

New Planar Cobalt(II) and Nickel(II) Complexes

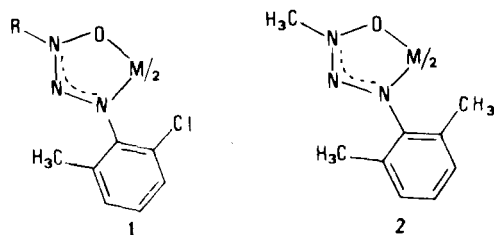
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Some planar complexes of cobalt(II) and nickel(II) derived from triazene 1-oxides are reported in this paper. The cobalt(II) complexes are very stable and are shown to be monomolecular in solution. Their magnetic moments lie in the range 2.08-2.19 BM. They show electronic spectra with many features in the range 4500-30,000 cm^{-1} . Probable assignment schemes are suggested on the basis of a strong field model. In one of these schemes the spectra of the cobalt(II) and nickel(II) complexes can be understood on the basis of a single set of crystal field and Slater-Condon parameters. In pyridine solution the cobalt(II) and nickel(II) species exist in equilibrium with high spin adducts. The thermodynamic parameters ΔH° and ΔS° for the equilibrium are determined for nickel(II) species from variable temperature magnetic data. It is shown that adduct formation is more extensive in the case of cobalt(II) than in the case of nickel(II).

Introduction

Planar cobalt(II) complexes are usually unstable to aerial oxidation and need careful handling. The number of definitive studies done on spectra, magnetochemistry and electronic structure of such species is very limited. In the course of our general research programme¹ on the complexes of triazene 1-oxides, we have discovered some planar four-coordinate cobalt(II) species which are remarkably stable in the crystalline state and in the solution phase. These systems together with their nickel(II) analogues are described in this paper. The complexes belong to the structural types 1 and 2. Specific examples of type 1 will be identified by the R group in the form of the notation 1(R).



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Experimental Section

Preparation of Compounds. The ligands were synthesized by reacting the appropriate diazonium salts with substituted hydroxylamines.^{1a} The complexes were prepared as crystalline solids by reacting an ethanolic or methanolic solution of the ligand (0.02 mole) with an aqueous solution of the appropriate metal acetate (0.01 mole). Recrystallizations were done from acetone.

Electronic Spectra were measured on a Cary 14 recording spectrophotometer. Solids were examined in Nujol mull. **Bulk Susceptibility** measurements were carried out on a sensitive Gouy balance. $\text{CoHg}(\text{SCN})_4$ and distilled water were used as standards for measurements on solids and solutions respectively. Solvents used for solution measurements were carefully purified and then distilled.

Proton magnetic resonance spectra were recorded on a Varian HR-100 spectrometer. **Molecular weight measurements** were carried out on a vapour pressure osmometer Model 301 A (Machrolab Inc.) in benzene solution.

Results

Syntheses. The cobalt(II) and nickel(II) complexes of type 1 and 2 were synthesized by straightforward reactions of ligands with metal acetates. The cobalt(II) complexes are perfectly stable in air both in the solid and in solution phases. Characterization data are set out in Table I.

Cobalt(II) Complexes. Magnetic data for the complexes are collected in Table II. The moments uniformly lie in the range 2.08 - 2.19 BM. In the solution phase the compounds are monomeric in benzene, e.g., 1(CH_3), Found, 445 (Calcd. 456); 1(C_2H_5), Found, 470 (Calcd. 484). Several electronic bands are seen in the near-ir, visible and near-uv regions. Spectral data are collected in Table III and Figure 1. When the complexes are dissolved in pyridine their magnetic moment increases to >4 BM (Table II). Electronic spectra in pyridine (Table III) are also substantially different from spectra in benzene.

Nickel(II) Complexes. These form green diamagnetic solids. They are also diamagnetic in benzene solution. Electronic spectral data are collected in Table IV. The most characteristic feature is a band

Table I. Characterization Data for Some Cobalt(II) and Nickel(II) Complexes.

