

A HIGH SPIN-LOW SPIN CONFORMATIONAL EQUILIBRIUM IN THE COMPLEX DITHIOCYANATOBIS(TRIETHYLPHOSPHINE)COBALT(II)

M. NICOLINI, C. PECILE AND A. TURCO*

Istituti di Chimica Generale e di Chimica Fisica, Università di Padova, Consiglio Nazionale delle Ricerche, Roma (Italy)

ABSTRACT

The magnetic moments, electronic and infrared spectra of the compound $[\text{Co}(\text{PEt}_3)_2(\text{NCS})_2]$ are found to depend markedly on temperature and concentration in solvents such as dichloromethane and dichloroethane. It is shown that these characteristics depend on a *monomeric (high spin) \rightleftharpoons dimeric (low spin)* equilibrium.

The high spin form is identified with a tetrahedral configuration about the cobalt atom. It is suggested that the low spin species is a dimer in which the cobalt atoms are linked by SCN bridges to give a pentacoordinate, approximately pyramidal, configuration. The values of the equilibrium constants for the solution equilibria derived from the temperature dependence of the magnetic susceptibilities are presented.

INTRODUCTION

The coordination compounds of cobalt(II) of the type L_2CoX_2 (where L is PCy_3 , PPh_3 , OPR_3 , and $\text{X} = \text{Cl}$, Br , I , NCS) have a tetrahedral structure, and magnetic moments in the range 4.4–4.8 $B.M.$ ¹ The complexes of cobalt(II) halides with *n*-alkyl phosphines are tetrahedral² whereas that of cobalt(II) thiocyanate, as we reported recently³, has a magnetic moment indicating the presence of only one unpaired electron.

We also found that dichloromethane solutions of the compound $[\text{Co}(\text{PEt}_3)_2(\text{NCS})_2]$ have a magnetic susceptibility larger than expected for the presence of one unpaired electron, but lower than expected for spin-free tetrahedral complexes. The visible spectra in dichloromethane solution are 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. The magnetic

* M. Nicolini and A. Turco, Istituto Chimica Generale, Università di Padova. C. Pecile, Istituto Chimica Fisica, Università di Padova.

and electronic spectral data showed that both high spin and low spin species are present in dichloromethane solution. The existence in solution of the equilibrium, diamagnetic \rightleftharpoons paramagnetic, has already been established for the quadricoordinate nickel(II) complexes⁴. A preliminary report indicates that a geometric isomerism between a square planar (diamagnetic) and a tetrahedral (paramagnetic) form occurs⁵ in $[\text{Ni}(\text{PPh}_2\text{Et})_2\text{Br}_2]$. The existence of an equilibrium low spin \rightleftharpoons high spin has never been reported previously for quadricoordinate cobalt(II) complexes. One case of equilibrium spin free \rightleftharpoons spin paired in the solid state has been reported for a six coordinate cobalt(II) compound⁶.

It is our purpose here to present evidence for the existence of a true chemical equilibrium in solutions of $[\text{Co}(\text{PEt}_3)_2(\text{NCS})_2]$, and to try to elucidate the nature of the chemical species present in solution.

RESULTS AND DISCUSSION

Table I lists a series of quadricoordinate cobalt(II) complexes of the type L_2CoX_2 , whose spectral and magnetic properties must be rationalized with a tetrahedral structure. The complex $[\text{Co}(\text{PEt}_3)_2(\text{NCS})_2]$ is the only case for which

TABLE I

STRUCTURE-MAGNETISM CORRELATIONS FOR SOME COBALT(II) COMPLEXES

Compound		Color	$\mu_{eff}(\text{B.M.})$	Structure
$[\text{Co}(\text{PR}_3)_2\text{X}_2]$				
R = ethyl;	X = Cl	blue	4.39 ^a ; 4.45	tetrahedral
	Br	blue	4.76 ^a	tetrahedral
	NCS	brown-red	2.20	planar
R = phenyl;	X = Cl	dark-blue	4.41 ^b	tetrahedral
	Br	blue-green	4.52 ^b	tetrahedral
	NCS	green	4.46 ^b	tetrahedral
R = cyclohexyl;	X = Cl	blue	4.45	tetrahedral
	Br	blue	4.61 ^b ; 4.50	tetrahedral
	NCS	green	4.40	tetrahedral
$[\text{Co}(\text{OPCy}_3)_2\text{X}_2]$				
	X = Cl	blue	4.70	tetrahedral
	Br	blue	4.75	tetrahedral
	NCS	blue	4.50	tetrahedral

^a W. E. HATFIELD AND J. T. YOKE, *Inorg. Chem.*, 1 (1962) 475.

