Spin Isomerism in Five-Coordinate Cobalt(II) Complexes of the Terdentate Ligands N-R-N-2-(diphenylphosphino)ethyl-N',N'-diethylethylenediamine (Donor Set NNP)

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The title ligands (R = H, H-NNP; R = Me, Me-NNP) form cobalt(II) complexes of general formula $CoLX_2$ (X = halogen, NCS). All the halo complexes are high spin and five-coordinate in the solid state; in solution they are partially (H-NNP) or entirely (Me-NNP) tetrahedral. The complex $Co(Me-NNP)(NCS)_2$ is also high spin and five-coordinate, whereas the corresponding H-NNP derivative in the solid state shows a temperature-dependent spin equilibrium between quadruplet and doublet ground states. In solution it is irreversibly oxidized to a cobalt(III) derivative $Co(H-NNP)(NCS)_3$ and a cobalt(II) phosphine oxide complex $Co(H-NNP(O))(NCS)_2$. Each of these compounds can be isolated with proper choice of the solvent.

## Introduction

Terdentate ligands of the type I are known to form neutral complexes having the formula $CoLX_2$ with cobalt(II) salts.

$$A{\overset{CH_2CH_2}{\diagup}}B{\overset{CH_2CH_2}{\diagup}}C$$

I
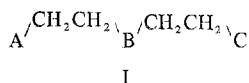
Both the overall steric requirements of the ligand and the nature of the donor groups A, B, and C have an important influence on the configuration and spin state of the resulting complex. Thus, for example, the ligands Et_4dien (A = C = NEt_2, B = NH) and Me_5dien (A = C = NMe_2, B = NMe) form high-spin five-coordinate complexes,[1,2] but ligands of the series PN(R)P (A = C = PPh_2, B = NH, NMe) give complexes of the same configuration though with low spin, a difference stemming from the difference between nitrogen and phosphorus as donor atoms.[3] When A = C = PPh_2 and B = N-cyclohexyl, tetrahedral complexes are formed.[3]

It therefore seemed interesting to study the complexes of cobalt(II) formed with ligands containing one phosphorus atom and two nitrogen atoms, a donor set NNP intermediate between the sets NNN and PNP previously studied. Such a series is exemplified by the ligands N-R-N-2-(diphenylphosphino)ethyl-N',N'-diethylethylenediamine (II). (Referring to formula I, A = NEt_2, C = PPh_2, B = NH, NMe.)

$$Et_2N{\overset{CH_2CH_2}{\diagup}}\underset{N}{\overset{R}{|}}{\overset{CH_2CH_2}{\diagup}}PPh_2$$

II
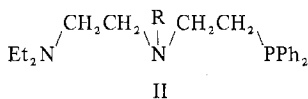
R = H, H-NNP
R = Me, Me-NNP

A preliminary account of the $Co(H-NNP)(NCS)_2$ complex has already been given.[4]

Results

The analytical data are given in Table I. The complexes are generally soluble in polar organic solvents, giving air-stable solutions, except in the case of $Co(H-NNP)(NCS)_2$ whose solutions change from violet to red on exposure to dry air. Physical measurements on the latter complex were carried out under nitrogen. The magnetic moment of this complex at room temperature is 3.79 BM and is temperature dependent, changing from 2.16 BM at 77°K to 4.32 BM at 418°K. Plots of $1/\chi_M$ and μ_{eff} against temperature are given in

Figure 1, with further details in Table II. The magnetic moments of the other complexes are normal for high-spin cobalt(II) complexes (Table I), with an orbital contribution that increases with decreasing ligand field strength, *i.e.*, in the order NCS, Cl, Br, I, as expected.[1]

Molecular weight and conductivity data indicate that all complexes are undissociated monomers in 1,2-dichloroethane and nitroethane. Partial solvation is observed in nitroethane, notably with $Co(H-NNP)I_2$. Electronic absorption spectra are shown in Figures 2–5, with further details in Table III.

