight measurements (carried out cryoscopically in $\text{C}_2\text{H}_4\text{Cl}_2$): concentration = 0.097 *m*, mol. wt. = 798, polymerization number (p. no., *i.e.*, mol. wt. (obsd.)/mol. wt. (calcd.)) = 1.94; concentration = 0.132 *m*, mol. wt. = 806, p. no. = 1.96. ^d 0.45 *M* in CH_2Cl_2 . ^e Recrystallized from hot absolute ethanol. ^f Prepared by addition of 13.5 mmoles of PCy_3 in ethanol-cyclohexane (300 ml., 4:1) to 6.74 mmoles of $\text{Co}(\text{CNS})_2$ in absolute ethanol (50 ml.). Molecular weight (measured at 25° using a Mechrolab osmometer): calcd., 736; found, 730. ^g 0.26 *M* in CH_2Cl_2 .

mmoles) in absolute ethanol (20–25 ml.) at room temperature. This solution was cooled at -60° for 5 min. and then brought again to room temperature and allowed to stand. Red-brown crystals separated from the green solution. The solid product was filtered, washed with small quantities of ice-cold absolute ethanol, and dried *in vacuo*. The compound reacts very rapidly with oxygen. The solid compound is stable under nitrogen.

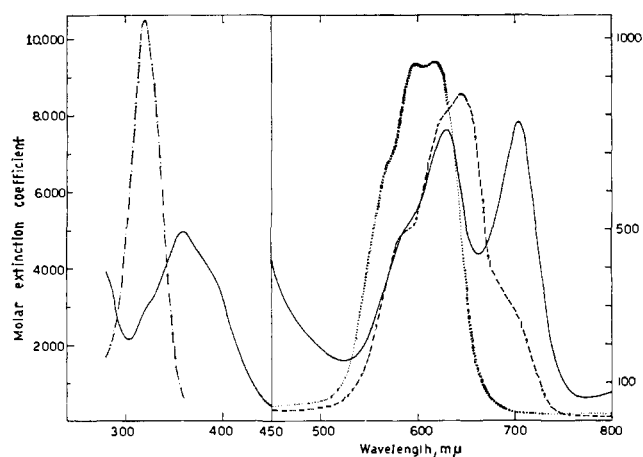


Figure 1. Absorption spectra in CH_2Cl_2 : $\text{Co}(\text{PEt}_3)_2(\text{NCS})_2$ (—), molar concentration = 6.1×10^{-4} (ultraviolet), 0.96×10^{-2} (visible); $\text{Co}(\text{PCy}_3)_2(\text{NCS})_2$ (---), molar concentration = 1.1×10^{-2} ; $\text{Co}(\text{OPCy}_3)_2(\text{NCS})_2$ (·····), molar concentration = 0.84×10^{-2} ; $[\text{Co}(\text{NCS})_4]^{2-}$ (-·-·-), molar concentration = 2.7×10^{-4} .

The molar conductance of a 2×10^{-3} *M* solution of CH_2Cl_2 , was 0.43 ohm^{-1} ; the molar conductance of a 1.8×10^{-3} *M* solution of $(\text{C}_2\text{H}_5)_4\text{NBr}$ was 13.2 ohm^{-1} , and that of a 10^{-3} *M* solution of $(\text{NEt}_3)_2\text{Co}(\text{NCS})_4$ was 10 ohm^{-1} . The low conductivity values indicate that the compound is a nonelectrolyte in CH_2Cl_2 and could arise either from partial rearrangement to give the ionic form $[\text{Co}(\text{PEt}_3)_4][\text{Co}(\text{NCS})_4]$ or from slight solvolysis in the very dilute solution. The presence of small amounts of $[\text{Co}$

$(\text{NCS})_4]^{2-}$ in solution is in agreement with the shoulder at about $320 \text{ m}\mu$ observed in the spectrum of $\text{Co}(\text{PEt}_3)_2(\text{NCS})_2$ in CH_2Cl_2 (Figure 1).

The average magnetic moment of samples obtained in seven different preparations was 2.21 ± 0.03 B.M., compared to 2.3 reported previously.⁵

Magnetic Measurements. Determinations of magnetic susceptibility were made at various temperatures and field strengths using the Gouy method. No dependence of susceptibility on field strength was observed in any case. The Gouy tubes were calibrated with solutions of NiCl_2 and solid copper(II) sulfate as previously reported.¹³ The magnetic moments were obtained by correcting measured susceptibility values for diamagnetism and using the equation $\mu = 2.84 \sqrt{\chi_{\text{mol}}^{\text{corr}} T}$.