^b F. A. COTTON *et al.*, *J. Am. Chem. Soc.*, 83 (1961) 4157.

a tetrahedral configuration cannot be assigned because it is spin-paired. Spin-paired complexes of both planar and octahedral types have been discussed by Figgis and Nyholm, who concluded that for spin-paired square complexes the moments ranged from 2.1 to 2.9 *B.M.* while spin-paired octahedral complexes have moments falling within the range 1.7–2.0 *B.M.* owing to the lower orbital contribution⁷.

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

The reflectance spectra of $[\text{Co}(\text{PEt}_3)_2(\text{NCS})_2]$ and those of $[\text{Co}(\text{diars})_2(\text{SCN})_2]$ and $[\text{Co}(\text{CNCH}_3)_4][\text{CdBr}_4]$ are shown in Fig. 1. The reflectance spectrum of the tetrahedral $[\text{Co}(\text{PCy}_3)_2(\text{NCS})_2]$ (Cy = cyclohexyl) has also been included for comparison. The spectra in dichloromethane of $[\text{Co}(\text{PEt}_3)_2(\text{NCS})_2]$ and of the tetrahedral compounds $[\text{Co}(\text{PCy}_3)_2(\text{NCS})_2]$ and $[\text{Co}(\text{OPCy}_3)_2(\text{NCS})_2]$ are shown in Fig. 2. Comparison of the spectra in solution with the reflectance spectra, shows that drastic structural changes occur upon solution of the solid compound. Indeed the spectra in dichloromethane in the range 500–800 $\text{m}\mu$ are clearly due to the presence of tetrahedral species as shown by the shape and by the intensity of the bands. Other features of the absorption spectra merit brief comment. The spectra of the tetrahedral compounds recorded in Fig. 1 and Fig. 2 show a very low

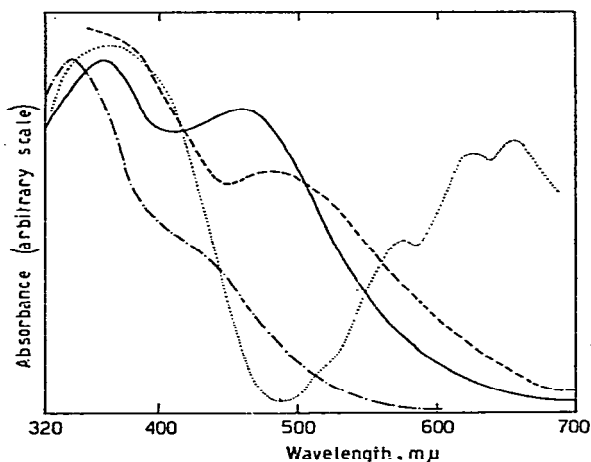


Fig. 1. Reflectance spectra of $[\text{Co}(\text{PEt}_3)_2(\text{NCS})_2]$ (—), $[\text{Co}(\text{diarsine})_2(\text{CNS})_2]$ (-.-.-), $[\text{Co}(\text{CNCH}_3)_4][\text{CdBr}_4]$ (---), $[\text{Co}(\text{PCy}_3)_2(\text{NCS})_2]$ (.....).

absorption in the 400–500 $\text{m}\mu$ region while the extinction coefficient of $[\text{Co}(\text{PEt}_3)_2(\text{NCS})_2]$ is greater than 150 in dichloromethane. This absorption can be attributed to the presence in solution of low-spin species. In fact the spectrum of the crystalline complex shows strong absorption bands in this region. Coming to the near ultra-violet region, comparison with the spectrum of $[\text{Co}(\text{NCS})_4]^{2-}$ reveals that very small amounts of this species are present in the solutions of $[\text{Co}(\text{PEt}_3)_2(\text{NCS})_2]$.