Compound ^a	Formula	MP, °C ^b	% C		% H		% N	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
Cobalt								
1(CH ₃)	C ₁₈ H ₁₈ N ₆ O ₂ Cl ₂ Co	188-189	42.11	42.38	3.95	4.10	18.39	18.53
1(C ₂ H ₅)	C ₁₈ H ₂₂ N ₆ O ₂ Cl ₂ Co	174-175	44.65	44.72	4.55	4.44	17.36	17.44
1(<i>n</i> -C ₃ H ₇)	C ₂₀ H ₂₆ N ₆ O ₂ Cl ₂ Co	182-183	46.88	46.30	5.08	5.12	16.41	16.71
2	C ₁₈ H ₂₄ N ₆ O ₂ Co	>260	52.07	52.25	5.79	5.70	20.25	20.67
6	C ₁₈ H ₁₈ N ₆ O ₂ Cl ₂ Co	182-183	42.11	42.21	3.95	3.98	18.39	18.30
Nickel								
1(CH ₃)	C ₁₈ H ₁₈ N ₆ O ₂ Cl ₂ Ni	209-210	42.13	42.17	3.95	3.70	18.44	18.00
1(C ₂ H ₅)	C ₁₈ H ₂₂ N ₆ O ₂ Cl ₂ Ni	190-191	44.67	45.00	4.55	4.63	17.38	17.11
1(<i>n</i> -C ₃ H ₇)	C ₂₀ H ₂₆ N ₆ O ₂ Cl ₂ Ni	220-221	46.90	47.35	5.08	5.23	16.42	16.06
2	C ₁₈ H ₂₄ N ₆ O ₂ Ni	>250	52.07	52.50	5.79	5.75	20.25	20.68
6	C ₁₈ H ₁₈ N ₆ O ₂ Cl ₂ Ni	187-188	42.13	42.45	3.95	4.02	18.44	18.72

^a Refer to the compound figure number in the text. ^b All melting points are uncorrected.

Table II. Magnetic susceptibility data for some cobalt(II) complexes.

Compound ^a	Temperature °K	Solid	μ _{eff} (BM)	Pyridine ^b solution
			Benzene solution ^b	
1(CH ₃)	300	2.08	2.15	4.32
1(C ₂ H ₅)	300	2.09	2.19	4.40
2	300	^c	2.10	4.11
	323			3.97
	343			3.85
	353			3.81

^a Refers to the compound Figure number in the text. ^b Concentration range 3-5 × 10⁻² M. ^c Measurement not made.

Table III. Frequencies (ν, cm⁻¹) and extinction coefficients ^a (ε, l.mol.⁻¹cm⁻¹) of electronic bands of some cobalt(II) complexes at room temperature (300-303°K).

Compound ^b	Medium	ν(ε)					
1(CH ₃)	benzene	4650(19) ^c	11,760(12)	16,100(44)	19,400(350) ^d	23,250(820) ^d	30,300(5800)
	pyridine	6600(7)	11,900(9)	13,890(10)	17,240(47) ^d	20,400(170) ^d	33,300(4400)
1(C ₂ H ₅)	benzene	<6250(3) ^e	11,760(11)	16,100(47)	19,400(330) ^d	23,250(910) ^d	30,300(5870)
1(<i>n</i> -C ₃ H ₇)	benzene	<6250(3) ^e	11,760(12)	16,100(46)	19,400(380) ^d	23,250(930) ^d	30,300(6110)
2	benzene	<6250(3) ^e	11,760(12)	16,300(46)	19,600(310) ^d	23,250(810) ^d	29,400(5860)
	pyridine	6600(5)	11,760(10)	14,080(8)	17,240(50) ^d	20,400(240) ^d	33,300(4400)

^a Solute concentrations were adjusted to get the optical density values in the range 0.5-1. ^b Refers to the compound figure number in the text. ^c This band was studied in chloroform solution. ^d Shoulder. ^e The band maximum lies at a lower energy.

Table IV. Frequencies (ν, cm⁻¹) and extinction coefficients ^a (ε, l.mol.⁻¹cm⁻¹) of electronic bands of some cobalt(II) complexes at room temperature (300-303°K).