Discussion

(H-NNP)-X Complexes. The electronic spectra of the complexes $Co(H-NNP)X_2$ (X = Cl, Br, I) are very similar to each other and are typical of high-spin five-coordinate cobalt-(II) complexes.[1,2,5] A neutral, monomeric structure $[Co(H-NNP)X_2]$ with donor set $NNPX_2$ is therefore assigned to each of these compounds. In the solid-state reflectance spectra the bands attributable to the transitions $^4A_2(F) \to {}^4E(F)$ and $^4A_2(F) \to {}^4E(P)$ are split (Table III),[5] and the splitting clearly indicates increasing geometrical distortion of the complex from the chloride to the bromide and iodide. A similar splitting was found in the spectra of the corresponding Et_4dien complexes.[1] In solution the absorption spectra do not show band splitting and thus indicate that lattice forces are in part responsible for the distortions in the crystalline state.

The solution spectrum of each complex is temperature dependent, as is illustrated in Figure 3. The observed variations clearly indicate the presence of an equilibrium between the five-coordinate species and a tetrahedral species whose concentration increases with temperature. As the solutions remain nonconducting, the tetrahedral species must be formed by detaching one of the donor atoms of the ligand. These results can be used to compare H-NNP with the ligands previously studied. On the one hand the complex Co-(Et_4dien)I_2 transforms completely into the tetrahedral species even at room temperature,[1] while on the other hand the complex $Co(H-PNP)I_2$ remains entirely in the five-coordinate form even at high temperatures.[3] This behavior suggests that for a given central atom and halide the internal strain of the complex decreases in the order Et_4dien > H-NNP > H-PNP, that is, as the NEt_2 groups are successively replaced by PPh_2 groups having different steric and electronic requirements. The effect is most clearly seen in the iodide complexes, for iodide, because of its size, induces more strain into the chelate rings than do the smaller halides.

(1) Z. Dori and H. B. Gray, *Inorg. Chem.*, 7, 889 (1968).
(2) M. Ciampolini and G. P. Speroni, *Inorg. Chem.*, 5, 45 (1966).
(3) L. Sacconi and R. Morassi, *J. Chem. Soc. A*, 2997 (1968).
(4) R. Morassi and L. Sacconi, *J. Amer. Chem. Soc.*, 92, 5241 (1970).

(5) M. Ciampolini and N. Nardi, *Inorg. Chem.*, 5, 41 (1966); M. Ciampolini and I. Bertini, *J. Chem. Soc. A*, 2997 (1968).

Table I. Analytical and Magnetic Data for the Complexes

Compound	Color	Mp, °C	% found				% calcd				μ_{eff}, BM[a]
			C	H	N	Metal	C	H	N	Metal	
[Co(H–NNP)Cl₂]	Purple	212–214	52.8	6.4	6.3	13.0	52.42	6.38	6.11	12.83	4.59 (21)
[Co(H–NNP)Br₂]	Purple	203–206	44.0	5.6	5.4	10.6	43.80	5.34	5.12	10.75	4.63 (21)
[Co(H–NNP)I₂]	Magenta	203–207	37.9	4.7	4.6	9.1	37.47	4.56	4.37	9.19	4.63 (21)
[Co(H–NNP)(NCS)₂]	Amethyst	178 dec	52.9	6.0	11.4	11.7	52.50	5.81	11.14	11.70	3.79 (21)
[Co(H–NNP(O))(NCS)₂] [b]	Violet	210–212	51.0	5.8	11.1	11.6	50.85	5.63	10.78	11.34	4.56 (30)
[Co(H–NNP)(NCS)₃] [c]	Red-brown	178–181	48.9	5.2	12.3	10.3	49.19	5.20	12.47	10.49	Diam (25)
[Co(Me–NNP)Cl₂]	Violet	166–168	53.1	6.7	6.0	12.8	53.40	6.62	5.93	12.47	4.55 (21)
[Co(Me–NNP)Br₂]	Violet	150–152	45.3	5.7	5.4	10.6	44.93	5.57	4.99	10.50	4.67 (21)
[Co(Me–NNP)(NCS)₂]	Light violet	178–182	53.8	6.3	10.7	11.6	53.40	6.04	10.80	11.38	4.47 (21)

[a] Temperature (°C) in parentheses. [b] Sulfur analysis: calcd, 12.34; found, 12.3. [c] Sulfur analysis: calcd, 17.13; found, 17.0.