The conclusions derived from the spectral data are confirmed by the value of the magnetic susceptibility of the solutions. Table VI shows that in contrast to the magnetic moment of $[\text{Co}(\text{PCy}_3)_2(\text{NCS})_2]$ (4.4 *B.M.* in the solid and in solution) the magnetic moment of $[\text{Co}(\text{PEt}_3)_2(\text{NCS})_2]$ is only 3.4 in 0.45 *M* dichloro-

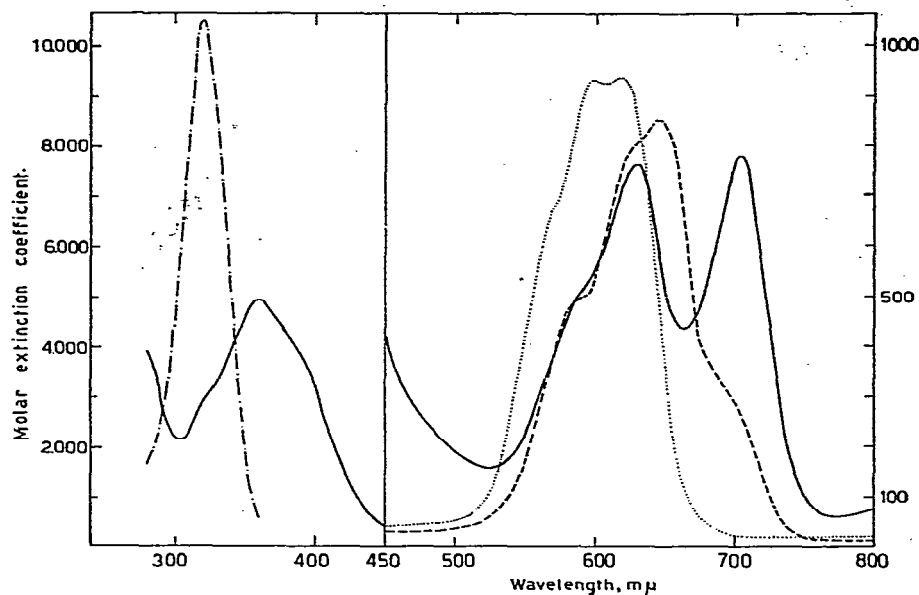


Fig. 2. Absorption spectra in CH_2Cl_2 : $[\text{Co}(\text{PEt}_3)_2(\text{NCS})_2]$ (—), molar concn. = $6.1 \cdot 10^{-4}$ (U.V.), $0.96 \cdot 10^{-2}$ (Vis.); $[\text{Co}(\text{PCy}_3)_2(\text{NCS})_2]$ (---), molar concn. = $1.1 \cdot 10^{-2}$; $[\text{Co}(\text{OPCy}_3)_2(\text{NCS})_2]$ (.....), molar concn. = $0.84 \cdot 10^{-2}$; $[\text{Co}(\text{NCS})_4]^{2-}$ (-.-.-), molar concn. = $2.7 \cdot 10^{-4}$.

methane 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 dichloromethane indicates that both high spin and low spin species are present in this solvent.

TABLE II

INFRARED ABSORPTION OF THE SCN GROUP IN SOME THIOCYANATO COMPLEXES IN SOLUTION

Compound	Solvent	$\nu_{\text{as}}(\text{NCS})$, (cm^{-1})	$\Delta\nu_{\frac{1}{2}}$, (cm^{-1})	ϵ_{max}^* , ($M^{-1}\text{cm}^{-1}$)	$A \times 10^{-4}^*$, ($M^{-1}\text{cm}^{-2}$)
KSCN	$\text{CH}_3\text{COC}_2\text{H}_5$	2060	16	760	4.4
$\text{K}_2\text{Pt}(\text{SCN})_4$	CH_3COCH_3	2112	12	477	1.8
$\text{K}_2\text{Pt}(\text{SCN})_6$	CH_3COCH_3	2120	14	207	1.03
$(\text{NEt}_3)_2\text{Co}(\text{NCS})_4$	$\text{CH}_3\text{COC}_2\text{H}_5$	2077	18	1320	11.7
$\text{trans}-(\text{PEt}_3)_2\text{Pt}(\text{NCS})_2$	$\text{CH}_3\text{COC}_2\text{H}_5$	2112	26	705	—
$\text{trans}-(\text{AsEt}_3)_2\text{Pt}(\text{NCS})_2$	$\text{CH}_3\text{COC}_2\text{H}_5$	2116	24	1340	—
$(\text{CH}_3\text{NC})_2\text{Pd}(\text{SCN})_2$	CHCl_3	2124	16	255	—
$(\text{PEt}_3)_2\text{Zn}(\text{NCS})_2$	$\text{ClCH}_2\text{CH}_2\text{Cl}$	2078 sh	—	—	—
		2062	32**	1130	—
$(\text{Cy}_3\text{PO})_2\text{Co}(\text{NCS})_2$	$\text{ClCH}_2\text{CH}_2\text{Cl}$	2080 sh	—	—	—
		2066	27**	1110	—
$(\text{Cy}_3\text{P})_2\text{Co}(\text{NCS})_2$	$\text{ClCH}_2\text{CH}_2\text{Cl}$	2060 sh	—	—	—
		2052	30**	1150	—

* Calculated per mole of coordinated SCN group.