Compound ^a	Medium	ν(ε)	
1(CH ₃)	benzene	13,990(67)	28,570(4740)
	pyridine	<6250(5) ^c	14,500(54), 29,850(5930)
1(C ₂ H ₅)	benzene	14,180(73)	29,410(6880)
	pyridine	<6250(6) ^c	14,500(54), 31,800(6230)
1(<i>n</i> -C ₃ H ₇)	benzene	14,280(70)	28,570(8650)
2	benzene	14,080(70)	27,780(5150)
	pyridine	14,180(65)	28,570(5150)

^a The concentration of the solution was adjusted to get the optical density values in the range 0.5-1. ^b Refers to the compound figure number in the text. ^c The band maximum lies at a lower energy.

at ~14,000 cm⁻¹ (ε ~ 70). In pyridine solution the complexes of the type 1 become partially paramagnetic (0 < μ_{eff} < 3.2) and the magnetic moment decreases with increasing temperature (Table V). Electronic spectral data in pyridine solution are shown in Table IV. The complex 2 does not become paramagnetic in pyridine solution.

Discussion

Magnetic Data: In Solid State and in Benzene Solution. Magnetic moments of low spin grossly planar cobalt(II) complexes usually lie in the range² 2.1 - 2.9

(2) R. L. Carlin, « Transition Metal Chemistry », Ed. R. L. Carlin, Marcel Dekker, Inc., New York, Vol. 1, 1969, p. 1.

Table V. Variable temperature magnetic susceptibility data and thermodynamic parameters for some nickel(II) complexes in pyridine.

Compound ^a	T (°K)	μ_{eff} (BM)	ΔH° (kcal mol ⁻¹)	ΔS° (eu)
1(CH ₃)	300	2.21	-5(±1)	-15(±5)
	313	2.08		
	323	1.93		
	333	1.83		
	343	1.70		
	353	1.58		
1(C ₂ H ₅)	298	2.10	-6(±1)	-19(±5)
	313	1.93		
	323	1.81		
	333	1.70		
	343	1.61		

^a Refer to compound figure number in the text.

BM. The cobalt(II) complexes of type 1 are monomolecular and their magnetic moments fall in the above range. They are most certainly grossly planar in the solid state and in benzene solution. The same comment applies to the nickel(II) species in view of their diamagnetism. It is expected that the complexes have trans CoN₂O₂ coordination sphere. The cis geometry is likely to be sterically unfavourable. Triazene 1-oxide complexes with cis stereochemistry enforced by ligand geometry was reported earlier.^{1e} Their spectral and magnetic behaviour are qualitatively the same as those of the present complexes.

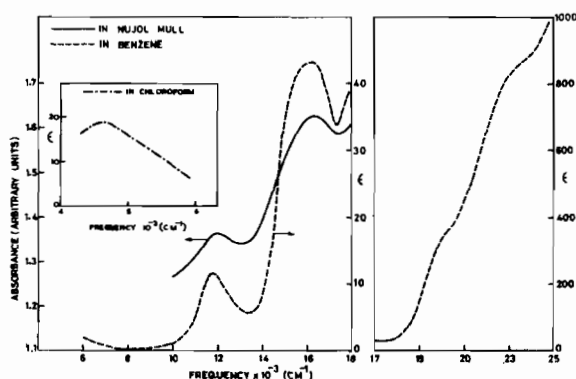


Figure 1. Electronic spectra of 1(CH₃) in solid and in solution phase at 300°K. The inset shows the low energy band.

Electronic Spectra: In Solid State and in Non-Coordinating Solvents.

(a) *Cobalt(II) Complexes.* The mull and solution spectra of these complexes are essentially the same. There are two bands (Table III and Figure 1) at $\sim 12,000$ cm⁻¹ and $\sim 16,000$ cm⁻¹ and two well defined shoulders at $\sim 20,000$ cm⁻¹ and $\sim 23,000$ cm⁻¹. In addition to this the absorption slowly increases at < 8000 cm⁻¹ and a maximum is located at 4700 cm⁻¹. Due to solvent interference this band is more clearly observed in chloroform than in benzene. The 4700 cm⁻¹ band is absent in the corresponding nickel(II) and copper(II) complexes and therefore this cannot be due to vibrations of ligands in the complex. The electronic spectra of the cobalt(II) complexes are thus

unusually rich in features. These complexes provide a unique opportunity to study the energy level scheme of low spin planar cobalt(II). Reported work in this area is meager and often fragmentary.