Electronic Spectra. The spectra in solution were recorded using a Beckman DK2A spectrophotometer equipped with a thermostated cell compartment. Standard cells with path lengths 0.1, 1.0, and 5.0 cm. were used for the low-concentrations range. Concentrated solutions were examined using a cell with path length of 0.03 mm. Reflectance spectra of the solid compounds were measured using a Beckman D.U. spectrophotometer with a standard reflectance attachment and magnesium carbonate as the reference sample.

Infrared Spectra. The spectra were recorded using a Perkin-Elmer Model 21 spectrophotometer equipped with a sodium chloride prism. The samples were examined either as solids in Nujol mulls or as solutions in fixed-thickness cells with calcium fluoride windows and Teflon spacers.

Molecular Weight Determinations. Reagent grade solvents were dried over Drierite and then distilled under nitrogen. Cryoscopic determinations in $\text{C}_2\text{H}_4\text{Cl}_2$ were made by a differential apparatus calibrated with solutions of dibenzyl.

Results and Discussion

Table I lists a series of quadricoordinate cobalt(II) complexes of the type L_2CoX_2 studied in the present

(13) A. Turco, C. Pecile, and M. Nicolini, *J. Chem. Soc.*, 3008 (1962).

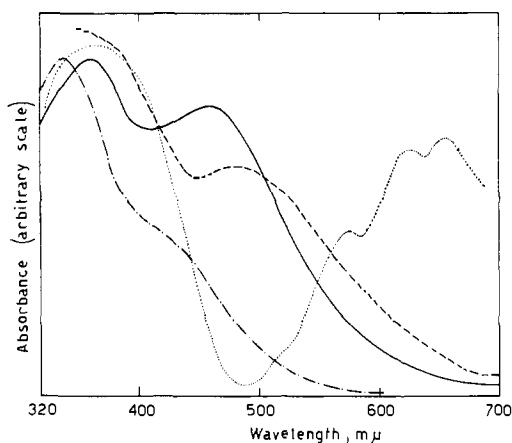


Figure 2. Reflectance spectra of $\text{Co}(\text{PEt}_3)_2(\text{NCS})_2$ (—), $\text{Co}(\text{diarsine})_2(\text{CNS})_2$ (---), $[\text{Co}(\text{CNCH}_3)_4][\text{CdBr}_4]$ (-·-·-·-), and $\text{Co}(\text{PCy}_3)_2(\text{NCS})_2$ (·····).

work, whose spectral and magnetic properties are well interpreted on the basis of a tetrahedral structure.¹⁴ The spin-paired complex $\text{Co}(\text{PEt}_3)_2(\text{NCS})_2$ is the only compound of the type L_2CoX_2 to which a tetrahedral configuration cannot be assigned. Spin-paired complexes of both planar and octahedral configurations have been discussed by Figgis and Nyholm, who concluded that for square complexes the moments range from 2.1 to 2.9 B.M., whereas octahedral complexes have moments falling in the range 1.7–2.0 B.M. because of the lower orbital contribution.¹⁵

The crystalline compound $\text{Co}(\text{PEt}_3)_2(\text{NCS})_2$ has a moment of 2.2 B.M., consistent with a spin-paired square-planar complex. However, on the basis of the magnetic data alone, a polymeric sexicovalent tetragonal structure with bridging thiocyanato groups cannot be ruled out (*vide infra*).

Comparison of the reflectance spectra (Figure 2) with the spectra in solution (Figure 1) shows that the solid compound undergoes drastic structural changes upon dissolution. In fact, in the region 500–800 $\text{m}\mu$ the spectra in CH_2Cl_2 clearly arise from the presence of tetrahedral species, as shown by the shape and intensity of the absorption bands. Other features of the absorption spectra merit brief comment. The spectra of the tetrahedral compounds shown in Figures 1 and 2 show a very low absorption in the 400–500- $\text{m}\mu$ region, while the extinction coefficient of $\text{Co}(\text{PEt}_3)_2(\text{NCS})_2$ in CH_2Cl_2 is greater than 150. This absorption can be attributed to the presence of low spin species in solution, and, in fact, the spectrum of the crystalline complex shows strong absorption bands in this region. In the near-ultraviolet region, comparison with the spectrum of $[\text{Co}(\text{NCS})_4]^{2-}$ reveals that a very small amount of this species is present in solutions of $\text{Co}(\text{PEt}_3)_2(\text{NCS})_2$.