** Values evaluated by graphic resolution.

The conclusions based on the visible spectra and on the magnetic data are supported by an analysis of 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 does not have absorption bands in the $2130\text{--}2160\text{ cm}^{-1}$ region. Two strong bands are observed at 830 and 795 cm^{-1} in the spectrum of $[\text{Co}(\text{PET}_3)_2(\text{NCS})_2]$ but are absent in the

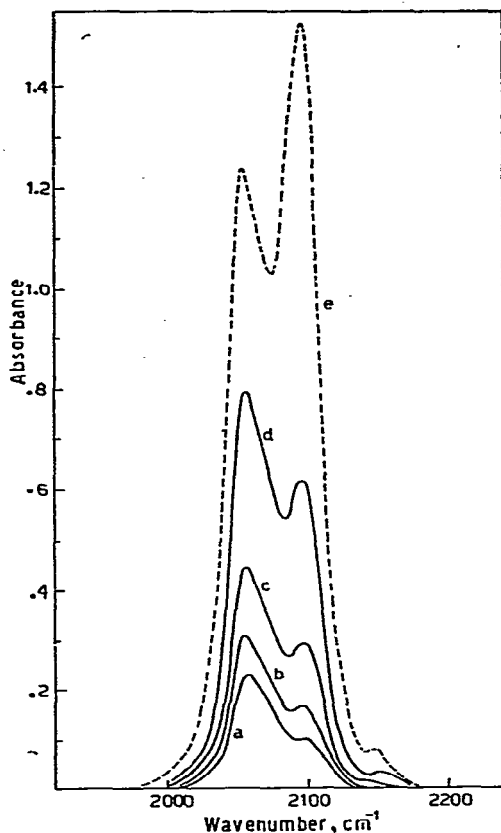


Fig. 3. Infrared spectra of $[\text{Co}(\text{PET}_3)_2(\text{NCS})_2]$ in CH_2Cl_2 . Molar concentration: a = 0.051; b = 0.076; c = 0.12; d = 0.25; e = 0.51.

spectra of $[\text{Co}(\text{PET}_3)_2\text{Cl}_2]$ and $[\text{Co}(\text{PET}_3)_2\text{Br}_2]$; they are assigned to the CS (pseudo-symmetrical N-C-S) stretching vibration of the NCS group in isothiocyanates. The infrared spectra in the region $2000\text{--}2100\text{ cm}^{-1}$ in dichloromethane solution are shown in Fig. 3. They consist of two bands at 2060 and 2090 cm^{-1} . The interpretation of the spectra requires a brief discussion of the infrared behaviour of other thiocyanato complexes.

The value of 2090 cm^{-1} found for the solid spectrum might indicate that there are no bridging thiocyanato groups in the compound $[\text{Co}(\text{PET}_3)_2(\text{NCS})_2]$ and exclude a polymeric structure. It has been shown⁸, for a number of thiocyanato complexes, that those compounds which contain strong thiocyanato

bridges display a maximum at a frequency some $30\text{--}60\text{ cm}^{-1}$ higher than a terminal thiocyanato group. We wish to point out that these criteria can be valid 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 statement is valid, for example, for the polymeric compounds $[\text{Co}(\text{pyridine})_2(\text{NCS})_2]$, ($2107, 2080\text{ cm}^{-1}$) and $[\text{Ag}(\text{Pr}_3\text{P})(\text{NCS})]$ (2090 cm^{-1}) when the metal atoms are linked by two $-\text{SCN}-$ groups forming 8-membered quasi-planar rings $..M(\text{SCN})_2M..$ ⁹.