Table II. Dependence of Magnetic Moment on Temperature for the [Co(H–NNP)(NCS)₂] Complex

Temp, °K	$10^6 \chi_M$, cgs emu	μ_{eff}	Temp, °K	$10^6 \chi_M$, cgs emu	μ_{eff}
79	7390	2.16	233	3715	2.64
88	6595	2.16	246	3982	2.80
100	5804	2.15	261	4561	3.10
116	5135	2.19	278	4968	3.34
128	4707	2.21	297	5373	3.60
140	4310	2.20	302	5464	3.65
154	3966	2.22	323	5764	3.87
170	3675	2.24	348	5860	4.05
189	3488	2.30	373	5865	4.20
206	3450	2.43	398	5789	4.30
220	3538	2.50	418	5553	4.32

Table III. Spectrophotometric Data for the Complexes

Compound	State[a]	Absorption max, kK, with ϵ_{molar} for soln in parentheses[b]
[Co(H–NNP)Cl₂]	R	5.6 br, 11.7, 14.3, 19.2
	D	5.9 br (24), 11.5 (30), 14.8 (96), 19.0 (207)
[Co(H–NNP)Br₂]	R	5.6 br, 11.0, 14.0, 18.6, 19.2 sh
	DB	5.9 br (32), 11.1 (41), 14.6 (126), 18.6 (237)
[Co(H–NNP)I₂]	R	5.4 br, 10.0 sh, 11.8 sh, 14.0, 17.6 sh, 18.8, 21.0 sh
	D	5.8 br (26), 11.1 (39), 14.3 (144), 16.0 sh, 18.8 (221)
[Co(H–NNP)(NCS)₂]	R	6.65 br, 10.9 sh, 15.9 sh, 19.5 sh, 20.7
	D[c]	5.9 br (62), 12.0 sh, 15.3 (163), 20.1 (303)
	D[d]	5.5 br (28), 12.5 (21), 16.8 (240), 18.9 (315)
[Co(H–NNP(O))(NCS)₂]	R	5.8 br, 11.0, 13.4 sh, 16.6, 18.5 sh, 19.6, 21.0
	D	5.5 br (33), 12.5 (26), 16.7 (202), 18.9 (133), 19.85 (138), 21.1 sh
[Co(H–NNP)(NCS)₃]	R	18.4, 26.0 sh
	D	19.0 (1860)
[Co(Me–NNP)Cl₂]	R	6.0 br, 9.5, 12.6 sh, 15.0, 17.8, 18.8 sh, 20.1
	D	5.9 br (30), 7.25 (35), 9.8 (26), 15.3 (226), 15.8 sh, 17.4 (238)
[Co(Me–NNP)Br₂]	R	5.9 br, 9.3, 12.5 sh, 15.1 sh, 17.5, 18.1 sh, 19.8
	D	5.8 br (29), 6.9 (37), 9.5 (30), 14.9 (312), 15.4 (305), 16.7 (286), 17.5 sh
[Co(Me–NNP)(NCS)₂]	R	5.9 br, 12.0 sh, 15.5, 19.0, 20.5 sh
	D	6.1 br (66), 12.5 (56), 15.25 (220), 18.8 (277)

[a] R, diffuse reflectance; DB, *o*-dichlorobenzene; D, 1,2-dichloroethane. [b] br, broad; sh, shoulder. [c] Under inert atmosphere. [d] After aerial oxidation.

(Me–NNP) Complexes. The complexes Co(Me–NNP)X₂ (X = Cl, Br, I) have reflectance spectra which indicate a five-coordinate structure but which differ sufficiently from those
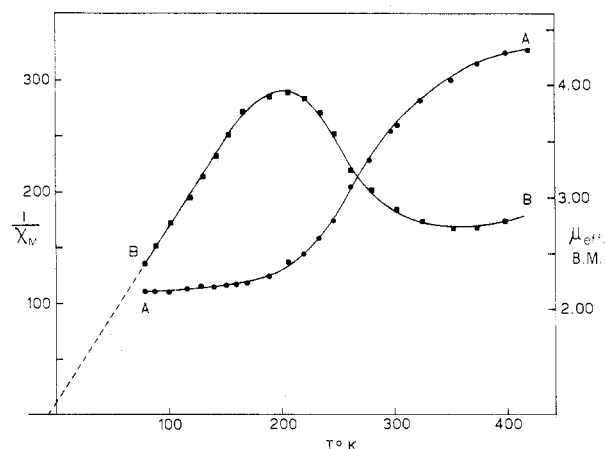