The values of the magnetic susceptibility of the solutions are in good agreement with the spectral data. The magnetic moment of $\text{Co}(\text{PEt}_3)_2(\text{NCS})_2$ is only 3.4 in 0.45 M CH_2Cl_2 solution, in contrast to the magnetic moment of $\text{Co}(\text{PCy}_3)_2(\text{NCS})_2$ which is 4.4 B.M., both in

(14) The magnetic moments (B.M.) of tetrahedral complexes of the same type reported by other authors are: $\text{Co}(\text{PEt}_3)_2\text{Br}_2$, 4.764; $\text{Co}(\text{PPh}_3)_2\text{X}_2$ ³⁰ where X = Br, 4.52; X = Cl, 4.41; X = NCS, 4.46 (Ph = phenyl).

(15) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 338 (1959).

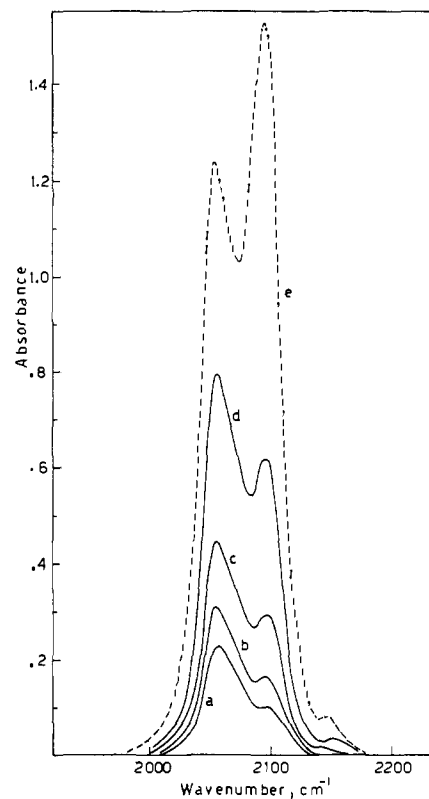


Figure 3. Infrared spectra of $\text{Co}(\text{PEt}_3)_2(\text{NCS})_2$ in CH_2Cl_2 . Molar concentration: a = 0.051; b = 0.076; c = 0.12; d = 0.25; e = 0.51.

the solid and in solution. If one makes the assumption that the moment of the (not isolated) tetrahedral isomer of $\text{Co}(\text{PEt}_3)_2(\text{NCS})_2$ is about 4.4 B.M., then the moment 3.4 found in CH_2Cl_2 indicates that both high spin and low spin species are present in this solvent.

The conclusions based on the visible spectra and the magnetic data are supported by the infrared absorption spectra of the compound. The spectrum of solid $\text{Co}(\text{PEt}_3)_2(\text{NCS})_2$ has a strong band at 2090 cm^{-1} , assigned to the CN stretching vibration of the SCN group, and shows no absorption bands in the 2130–2160- cm^{-1} region. These data might indicate that there are no bridging thiocyanato groups in the compound $\text{Co}(\text{PEt}_3)_2(\text{NCS})_2$ in the solid state and exclude a polymeric structure. Although it has been shown¹⁶ that thiocyanato complexes containing thiocyanato bridges display a maximum at a frequency some 30–60 cm^{-1} higher than those with terminal thiocyanato groups, we wish to point out that this is observed only for *strong* thiocyanato bridges. When the bridges are *weak*, the CN stretching may well give rise to absorption in the same region as the terminal groups. This is the case, for example, for the polymeric compounds $\text{Co}(\text{pyridine})_2(\text{NCS})_2$ (2107, 2080 cm^{-1}) and $\text{Ag}(\text{Pr}_3\text{P})(\text{NCS})$ (2090 cm^{-1}), in which adjacent metal atoms are linked by two $-\text{SCN}-$ bridging groups to form quasi-planar eight-membered rings $\cdots\text{M}(\text{SCN})_2\text{M}\cdots$ ¹⁷

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Table II. Magnetic Data at Various Temperatures for $\text{Co}(\text{PEt}_3)_2(\text{NCS})_2$ in CH_2Cl_2