Grossly planar salicylalimine and β -ketoamine complexes of cobalt(II) show^{3,4} a narrow and relatively weak band at 8500 cm⁻¹. Recently Hipp and Baker⁵ reported the identification of three additional ligand field bands using circular dichroism spectra. They suggest⁵ the order: $d_{x^2-y^2} > d_{xy} > d_{xz} \sim d_{yz} > d_{z^2}$. The electronic bands^{6,7} of planar^{6,8} bis(dithioacetone)-cobalt(II) are as yet unassigned. The trans complexes of the type (aryl)₂(phosphine)₂Co have⁹ the highest two levels ordered as $d_{x^2-y^2} > d_{z^2}$. The same applies to cobalt(II) phthalocyanine^{10,11} and a few other systems¹² having the CoN₄ coordination sphere.

We shall now examine the possibility of understanding the gross spectral features of 1 and 2 on the basis of simple models in which the crystal field is assumed to be « strong » and to have an effective D_{4h} symmetry. Spin orbit interactions and two electron transitions are ignored.

Since the ligands are on the x and y axes, the $d_{x^2-y^2}$ orbital may be expected to be highest in energy. This is found to be true without exception for planar four coordinate complexes.¹³⁻¹⁶ The ordering of the remaining levels cannot be decided *a priori*. We considered several different orderings of levels.¹⁷ Good to satisfactory agreement with experimental results was obtained from the schemes shown in Figure 2. The energies of the ground and excited states were computed¹⁷ using the strong field approximation for the

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Table VI. Transition energies and assignments of bands in cobalt(II) species.

Scheme	Transition ^a	Energy Expression ^b	Energy (cm ⁻¹)	
			Calculated	Observed
A	$xz,yz \rightarrow z^2$	$\Delta_2 + \Delta_3 + 5F_2 - 25F_4$	5,300	4,700
	$xy \rightarrow z^2$	$\Delta_2 + 20F_2 - 100F_4$	11,300	12,000
	$z^2 \rightarrow x^2 - y^2$	Δ_1	16,000	
	$xy \rightarrow x^2 - y^2$ ^{1d}	$\Delta_1 + \Delta_2 - 35F_4$	15,400	16,000
	$xz,yz \rightarrow x^2 - y^2$ ^{1d}	$\Delta_1 + \Delta_2 + \Delta_3 + 4F_2 - 55F_4 - G$ ^e	16,500	
	$xy \rightarrow x^2 - y^2$ ^{11d}	$\Delta_1 + \Delta_2 + 8F_2 - 75F_4$	19,000	
	$xz,yz \rightarrow x^2 - y^2$ ^{11d}	$\Delta_1 + \Delta_2 + \Delta_3 + 4F_2 - 55F_4 + G$ ^e	18,800	19,400
B	$xz,yz \rightarrow xy$	$\omega_2 - 15F_2 + 75F_4$	6,600	
	$z^2 \rightarrow xy$	$\omega_2 + \omega_3 - 20F_2 + 100F_4$	5,500	4,700
	$xy \rightarrow x^2 - y^2$	ω_1	12,000	12,000
	$xz,yz \rightarrow x^2 - y^2$ ^{1d}	$\omega_1 + \omega_2 - 15F_2 + 40F_4$	15,600	
	$z^2 \rightarrow x^2 - y^2$ ^{1d}	$\omega_1 + \omega_2 + \omega_3 - 20F_2 + 65F_4$	14,500	16,000
	$xz,yz \rightarrow x^2 - y^2$ ^{11d}	$\omega_1 + \omega_2 - 9F_2 + 10F_4$	17,900	
	$z^2 \rightarrow x^2 - y^2$ ^{11d}	$\omega_1 + \omega_2 + \omega_3 - 12F_2 + 25F_4$	18,200	19,400

^a Only spin allowed transitions are considered. ^b F_2 and F_4 are Slater-Condon parameters. For scheme A the parameters used in cm⁻¹ are $\Delta_1 = 16,000$; $\Delta_2 = 2500$; $\Delta_3 = 500$; $F_2 = 10F_4 = 900$; for scheme B they are: $\omega_1 = 12,000$; $\omega_2 = 13,000$; $\omega_3 = 1000$; $F_2 = 10F_4 = 850$. ^d I and II arise due to configuration interaction. ^e $G = (7F_2^2 + 175F_4^2 - 70F_2F_4)^{1/2}$.

Table VII. Transition energies for nickel(II) species.