Figure 1. Plots of μ_{eff} (A, right-hand scale) and $1/\chi_M$ (B, left-hand scale) *vs.* absolute temperature for Co(H–NNP)(NCS)₂.
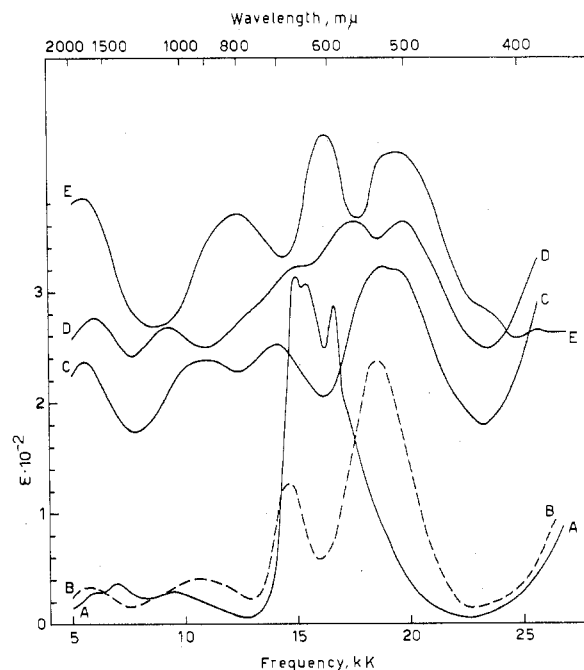

Figure 2. Absorption spectra: A, Co(Me–NNP)Br₂ (in 1,2-dichloroethane); B, Co(H–NNP)Br₂ (in *o*-dichlorobenzene). Reflectance spectra (arbitrary scale): C, Co(H–NNP)Br₂; D, Co(Me–NNP)Br₂; E, [Co(Me₆tren)Br] Br (from ref 5).

of the H–NNP complexes to suggest a substantial geometrical difference (Figure 2). The absorption spectra, moreover, show that even at room temperature the complexes assume an entirely tetrahedral form in solution (Figure 2). The ligand is bidentate in this case, too, since the complexes are not ionic. Thus, the replacement of the hydrogen atom on the central nitrogen atom by a methyl group favors the for-
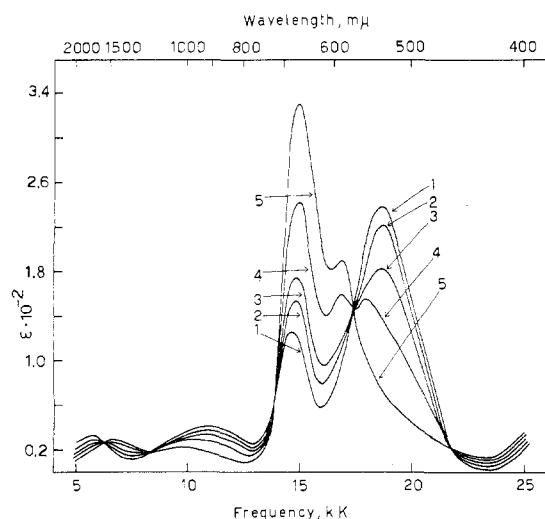
Figure 3. Absorption spectra of Co(H–NNP)Br$_2$ in o-dichloro-benzene solution: 1, 19°; 2, 60°; 3, 80°; 4, 110°; 5, 130°.

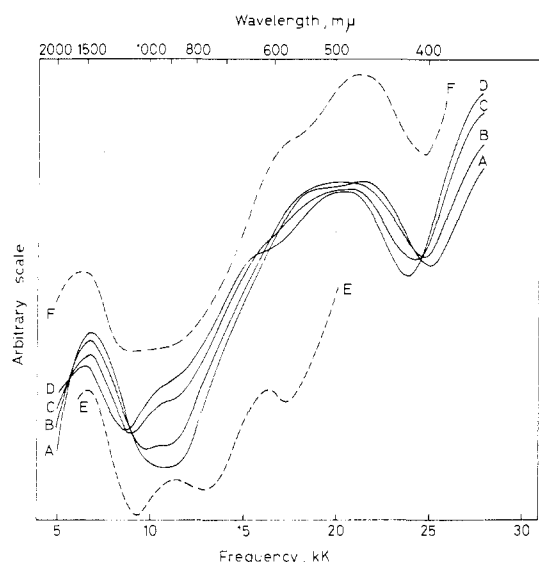**Figure 4.** Electronic spectra (solid state) of Co(H–NNP)(NCS)$_2$: A, 168°K; B, 223°K; C, 294°K; D, 338°K. Reflectance spectra: E, [5-Cl-SALen-NEt$_2$]$_2$Co (from ref 10); F, [Co(PNNP)Br]BPh$_4$ (from ref 11).