T , °K.	$C_z \times$ 10^2 ^a	$\chi_M \times$ 10^6 (corr.) ^b	μ_{eff} B.M.	μ_{eff} (solid), B.M.	f ^c	$K_z \times$ 10^2 ^d
298	2.70	4820	3.40	2.21	0.465	2.18
298	2.84	4830	3.40	2.21	0.468	2.33
298	3.66	4530	3.30	2.21	0.422	2.25
298	4.18	4360	3.24	2.21	0.390	2.10
293	2.55	4973	3.42	2.19	0.473	2.17
283	2.55	4790	3.31	2.17	0.422	1.57
273	2.55	4617	3.22	2.19	0.381	1.20
263	2.55	4500	3.09	2.21	0.325	0.802
253	2.55	4375	3.00	2.21	0.287	0.589
243	2.55	4330	2.91	2.18	0.250	0.425
231	2.55	4240	2.80	2.18	0.207	0.276

^a C_z = mole fraction of complex. ^b Diamagnetic correction = 274×10^{-6} c.g.s. unit. ^c f = fraction of tetrahedral (high spin) species; f has been calculated assuming $\mu_{\text{eff}} = 4.4$ B.M. for the high spin species, $\mu_{\text{eff}} = 2.2$ B.M. for the low spin species. ^d The equilibrium constants K_z have been calculated for the reaction: $[\text{Co}(\text{PEt}_3)_2(\text{NCS})_2]_2 \rightleftharpoons 2\text{Co}(\text{PEt}_3)_2(\text{NCS})_2$.

In both these compounds the metal-sulfur bond lengths are found to be considerably greater than that expected for a covalent bond. Thus, the value of 2090 cm^{-1} found for $\text{Co}(\text{PEt}_3)_2(\text{NCS})_2$, while it does not rule out the possibility of a weak sulfur-cobalt bonding interaction, seems to indicate that the cobalt-nitrogen bond is of relatively greater importance. The infrared spectra in the region 2000–2100 cm^{-1} in CH_2Cl_2 solution are shown in Figure 3 and consist of two bands at 2060 and 2090 cm^{-1} . The spectra of some tetrahedral thiocyanates of the type $\text{L}_2\text{M}(\text{NCS})_2$ in

that the species absorbing at 2090 cm^{-1} is the low spin complex present in the solid (or at least similar to it), we may logically conclude that the low spin species derives from the association of the high spin molecules.

The conclusion is confirmed by the visible spectra and by the magnetic susceptibility values at various concentrations in CH_2Cl_2 . Spectra of $\text{Co}(\text{PEt}_3)_2(\text{NCS})_2$ in CH_2Cl_2 solutions at different concentrations are shown in Figure 5. The deviation from Beer's

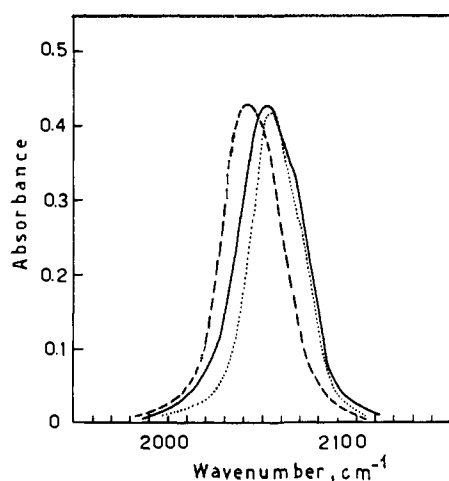


Figure 4. Infrared absorption of 0.1 M CH_2Cl_2 solutions of tetrahedral isothiocyanates in the 2000–2100- cm^{-1} range: —, $\text{Co}(\text{OPCy}_3)_2(\text{NCS})_2$; ----, $\text{Co}(\text{PCy}_3)_2(\text{NCS})_2$; ·····, $\text{Zn}(\text{PEt}_3)_2(\text{NCS})_2$; cell thickness, 0.019 mm.

the same region are shown in Figure 4 for comparison. We assign the absorption band at 2060 cm^{-1} to the tetrahedral species $\text{Co}(\text{PEt}_3)_2(\text{NCS})_2$. The intensity of this absorption shows that the NCS group is attached to cobalt(II) through the nitrogen atom.¹⁸ The band at 2090 cm^{-1} is attributed to nontetrahedral species. As shown in Figure 3, the relative intensities of the two bands vary with the concentration, indicating that the nontetrahedral species, which absorbs at 2090 cm^{-1} , predominates in concentrated solution, whereas the reverse is true in dilute solution. If we now assume