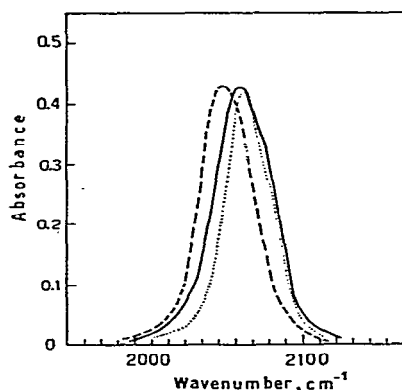


Fig. 4. Infrared absorption of $0.1\text{ M C}_2\text{H}_4\text{Cl}_2$ solutions of tetrahedral isothiocyanates in the $2000\text{--}2100\text{ cm}^{-1}$ range:

(—), $[\text{Co}(\text{OPCy}_3)_2(\text{NCS})_2]$;

(---), $[\text{Co}(\text{PCy}_3)_2(\text{NCS})_2]$;

(.....), $[\text{Zn}(\text{PEt}_3)_2(\text{NCS})_2]$; (cell thickness, 0.019 mm).

In both cases the metal-sulphur bond length is considerably greater than the distance expected for a covalent bond. In the compound $[\text{Ag}(\text{Pr}_3\text{P})(\text{NCS})]$ the Ag-S bond length is about 2.75 \AA while in the polymeric AgSCN the length of the same bond is only 2.43 \AA . Thus the value of 2090 cm^{-1} found for $[\text{Co}(\text{PET}_3)_2(\text{NCS})_2]$ cannot, in our opinion, rule out the possibility of a weak sulphur-cobalt bond interaction. However, it can indicate that the cobalt-nitrogen bond must be of relatively greater importance. The values of 830 and 795 cm^{-1} for the CS stretch, are in the region of M-NCS coordination. The possible existence of $-\text{NCS}-$ bridges makes less certain, however, the application of this criterion in the present case. The doublet structure might indicate that there are two different types of NCS groups; one of them functioning as a bridging group, the other as a terminal Co-NCS group.

The band at 2090 cm^{-1} found in dichloromethane solution (Fig. 3) is attributed to species similar to those present in the crystalline compound. The other band in dichloromethane at 2060 cm^{-1} must be attributed to species of a conformation different from that of the solid compound. The spectra in the same region of some tetrahedral thiocyanates of the type $\text{L}_2\text{M}(\text{NCS})_2$ are reproduced in Fig. 4. These, in combination with the visible spectra, which clearly indicate the presence of tetrahedral species in solution, allow us to attribute the absorption at 2060 cm^{-1} to tetrahedral molecules of $[\text{Co}(\text{PET}_3)_2(\text{NCS})_2]$. The intensity of the absorption at 2060 cm^{-1} shows that the NCS group is bound to cobalt through its

nitrogen end¹⁰. Comparison of the values of the integrated intensity A ($M^{-1}\text{cm}^{-2}$) in a series of isothiocyanato- and thiocyanato complexes, shows that the two types of coordination can easily be differentiated. The A values per single coordinated SCN group, fall in the range $0.8\text{--}2.3 \times 10^4 M^{-1}\text{cm}^{-2}$ for the $M\text{--SCN}$ compounds, and in the range $9\text{--}12 \times 10^4 M^{-1}\text{cm}^{-2}$ for $M\text{--NCS}$ compounds. When the value of A is not available, it can be advantageously replaced by the product $\epsilon_{\text{max}} \times \Delta\nu_{\frac{1}{2}}$ ($\Delta\nu_{\frac{1}{2}}$ = half band width) which can also be taken as indicative of the relative intensities of the absorption, and therefore of the type of coordination. When

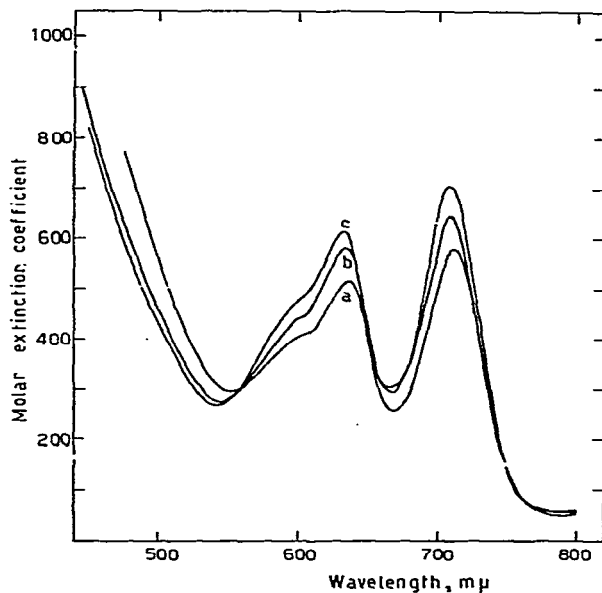


Fig. 5. Visible spectra of $[\text{Co}(\text{PEt}_3)_2(\text{NCS})_2]$ in CH_2Cl_2 solution. Molar concentration: a = 0.40; b = 0.265; c = 0.15.