mation of the tetrahedral species, as was observed in the analogous complexes with the ligands H-PNP and Me-PNP.[3] This replacement, in spite of the increased electron release, causes a general increase in steric hindrance which is mainly due to the short distance between the methyl group and nearby halogen, as shown by the structural data for the complexes Co(Et$_4$dien)Cl$_2$[6] and Co(Me$_5$dien)X$_2$:[7] for example, the length of the bond between the metal and central nitrogen atom is longer than in the unsubstituted case. It follows that this bond is the one most likely to be broken when the tetrahedral species is formed, as is the case also in the R-PNP complexes.[3] The complexes of Me-PNP, in which NEt$_2$ group of Me-NNP is replaced by a PPh$_2$ group, are subject to less internal strain as noted above and in fact are tetrahedral in solution only at high temperatures.[3]

The role of the anion X in determining the stereochemistry is well demonstrated by contrasting the halide complexes with the thiocyanate complex Co(Me-NNP)(NCS)$_2$. This
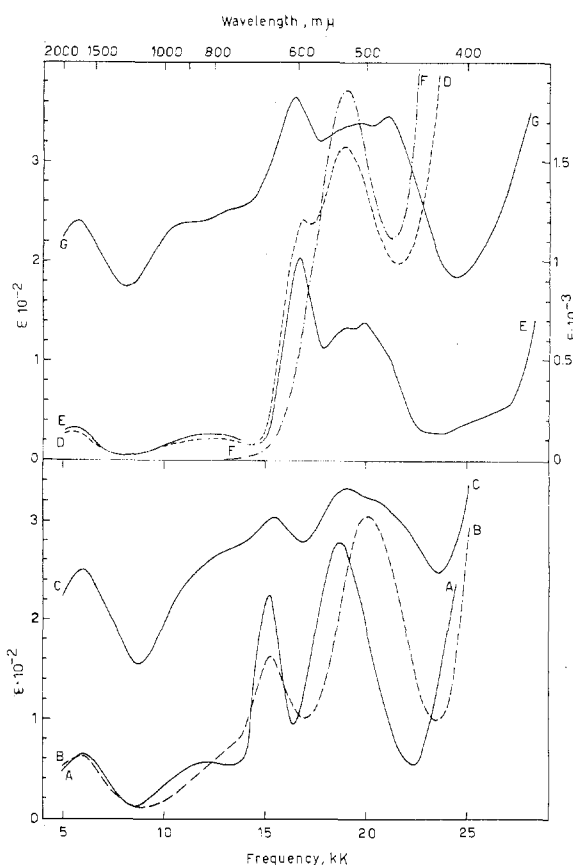
Figure 5. Absorption spectra of 1,2-dichloroethane solutions: A, Co(Me-NNP)(NCS)$_2$; B, Co(H-NNP)(NCS)$_2$ under nitrogen; D, Co(H-NNP)(NCS)$_2$ after aerial oxidation; E, Co(H-NNP(O))(NCS)$_2$; F, Co(H-NNP)(NCS)$_3$ (right-hand scale). Reflectance spectra (arbitrary scale): C, Co(Me-NNP)(NCS)$_2$; G, Co(H-NNP(O))(NCS)$_2$.

complex remains five-coordinate in solution (Figure 5) and gives tetrahedral species only at high temperatures. This is probably due to the different electronic characteristics and the small steric encumbrance of the thiocyanate group compared to that of the halides.