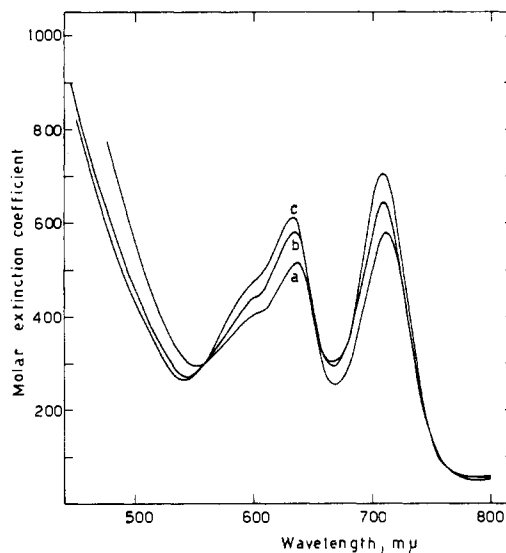


Figure 5. Visible spectra of $\text{Co}(\text{PEt}_3)_2(\text{NCS})_2$ in CH_2Cl_2 solution. Molar concentration: a = 0.40; b = 0.265; c = 0.15.

law is very striking, qualitatively supporting the existence of a concentration-dependent molecular association process. Here again one can see that the concentration of the tetrahedral species decreases when the total concentration of complex increases.

The concentration dependence of spectral (Figures 3 and 5) and magnetic (Table II) properties of $\text{Co}(\text{PEt}_3)_2(\text{NCS})_2$ in CH_2Cl_2 at various concentrations also consistently points out the same conclusion, namely, that the high spin (tetrahedral species) predominates at low concentrations, and the low spin species, at high concentrations.

The spectra of $\text{Co}(\text{PEt}_3)_2(\text{NCS})_2$ in CH_2Cl_2 solution at various temperatures are shown in Figure 6. On

(18) C. Pecile and A. Turco, to be published.

decreasing the temperature, the relative intensity of the absorption attributed to the tetrahedral species decreases while that corresponding to the low spin species increases. Also, the ratio of tetrahedral/nontetrahedral species at a given concentration depends only upon the temperature. Thus, high spin and low spin species transform reversibly one into the other on changing the temperature.

To determine the applicability of the concept of an equilibrium mixture of the two species in different spin states, the magnetic susceptibility of relatively concentrated solutions has been determined as a function of temperature over a range of about 70°. The results are summarized in Table II. The mole fractions of the two species were calculated for each temperature on the assumption that the magnetic moment of the tetrahedral species is 4.4 B.M. and that of the low spin species is 2.2 B.M., similar to the value of the crystalline compound. Since the molecular weight measurements (Table I) indicate that the low spin species exist primarily as a dimer in $C_2H_4Cl_2$, the equilibrium constant was then calculated for the reaction $[Co(PEt_3)_2(NCS)_2]_2 \rightleftharpoons 2[Co(PEt_3)_2(NCS)_2]$. The simplified treatment adopted in the calculation of the stability constant does not take into account the temperature dependence of the magnetic moment of the different species in equilibrium. However, this approximation should introduce only negligible errors in the present case, and the main source of error in determining the stability constants probably arises from the uncertainty of the values of the magnetic moments assigned to the two different spin states. In spite of these limitations there is no doubt as to the validity of the general interpretation, which is supported by the satisfactory fitting of the data in the graph of $\log K$ vs. $1/T$. The values at 298°K. in Table II also show that the equilibrium constant K is reasonably independent of the concentration, the differences among the calculated values being within experimental error. Although the concentration range studied is rather narrow owing to experimental limitations, it still shows that any other value of the association number n does not satisfy a hypothetical equilibrium constant K_n . While the precision of the data at hand cannot rule out the existence in solution of small amounts of higher oligomers, it appears clearly from the available evidence that the dimer is the most stable oligomeric species. The enthalpy of dissociation per dimer unit is 4.0 kcal./mole, based on the data in the temperature range 231–263°K.