more than one band is present, depending on the particular symmetry of the molecule, in the $2050\text{--}2120\text{ cm}^{-1}$ region, the product $\epsilon_{\text{max}} \times \Delta\nu_{\frac{1}{2}}$ is still sufficiently indicative of the type of bonding (Table II). Fig. 3 shows that the relative intensities of the two bands depend drastically on the concentration. Thus the infrared spectra indicate that the non tetrahedral species, which absorb at 2090 cm^{-1} , predominate in concentrated solutions, whereas the reverse is true in dilute solutions.

This conclusion is confirmed by the visible spectra and magnetic susceptibility at various concentrations in dichloromethane. Spectra of $[\text{Co}(\text{PEt}_3)_2(\text{NCS})_2]$ in solutions of different concentrations are shown in Fig. 5. The deviation from Beer's law is very striking, qualitatively supporting the conclusion that there is 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 and magnetic properties of $[\text{Co}(\text{PEt}_3)_2(\text{NCS})_2]$ in dichloromethane at various concentrations is summarized in Table III. The values of the magnetic moment and the spectral data consistently point to the same conclusion, namely that the high spin (tetrahedral species)

TABLE III

OBSERVED EXTINCTION* AT VARIOUS WAVELENGTHS FOR $[\text{Co}(\text{PEt}_3)_2(\text{NCS})_2]$ IN CH_2Cl_2 AT 25°

Mol.concn.	μ_{eff}	$^a\epsilon_{710}(\text{m}\mu)$	$^a\epsilon_{2080}(\text{cm}^{-1})$	$^a\epsilon_{2090}(\text{cm}^{-1})$	$\epsilon_{2080}/\epsilon_{2090}$
0.68	3.24	—	—	—	—
0.59	3.31	—	—	—	—
0.51	—	—	950	1173	0.81
0.44	3.40	—	—	—	—
0.40	—	580	—	—	—
0.26	—	630	—	—	—
0.25	—	—	1247	965	1.29
0.15	—	705	—	—	—
0.12	—	—	1454	915	1.59
0.076	—	—	1600	851	1.88
0.051	—	—	1770	769	2.30

* $^a\epsilon = A/lc_M$, where A = absorbance, l is path length, c_M is molar concn. of Co(II).

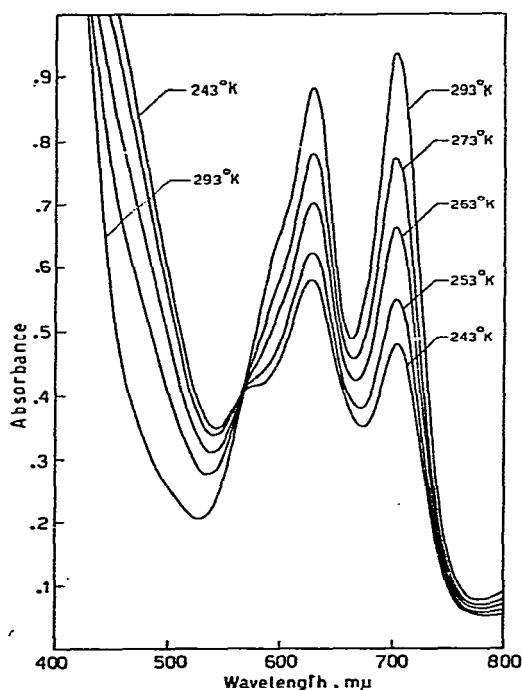


Fig. 6. Visible spectra of $[\text{Co}(\text{PEt}_3)_2(\text{NCS})_2]$ in CH_2Cl_2 solution, in the temperature range 243–293 °K. Molar concentration = $1.1 \cdot 10^{-2}$.

predominates at low concentrations, whereas the low spin species is formed at high concentrations.