Transition	Energy Expression ^{a,b}		Calculated Energy (cm ⁻¹)	
	Scheme A	Scheme B	Scheme A ^c	Scheme B ^c
$xy \rightarrow x^2 - y^2$	$\Delta_1 + \Delta_2 - 35F_4$	$\omega_1 - 35F_4$	15,300	10,000
$xz,yz \rightarrow x^2 - y^2$	$\Delta_1 + \Delta_2 + \Delta_3 - 3F_2 - 20F_4$	$\omega_1 + \omega_2 - 3F_2 - 20F_4$	14,700	20,700
$z^2 \rightarrow x^2 - y^2$	$\Delta_1 + 4F_2 - 15F_4$	$\omega_1 + \omega_2 + \omega_3 - 4F_2 - 15F_4$	11,300	21,300

^a F_2 and F_4 are Slater Condon parameters. ^b H.B. Gray and C.J. Ballhausen, *J. Am. Chem. Soc.*, 85, 260 (1963). ^c Values of parameters used are same as those in Table VI.

three hole (d^7) configuration. From these the various transition energies were calculated for both schemes.

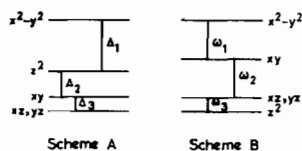


Figure 2. Schemes of energy levels in planar low spin cobalt(II) complexes (not drawn to scale).

These are set out in Table VI. Also shown in this table are the fits of calculated and experimental band positions. The values of the parameters can be varied within small limits without upsetting the fits too much. The experimental spectra fit better with scheme A than with scheme B (Table VI). One further advantage of scheme A will be pointed out a little later. We believe that scheme A is more probable than scheme B. Electron spin resonance work, now in progress, will hopefully establish the identity of the ground state with finality.

In these assignment schemes the shoulder at $\sim 23,000$ cm⁻¹ is not considered to be of crystal field origin. The same is true of a band in the ultraviolet at $30,000$ cm⁻¹ ($\epsilon \sim 6000$). The two bands ($23,000$ cm⁻¹ and $30,000$ cm⁻¹) can very well be due to ligand \rightarrow metal charge transfer transitions. In this respect it may be significant that the corresponding nickel(II) and copper(II) species having holes in the

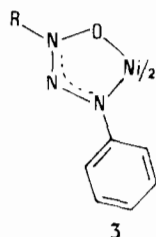
$d_{x^2-y^2}$ orbitals alone show only one transition believed to be of ligand \rightarrow metal origin at $\sim 29,000$ cm⁻¹ and $\sim 26,000$ cm⁻¹ respectively. We have assigned the observed cobalt(II) bands to spin allowed transitions only. This is justified by the intensities of the bands. We believe that the spin-forbidden transitions are not observed.

(b) *Nickel(II) Complexes.* One merit of the assignment scheme A (Table VI) is that it provides a unification of spectral data of nickel(II) and cobalt(II) complexes on the basis of a single set of parameters. The energy expressions (strong field approximation) for spin allowed transitions in low spin planar nickel(II) species are well known¹⁸ and are collected in Table VII for ready reference. If it is assumed that the values of the crystal field and Slater-Condon parameters do not undergo much change in going from cobalt(II) to nickel(II) species, the transition energies of the latter can be calculated using the energy expressions. The energies of the three bands are predicted to lie in the range $11,000$ - $15,000$ cm⁻¹ and $10,000$ - $21,000$ cm⁻¹ in schemes A and B respectively (Table VII). The experimental spectra show only one region of crystal field absorption at $\sim 14,000$ cm⁻¹. It is conceivable that the three predicted bands of scheme A cluster together showing only one feature at room temperature. Scheme B requires the observation of two widely separated regions of absorption: at $\sim 10,000$ and $\sim 21,000$ cm⁻¹.

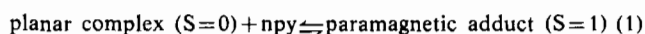
(18) H. B. Gray and C. J. Ballhausen, *J. Am. Chem. Soc.*, 85, 260 (1963).

Behaviour in Pyridine Solution: (a) *Nickel(II) Complexes.* The compounds of type 1 dissolve in pyridine giving green solutions which are partially paramagnetic ($0 < \mu_{\text{eff}} < 3.2$ BM), the magnetism being temperature dependent (Table V). These partially paramagnetic solutions show in addition to the planar ligand field band at $\sim 14,000$ cm^{-1} (intensity less than that in benzene) a new band whose maximum lies at < 6250 cm^{-1} (Table IV).