Co(H-NNP)(NCS)$_2$ Complex. The variation with temperature of the magnetic properties of this complex (Figure 1, Table II), which has been briefly reported,[4] shows that this complex is the only one in which a spin equilibrium obtains in the solid state between quadruplet and doublet ground states. The log K_{eq} vs. $1/T$ plot, assuming limiting values of 2.16 and 4.50 BM for the low- and high-spin forms, respectively, is linear above ca. 230°K (below this temperature, conversion into the low-spin form is virtually complete). From the linear portion of this plot, $\Delta H = 4.2$ kcal mol^{-1}, which is close to the values found for the few other known cases of spin isomerism in five-coordinate complexes.[8] The value of the overall nucleophilicity constant $\Sigma n°$ of the donor set NNP(NCS)$_2$ is intermediate between those of the sets in (high-spin) complexes of the ligand Me$_5$dien and (low-spin) complexes of the ligands R-PNP and is in the range where the magnetic crossover is predicted.[4,9] It is therefore not surprising that spin equilibrium is observed.

The variation of spin state with temperature is accompanied by substantial and reversible spectral changes in the visible and ir regions (ν(N–H) and ν(C=N)bands).[4] The changes

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(7) M. Di Vaira and P. L. Orioli, *Inorg. Chem.*, **8**, 2729 (1969).

(8) W. S. J. Kelly, G. H. Ford, and S. M. Nelson, *J. Chem. Soc. A*, 388 (1971); W. V. Dahlhoff and S. M. Nelson, *ibid.*, 2184 (1971); L. G. Marzilli and P. A. Marzilli, *Inorg. Chem.*, **11**, 457 (1972).

(9) L. Sacconi, *J. Chem. Soc. A*, 248 (1970).

in the electronic spectrum are shown in Figure 4. The positions of the bands at high temperatures can be correlated with those found in the spectra of high-spin distorted square-pyramidal cobalt(II) complexes,[10] while at low temperatures there is a correlation with the spectra of some low-spin square-pyramidal complexes.[11] These results suggest that the conversion of the high-spin form to a low-spin form is accompanied by variations in the structural parameters and possibly also in the intermolecular interactions of the complex. Such variations, which may affect both the vibrational and electronic energy levels, have been observed in other cases of spin isomerism.[8,12] In this connection we recall that the introduction of a methyl group on the central nitrogen atom in the complex Co(Me-NNP)(NCS)$_2$ causes sufficient structural changes for the complex to be completely high spin (Figure 5). Preliminary X-ray investigations have shown that these two complexes have five-coordinate "intermediate" geometries (III), that of the H-NNP derivative being distorted toward square pyramidal, while that of the Me-NNP analog is tetrahedrally distorted.[13] Thus, when the donor atoms engender a crystal field close to the value at the magnetic crossover, the geometry of the complex has the determining influence on the spin state obtaining.

III
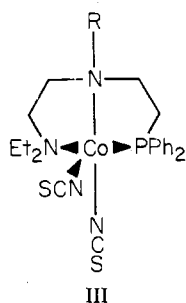
The behavior of the complex Co(H-NNP)(NCS)$_2$ in solution is most unusual. The absorption spectrum in various solvents (*e.g.*, acetone or 1,2-dichloroethane) is fairly similar to the limiting reflectance spectrum of the high-spin form. The solutions, which thus contain a predominant proportion of the high-spin five-coordinate species, are rapidly oxidized by dry air, when they change color from violet to red. The spectrum of the oxidized solution differs significantly from the spectrum of an unoxidized solution, particularly in the region 15–20 kK (Figure 5). The products obtained by concentrating the oxidized solutions are different according to the solvent.

The violet crystals obtained from acetone, methanol, and ethanol have the formula Co(H-NNP(O))(NCS)$_2$; that is, the atom which has been oxidized is the phosphorus atom of the diphenylphosphine group, which has thus become a phosphine oxide. This compound has an electronic spectrum characteristic of a high-spin five-coordinate cobalt(II) complex (Figure 5) and a temperature-independent magnetic moment of 4.56 BM. X-Ray structural data have shown that the complex has a distorted trigonal-bipyramidal structure with one thiocyanate group and the secondary amine nitro-

gen in the axial positions (IV).[14]

IV
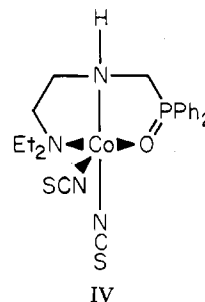
The product which crystallizes from the oxidized solutions in 1,2-dichloroethane or chloroform is red-brown and diamagnetic, with a formula Co(H-NNP)(NCS)$_3$. The solution spectrum of the pure compound shows a single band at 19.0 kK (Figure 5) characteristic of a cobalt(III) complex. This band corresponds in shape and position to the most intense band of the oxidized solutions. The other bands in the spectra of the oxidized solutions are identical with those exhibited by Co(H-NNP(O))(NCS)$_2$ (Figure 5). The observed spectrum can in fact be reconstructed by assuming that Co(H-NNP)(NCS)$_3$ and Co(H-NNP(O))(NCS)$_2$ are present in the ratio *ca.* 1:9.