A record of the spectrum of $[\text{Co}(\text{PEt}_3)_2(\text{NCS})_2]$ in dichloromethane at various temperatures is shown in Fig. 6. The apparent extinction coefficient of the tetrahedral species becomes smaller at lower temperatures (lowering of the temperature causes absorption to decrease in the 600–800 $\text{m}\mu$ region) but it becomes greater at wave-lengths shorter than the isosbestic point where the low spin species absorb. Moreover, the ratio of tetrahedral/non-tetrahedral 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.

In order 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 almost 70° . The results are summarised in Table IV. By assuming

TABLE IV

MAGNETIC DATA AT VARIOUS TEMPERATURES FOR $[\text{Co}(\text{PEt}_3)_2(\text{NCS})_2]$ IN CH_2Cl_2

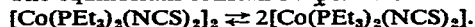
$T, ^\circ\text{K}$	$^a C_x \cdot 10^2$	$^b 10 \chi_M(\text{corr.})$	$\mu_{\text{eff}}, B.M.$	$\mu_{\text{eff}}(\text{solid})$	c_f	$^d K_x \cdot 10^2$
298	2.70	4820	3.40	2.21	0.465	2.18
298	2.84	4830	3.40	2.21	0.468	2.33
298	3.66	4530	3.30	2.21	0.422	2.25
298	4.18	4360	3.24	2.21	0.390	2.10
293	2.55	4973	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_x is the mole fraction of complex.

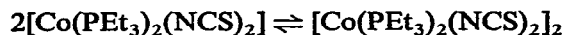
^b diam. corr. = 274×10^{-6} c.g.s. units.

^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_x have been calculated for the reaction:



a magnetic moment of $4.4 B.M.$ for the tetrahedral species and $2.2 B.M.$ for the low spin species (the value for the crystalline compound), the mole fraction of the two states was calculated for each temperature at which the determination was made. The equilibrium constant was calculated for the reaction



since the molecular weight measurements, Table V, indicate that the low spin species exists primarily as a dimer in solution. The values thus calculated for the equilibrium constants can be affected by the approximation introduced in this simplified treatment. Thus the treatment given ignores the variation with temper-

TABLE V

CRYSCOPIC MOLECULAR WEIGHT MEASUREMENTS ON $[\text{Co}(\text{PEt}_3)_2(\text{NCS})_2]$ IN ETHYLENEDICHLORIDE AT ABOUT -35°

concn. ^a	Mol. wt. ^b	Polymerisation No. ^c
0.097	798	1.94
0.132	806	1.96

^a concn. = moles of $[\text{Co}(\text{PEt}_3)_2(\text{NCS})_2]$ in 1000 g of ethylenedichloride.^b Theory for $[\text{Co}(\text{PEt}_3)_2(\text{NCS})_2]$: 411.4.^c Polymerisation number equals observed molecular weight/411.4.

ature of the moment assigned to the different species in equilibrium. However this approximation can only introduce negligible errors in the present case. Indeed the main source of error is probably due to the uncertainty in the *true* values of the magnetic moments in the two different spin states. Thus, whereas the value of 4.4 *B.M.* for the tetrahedral species is probably very near to the *true* value, one cannot be sure *a priori* that the magnetic moment of the low spin species is 2.2 *B.M.*, in view of the existing uncertainty about the structural identity in the solid and in solution. In spite of these limitations there is no doubt as to the veracity of the over-all interpretation, as shown for example by the satisfactory fitting of the data in the graph of $\log K$ vs. $1/T$. The enthalpy of dissociation per dimer unit is 4.0 kcal/mole based on the data in the temperature range 231–263°K.

The dimeric species in solution is likely to be structurally similar to the crystalline compound, and we suggest that the solid compound has a polymeric structure in which the cobalt atoms have a coordination number greater than four. Apparently this conclusion is not in agreement with the empirical rule⁷ which assigns a square planar structure to cobalt(II) compounds having magnetic moments greater than 2.0. However, we wish to point out that there is insufficient structural information concerning spin-paired cobalt(II) complexes to rule out the possibility that, in the borderline region of 2.0–2.3 *B.M.*, this empirical stereochemical rule does not apply. Thus we believe that the value of 2.2 *B.M.* found for $[\text{Co}(\text{PEt}_3)_2(\text{NCS})_2]$ cannot exclude a coordination number greater than four in the solid state. It might easily be six giving a polymeric arrangement of the type found for $[\text{Co}(\text{pyridine})_2(\text{SCN})_2]$. The structure of the molecule consists essentially of a square planar arrangement of four nitrogens around the metal, with two sulphur atoms loosely bonded perpendicular to the plane to give a tetragonally distorted octahedron. The structure of solid $[\text{Co}(\text{PEt}_3)_2(\text{NCS})_2]$ might easily be of this type.