The validity of the equilibrium constants K_x was tested by comparing the magnetic and spectral results. Since only the tetrahedral species absorbs at 705 $m\mu$, the ratio R_A between the optical densities at this wavelength at two different temperatures is equal to the ratio R_T of the concentrations of the tetrahedral monomer. Using the values of K_x obtained from magnetic data the amount of monomer present at each temperature was calculated for the concentration at which the spectra in Figure 6 were recorded. The ratios R_T thus obtained are in good agreement with the corresponding values of R_A , showing that the overall interpretation of the equilibria is correct and indirectly indicating that the magnetic moment of the low spin species in solution cannot differ greatly from

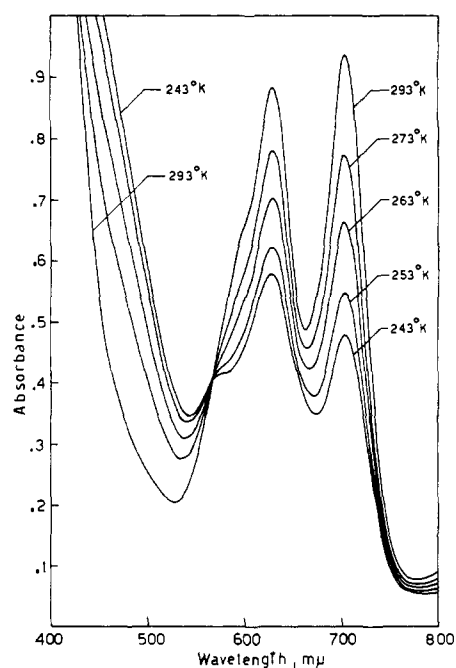


Figure 6. Visible spectra of $Co(PEt_3)_2(NCS)_2$ in CH_2Cl_2 solution, in the temperature range 243–293°K. Molar concentration = 1.1×10^{-2} .

the assumed value of 2.2 B.M. The dimeric species in solution is therefore likely to be structurally similar to the crystalline compound, which may be considered to be a polymer with the cobalt atoms having a coordination number >4 . Although a widely accepted empirical rule assigns a planar structure to cobalt(II) compounds having magnetic moments greater than 2.0,¹⁵ we feel that there is still insufficient structural information concerning spin-paired cobalt(II) complexes and that it is very possible that such an empirical rule does not hold in the borderline region of 2.0–2.3 B.M. In fact, recent work indicates that the compound $Co(diarsine)_2(CNS)_2$, which has a magnetic moment of 2.3 B.M. and which was therefore considered to be square-planar,¹⁹ has a coordination number greater than 4, and probably 6.²⁰ Similarly, the value of 2.2 B.M. found for $Co(PEt_3)_2(NCS)_2$ does not exclude a coordination number greater than 4 in the solid state. A polymeric arrangement of the type found for $Co(pyridine)_2(SCN)_2$, consisting essentially of a square-planar arrangement of four nitrogens around the metal, with two more loosely bonded sulfur atoms above and below the plane to give a tetragonally distorted octahedron, would satisfactorily account for the properties of the solid $Co(PEt_3)_2(NCS)_2$.

In solution, a discussion of the possible structure of the low spin dimer and of the equilibria, can only be based on indirect arguments. There are at least two possible ways to describe the process of molecular association and the equilibrium between the high spin and low spin species: (a) the presence of high spin and low spin molecules is regulated by a thermal Boltzmann distribution; (b) spin pairing is a consequence of the association of high spin monomers.

(19) R. S. Nyholm, *J. Chem. Soc.*, 2071 (1950).

(20) C. M. Harris, T. N. Lokyer, and R. S. Nyholm, unpublished work, communication of E. D. McKenzie.