The oxidation of Co(H-NNP)(NCS)$_2$ in solution by air therefore involves both cobalt and phosphorus atoms. The competition between the two oxidation reactions is controlled by the nature of the solvent, so that different products can be isolated from different solvents.

The complex Co(Me-NNP)(NCS)$_2$ does not undergo aerial oxidation in solution. The different redox behaviors of the two thiocyanate complexes are surprising in view of the general similarity of the donor atom set and solution spectra (Figure 5), suggesting a similar structure. The principal difference between the two compounds resides in their magnetic behavior, which can therefore be held to be a factor essential to the oxidation process. Indeed, the solutions of Co(H-NNP)(NCS)$_2$ must contain a proportion, however small, of the low-spin form. One recalls that high-spin complexes such as Co(Me$_5$dien)X$_2$ and Co(Et$_4$dien)X$_2$ are air stable in solution,[1,2] while low-spin complexes such as Co(R-PNP)X$_2$ are rapidly oxidized by air.[3]

Experimental Section

Synthesis of the Ligands. H-NNP. The synthesis of *N*-2-(diphenylphosphino)ethyl-*N'*,*N'*-diethylethylenediamine (H-NNP) has been reported previously.[15]

Me-NNP. Treatment of *N*-methyl-*N*-2-(diethylamino)ethyl-ethanolamine[16] with thionyl chloride gave *N*-methyl-*N*-2-chloroethyl-*N'*,*N'*-diethylethylenediamine dihydrochloride.

Anal. Calcd for C$_9$H$_{23}$N$_2$Cl$_3$: C, 40.69; H, 8.72; N, 10.54; Cl, 40.03. Found: C, 40.9; H, 9.0; N, 10.3; Cl, 40.8 (mp 178–180°). The ligand *N*-methyl-*N*-2-(diphenylphosphino)ethyl-*N'*,*N'*-diethyl-ethylenediamine (Me-NNP) was synthesized from this hydrochloride and KPPh$_2$·2(dioxane) with the same procedure reported for H-NNP.[15]

Anal. Calcd for C$_{21}$H$_{31}$N$_2$P: C, 73.60; H, 9.12; N, 8.18; P, 9.04. Found: C, 72.5; H, 9.1; N, 8.3; P, 9.2 (bp 180–182° (0.1 Torr)).

Preparation of the Complexes. To a hot solution of the metal salt (5 mmol) in butan-1-ol (10 ml) was added the ligand (5 mmol) dissolved in 10 ml of the same solvent. The solution was filtered and concentrated until the crystals separated. Cyclohexane was eventually added to induce crystallization. The complex Co(H-NNP)(NCS)$_2$

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(16) K. Nakajima, *Bull. Chem. Soc. Jap.*, 34, 655 (1961).

was obtained from hot butan-1-ol or ethanol solutions and recrystallized from acetone or ethanol under nitrogen. Recrystallization from acetone, ethanol, or methanol under aerial conditions gave Co(H–NNP(O))(NCS)$_2$. From concentrated solutions of Co(H–NNP)(NCS)$_2$ in chloroform or 1,2-dichloroethane, fine red-brown crystals of Co(H–NNP)(NCS)$_3$ separated upon standing.