Unsubstituted triazene 1-oxide complexes of the type 3 become¹⁹ fully paramagnetic ($\mu_{\text{eff}} \sim 3.2$ BM)



in pyridine solution giving rise to pseudooctahedral (presumably *trans*) bis adducts. These show electronic bands at 9900 cm^{-1} and $17,200$ cm^{-1} assignable to octahedral ν_1 and ν_2 transitions. The pyridine protons in such adducts undergo pmr contact shifts¹⁹ due to delocalization of unpaired metal electrons into the pyridine ring. The type 1 complexes also give rise to similar shifts of pyridine protons but the magnitudes of the shifts are only 40% of those obtained using type 3 complexes. These results are in line with the observed partial paramagnetism and clearly show that *pyridine is bound to the nickel(II) centre* in solutions of 1. This information is important because the electronic spectra of 1 in pyridine solution show a band at unusually low energy. We can express the partial paramagnetism of 1 in terms of the equilibrium:



If the geometry of the adduct is assumed to be pseudooctahedral ($n=2$ in Eq. 1) an unrealistically low value for Dq results: $\nu_1 = 10 Dq < 6250$ cm^{-1} . This is possible only if the Ni-py bonds are very long and yet the average environment is octahedral. On the other hand five-coordinated high spin nickel(II) species are known to have absorption bands in the near-ir region.²⁰ The results strongly suggest that a five-coordinated adduct ($n=1$) makes a major contribution to solution composition.

In view of the large concentration of pyridine, the equilibrium constant for the reaction (1) can be approximated as:

$$K = \frac{(\text{paramagnetic})}{(\text{diamagnetic})} = \frac{\mu_{\text{eff}}^2}{\mu_0^2 - \mu_{\text{eff}}^2} \quad (2)$$

where μ_{eff} is the observed magnetic moment and μ_0 is the magnetic moment of the paramagnetic species. The value of μ_0 will be assumed to be equal to 3.3

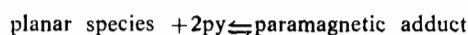
BM which is appropriate for pentacoordinated species having nitrogen-oxygen donors.²⁰

Plots of $\log K$ versus $1/T$ yielded good straight lines and values of ΔH° and ΔS° were extracted from the equality:

$$\frac{\Delta H^\circ}{T} = \Delta S^\circ - R \ln K \quad (3)$$

Values of ΔH° and ΔS° are shown in Table V. It is significant that the entropy term is negative. This is understandable since independent motion of constituent molecules is at least partially lost on adduct formation. The change in spin multiplicity on adduct formation makes a small and positive ($R \ln 3 = 2.2$ eu) contribution to the entropy change.

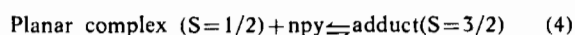
Equilibria of the type



have been thermodynamically characterized in several cases.^{21,22} The ΔH° and ΔS° values lie in the ranges -15 to -4 kcal. mole⁻¹ and -25 to -39 eu respectively.

The spectra of the nickel complex 2 in benzene and in pyridine are essentially the same. In this case adduct formation does not occur at all.

(b) *Cobalt(II) Complexes.* When the complexes 1 and 2 are dissolved in pyridine their magnetic moment increases to > 4 BM (Table II) showing that the spin state $S=3/2$ makes the major contribution. On increasing the temperature there is a small but systematic decrease in magnetic moment as indicated by the data for 2 (Table II). We suspect the presence of the equilibrium:



shifted heavily towards the adduct. A problem similar to that for nickel(II) complexes exists with respect to the identity of the value of n and the stereochemistry of the adduct.

If the adduct is pseudooctahedral ($n=2$ in Eq. (5)) the bands in near-ir (6600 cm^{-1}) and visible ($\sim 12,000$ cm^{-1}) are to be assigned to components of the ν_1 band split by the tetragonal ligand field. The narrow band at $\sim 14,000$ cm^{-1} could either be due to the ν_2 transition or to spin forbidden transitions. However, such a large tetragonal splitting does not appear to be reasonable. The near-ir and visible bands are best reconciled in terms of a five-coordinated geometry²³ ($n=1$ in Eq. (5)). We are ignoring any contribution to spectra due to the planar complex since its equilibrium concentration is small.