We shall now discuss the most probable structures of the species present in solution. There can be little doubt that the high spin species is a tetrahedral monomer with the NCS groups linked to cobalt through their nitrogen ends. Speculation as to the structure of the low spin dimer can only be based on indirect arguments and there are at least two possible ways of describing the process of molecular association and the equilibrium between the two species.

First there is the possibility that the energy difference between the doublet and quartet states is comparable to thermal energies. Thus a temperature-dependent Boltzmann distribution of molecules between the doublet and quartet state will occur. Consequently also temperature dependent structural change will occur because the stable structure for the doublet state is square planar, while it is tetrahedral for the quartet state. In this case the association process of the low spin molecules may be explained by a strong tendency of planar cobalt(II) to further coordinate one or two more ligands. Although direct cobalt-cobalt interaction cannot be excluded, association could more easily occur by formation of bonds between the cobalt atom of one molecule and the sulphur end of the SCN of another molecule. In principle, this interpretation seems correct, however we find it difficult to explain the absence of a similar behaviour in the case of $[\text{Co}(\text{PCy}_3)_2(\text{NCS})_2]$. One can see in Table VI that the magnetic moment of the compound is

TABLE VI

MAGNETIC DATA FOR $[\text{Co}(\text{PEt}_3)_2(\text{NCS})_2]$ AND $[\text{Co}(\text{PCy}_3)_2(\text{NCS})_2]$ AT 25 °C

Compound	μ_{eff} , B.M.	Mol. weight
$[\text{Co}(\text{PEt}_3)_2(\text{NCS})_2]$		
solid	2.21	
0.45 M, CH_2Cl_2	3.41	—
$[\text{Co}(\text{PCy}_3)_2(\text{NCS})_2]$		
solid	4.40	
0.26 M, CH_2Cl_2	4.40	730 ^a

^a Mechrolab Inc. apparatus; theory for $[\text{Co}(\text{PCy}_3)_2(\text{NCS})_2]$: 736.

4.4 both in the solid and in solution, 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 change appreciably 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 PCy_3 ligands cannot be relevant for the stability of the square planar molecule as shown by the fact that the nickel(II) complexes of the type $[\text{Ni}(\text{R}_3\text{P})_2(\text{CNS})_2]$ are all square planar. Nor can electronic factors be of importance, since the behavior of PCy_3 and PEt_3 as ligands is essentially the same in this respect¹⁰. However, the greater bulk of the PCy_3 ligands can be of importance in preventing one molecule approach another sufficiently to produce association. This suggests that association is the critical factor which stabilises 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 cases^{9a,11} we suggest that in the present case molecular association also 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 atoms can only be five-coordinate in solution

(ignoring solvent coordination) and we suggest that in this case each cobalt atom has four good bonds made by two nitrogen and two phosphorus atoms and one loose bond made by the sulfur end of an NCS group.

This tetragonal (or pyramidal) perturbation from the sulfur end of one complex molecule to the cobalt atom of another tetrahedral molecule will cause the four main bonds to distort from a tetrahedral to a planar configuration. At a certain stage of the distortion pairing of the spins can occur, when the four main bonds are sufficiently distorted. The situation is structurally very similar to that of the pyridine compound $[\text{Co}(\text{pyridine})_2(\text{NCS})_2]$. This is tetrahedral in nitrobenzene¹² and in going to the solid state must distort the four Co-N bonds towards a planar configuration. However, the presence in the compound of two pyridine molecules in the place of two phosphine molecules gives a ligand field weaker than that in $[\text{Co}(\text{PET}_3)_2(\text{NCS})_2]$ and thus $[\text{Co}(\text{pyridine})_2(\text{NCS})_2]$ is high spin both in the solid and in solution¹². In the absence of any direct structural information, speculation as to actual structure of the spin-paired species may seem somewhat hazardous. However we believe that the interpretation presented here is in accordance with the extensive experimental facts reported above.

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Figs. 1-6 and Table IV are reproduced, with permission, from A. TURCO *et al.*, *J. Am. Chem. Soc.*, 87 (1965) 2379.

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