Materials and Physical Measurements. All solvents were reagent grade. Physical measurements were carried out as described previously.[3] Magnetic susceptibilities at various temperatures were measured with the Gouy balance already described.[17]

Registry No. Cl(CH$_2$)$_2$N(Me)CH$_2$CH$_2$NEt$_2$·2HCl, 38127-

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70-7; Me-NNP, 38127-71-8; Co(H-NNP)Cl$_2$, 38127-72-9; Co-(H-NNP)Br$_2$, 38127-73-0; Co(H-NNP)I$_2$, 38127-74-1; Co-(H-NNP)(NCS)$_2$, 29993-37-1; Co[H-NNP(O)](NCS)$_2$, 38127-76-3; Co(H-NNP)(NCS)$_3$, 38127-77-4; Co(Me-NNP)Cl$_2$ (5-coordinate), 38127-78-5; Co(Me-NNP)Cl$_2$ (4-coordinate), 38127-79-6; Co(Me-NNP)Br$_2$ (5-coordinate), 38127-80-9; Co(Me-NNP)Br$_2$ (4-coordinate), 38127-81-0; Co(Me-NNP)-(NCS)$_2$, 29993-38-2.

Stereochemical Studies of *N*-Methyl-(*S*)-alaninatocobalt(III) Complexes with Chiral Tetramines. I. Cobalt(III)–*N*-Methyl-(*S*)-alaninato-5(*R*)- and -5(*S*)-methyl-1,4,7,10-tetraazadecane Systems

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The preparations and structural assignments of *N*-methyl-(*S*)-alaninatocobalt(III) complexes with 5(*R*)- and 5(*S*)-methyl-1,4,7,10-tetraazadecane (abbreviated as 5(*R*)- and 5(*S*)-metrien) are described. The Λ-β_2-*SSR* isomer has been obtained for Co(5(*R*)-metrien)(*N*-Me-(*S*)-ala)$^{2+}$ ion. The two isomers, which have been observed for the Co(5(*S*)-metrien)(*N*-Me-(*S*)-ala)$^{2+}$ ion under equilibrium condition at pH 7, are assigned as Δ-β_2-*RRS* and Δ-β_2-*RRR* configurations, based on the stereospecific coordination of 5(*S*)-metrien. The analogous arguments have been applied for the Δ-β_2 isomers of Co(trien)-(*N*-Me-(*S*)-ala)$^{2+}$ ion. The individual species noted in pmr measurements are assigned tentatively to Δ-β_2-*RRS* and Δ-β_2-*RRR* structures, respectively.

Introduction

In recent papers, cobalt(III) complexes with bidentate ligands containing coordinated secondary nitrogen atom(s), such as N-substituted amino acidates (sarcosinate,[1,2] (*S*)-prolinate,[3–6] and *N*-methyl-(*S*)-alaninate[6,7]) and N-substituted 1,2-diamines (*N*-methylethylenediamine,[8] *N*-methyl-(*S*)-propylenediamines,[9] and *N*,*N*'-dimethylethylenediamine[10,11]), have been investigated from stereochemical points of view. The study on the sarcosinatobis(ethylenediamine)cobalt(III) ion[1] first provided the possibility of stereoselective coordination of the N-substituted methyl group in tris chelate complexes due to steric repulsions between the *N*-methyl group and the adjacent chelate rings. It was indicated from an X-ray analysis study[12] that the

coordinated secondary N center of sarcosinate takes stereoselectively the *S*[13] configuration in the Λ[14] enantiomer of the Co(en)$_2$(sar)$^{2+}$ ion. The restricted orientation of the *N*-methyl group of sarcosinate chelate was also supposed for the β_2[15] isomer of the Co(trien)(sar)$^{2+}$ ion[2] (trien = triethylenetetramine).

It was observed that the bis(ethylenediamine)cobalt(III) complex of (*S*)-proline arises only in the Δ configuration stereoselectively.[6,16] Corresponding (*S*)-pipecolic acid and *N*-methyl-(*S*)-alanine complexes, in which both the amino acids have the asymmetric secondary N center with *R* configuration, gave rise to the Λ absolute configurations. This suggests that the absolute configuration of bis(en) complexes with N-substituted amino acids is controlled by the configuration of the secondary N center of amino acids.[6] When the asymmetric secondary N atom has the *R* configuration, the Λ absolute configuration is preferred for the bis(en) complex.

However, the stereoselective formation has not been observed in the case of trien–cobalt(III) complexes with (*S*)-proline[3] and *N*-methyl-(*S*)-alanine.[7] Under the reported preparative conditions, which are kinetically controlled, the above complexes were yielded in mixtures of Λ and Δ isomers in almost equal amounts. For the latter complex, the base-

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