If the energy difference between the doublet and quartet state of cobalt(II) is comparable to thermal energies, a temperature-dependent Boltzmann distribution of molecules between the doublet and quartet state will result, and, since the most stable configuration is square-planar for the doublet state, but tetrahedral for the quartet state, the structural change will also be temperature dependent. In this case the association process of the low spin molecules may be explained on the basis of a strong tendency of planar cobalt(II) to further coordinate one or two more ligands. Although direct cobalt-cobalt interaction cannot be excluded, we believe it more likely that association occurs by formation of bonds between the cobalt atom of one molecule and the sulfur end of the SCN of another molecule. It is of interest to note that the compound $\text{Co}(\text{PCy}_3)_2(\text{NCS})_2$ exhibits a different behavior. The magnetic moment of the compound is 4.4 both in the solid and in CH_2Cl_2 (Table I), and thus there is no evidence for the existence of low spin isomers in solution at 25° . Moreover, the spectrum in the same solvent does not show important changes as the temperature decreases from $+25$ to -25° (there is a 10% increase in ϵ_{max} accompanied by a decrease of the bands width). Steric hindrance caused by the bulky $\text{P}(\text{C}_6\text{H}_{11})_3$ ligands cannot be of relevant importance for the stability of the planar molecule, as shown by the fact that the nickel(II) complexes of the type $\text{Ni}(\text{PR}_3)_2(\text{CNS})_2$ are all planar, nor can electronic factors be of great importance since the behavior of $\text{P}(\text{C}_6\text{H}_{11})_3$ and $\text{P}(\text{C}_2\text{H}_5)_3$ as ligands is essentially the same in this respect.^{3a} However, the greater bulk of the $\text{P}(\text{C}_6\text{H}_{11})_3$ ligands can be of relevant importance in preventing one molecule from approaching another sufficiently to produce association. This suggests that association is the critical factor which stabilizes the low spin state, and this observation invalidates the simple picture of a thermal distribution of molecules between doublet and quartet state.

Since SCN bridges are easily formed by cobalt(II) in a number of compounds,^{17a,21} we believe that also, in the present example, molecular association occurs through formation of SCN bridges between the cobalt atoms of two different molecules. For steric reasons, only two of the four NCS groups can function as a bridge in the dimeric molecule. Thus, the cobalt

(21) F. A. Cotton and R. H. Holm, *J. Am. Chem. Soc.*, **82**, 2983 (1960).

atoms can only be five-coordinate in solution (ignoring solvent coordination), and we suggest that in this case each cobalt atom forms four stronger bonds with two nitrogen and two phosphorus atoms and one weaker bond with the sulfur atom of an NCS group. The perturbation caused by one of the sulfur atoms of one molecule on the cobalt atom of another tetrahedral molecule will cause the four main bonds to distort from an essentially tetrahedral to a nearly planar configuration. At a certain stage of the distortion, when the four main bonds are sufficiently distorted, spin pairing can occur. The situation is structurally very similar to that of the compound $\text{Co}(\text{pyridine})_2(\text{CNS})_2$ which is tetrahedral in nitrobenzene.²² In the solid state, tetragonal perturbation by the terminal sulfur atoms results in the distortion of the four Co-N bonds to a planar configuration. However, since pyridine produces a ligand field weaker than phosphine, the compound $\text{Co}(\text{pyridine})_2(\text{NCS})_2$ has high spin both in the solid and in solution.²² In the absence of any direct structural information, a discussion of the structure of the spin-paired species may seem somewhat speculative. However, the interpretation presented here is in accordance with the extensive experimental facts reported above. Thus, for example, one can readily explain that the compound $\text{Co}(\text{PCy}_3)_2(\text{NCS})_2$ remains tetrahedral and spin-free both in the solid and in solution because the greater bulk of the phosphine ligands does not allow the sulfur ends to approach the cobalt sufficiently close to produce adequate perturbation.

Finally, with regard to the structure of $\text{Co}(\text{PEt}_3)_2(\text{NCS})_2$ in the solid state a comparison between the electronic reflectance spectra of $\text{Co}(\text{PEt}_3)_2(\text{NCS})_2$ (Figure 2) and of the spin-paired compounds $\text{Co}(\text{diarsine})_2(\text{CNS})_2$ ²⁰ and $\text{Co}(\text{CN-CH}_3)_4\text{CdBr}_4$,²³ both believed to be six-coordinate, shows that the three compounds all display one band in the 440–500 $\text{m}\mu$ region and one stronger band in the 330–380 $\text{m}\mu$ range. Thus, although only a qualitative significance can be attached to such a comparison, the general features of the spectra strongly suggest that the type of coordination is similar in the three compounds, and there is the possibility that $\text{Co}(\text{PEt}_3)_2(\text{NCS})_2$ may, in the solid state, achieve six-coordination by thiocyanate bridging between dimeric units.

(22) N. S. Gill and R. S. Nyholm, *J. Inorg. Nucl. Chem.*, **18**, 88 (1961).

(23) A. Sacco and F. A. Cotton, *J. Am. Chem. Soc.*, **84**, 2043 (1962).