The percentage x of high spin species existing in equilibrium can be obtained from the relation

$$x = \frac{\mu_{\text{eff}}^2 - \mu_0^2}{\mu_0^2 - \mu_p^2} \times 100 \quad (5)$$

(21) T. S. Kannan and A. Chakravorty, *Inorg. Chem.*, 9, 1153 (1971).

(22) L. Sacconi, G. Lombardo and P. Paoletti, *J. Chem. Soc.*, 848 (1958).

(23) L. Sacconi, M. Cliampolini and G. P. Speroni, *Inorg. Chem.*, 4, 1116 (1965).

(19) P. S. Zacharias and A. Chakravorty, *Indian J. Chem.*, 9, 1148 (1971).

(20) L. Sacconi, « *Transition Metal Chemistry* », Ed. R. L. Carlin, Marcel Dekker Inc. New York, 1968, Vol. 4, p. 299.

were μ_p and μ_o are the magnetic moments of the planar complex (2.1 BM) and paramagnetic adduct (4.8 BM) respectively and μ_{eff} is the observed magnetic moment. A comparison of the population of high spin species for nickel(II) and cobalt(II) complexes can be made from the data shown in Table VIII.

Table VIII Population of high spin species for Nickel(II) and Cobalt(II) in Pyridine.

Compound ^a	Metal	% high spin species in pyridine at 300°K
1(CH ₃)	Ni	48
1(CH ₃)	Co	77
2	Ni	0
2	Co	67

^a Refers to the compound figure number in the text.

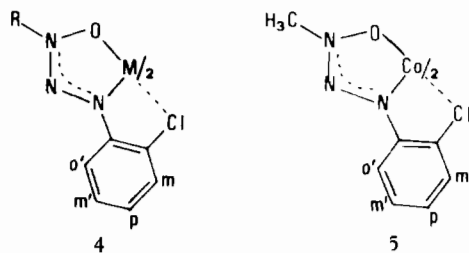
Table IX. Magnetic and Spectral Data for Type 6 ^a Complexes at 300°K.

Metal	Medium	μ_{eff} (BM)	Spectral data $\nu(\epsilon)$ (ν , cm ⁻¹ ; ϵ , l.mol ⁻¹ cm ⁻¹)
Nickel	benzene	1.38	9170(12), 13,800(83), 20,400(150), 28,990(8380)
Cobalt	benzene	4.75	7880(34) 10,100(25), 13,890(6), 15,630(7), 21,280(250), 32,260(46,800)

^a Refers to the compound figure number in the text.

Steric Factors and Stereochemistry

In a previous paper¹⁵ the magnetic and spectral properties of the triazene 1-oxide complexes of type 4 were delineated. Examination of models based on the known^{18,24} structure of 5 suggests that a methyl substituent in the *ortho*' position in 5 will sterically interact with the triazene ring.



One way of relieving this interaction, at least partially will be to put the benzene ring perpendicular to the triazene ring. In this arrangement the chloro group can no longer coordinate and a grossly planar co-

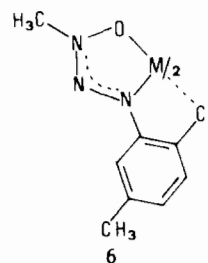
(24) G. L. Dwivedi and R. C. Srivastava, *Acta Cryst.*, B27, 2316 (1971).

ordination sphere for the complex is predicted. Such a change in geometry due to steric effect of substitution is considered likely particularly because the metal-chlorine bond is known^{18,24} to be weak. The results described in this paper show that these expectations are experimentally realized. If in 1 and 2 the benzene rings are indeed roughly perpendicular to the triazene ring, axial approach of donor solvent molecules may be hindered. The observed incomplete axial coordination in pyridine solution may thus be rationalized.

For a given ligand the extent of halo coordination in 4 follows¹⁵ the order cobalt(II) \gg nickel(II). Thus while the nickel(II) complex of type 4 shows planar-octahedral equilibrium in solution, the corresponding cobalt(II) complex exists essentially \sim 100% as the high-spin octahedral form¹⁵. The preference for the high-spin form in pyridine solution of the complexes

of type 1 and 2 is clearly parallel (Table VIII).

The steric effect present in 1 and 2 should be absent in the meta' substituted species 6. Indeed the behaviour of these complexes is closely



parallel to that of the corresponding complexes 4 as can be seen from comparison of the data presented in Table IX with those¹⁵ of 4.

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