

magnitude of this interaction,⁹ simply subtracting the three CH repulsions would reduce the stretching force constant to 2.77 mdyne/A. This is more nearly comparable to the value of 2.52 mdyne/A found for the central C-C stretching force constant.¹⁴

The value of 2.50 mdyne/A for $K(\text{Pt}-\text{C})$ is very similar to that of 2.46 mdyne/A for $K(\text{Pt}-\text{O})$ previously determined.⁹ This result is at least consistent with the chemical observation that both types of coordinate bonds are formed not only under the same conditions

but also in the same reaction mixture.³ This result may suggest that the order of the strength of these coordinate bonds⁹ may be $\text{Pt}-\text{CN} \gg \text{Pt}-\text{C}(\text{acac}) \approx \text{Pt}-\text{O}(\text{acac}) > \text{Pt}-\text{NH}_3$.

The bending and repulsive force constants are similar to those obtained previously.⁹ The changes observed are those expected due to changes in structure. For example, the value of 0.26 mdyne/A used previously for $H(\text{C}^{\cdots}\text{C}^{\cdots}\text{C})$ was reduced to 0.16 mdyne/A in this case.

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Complexes of Bivalent Iron, Cobalt, Nickel, and Copper with Bis(2-dimethylaminoethyl) Oxide

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The potentially tridentate ligand bis(2-dimethylaminoethyl) oxide (Me_4daeo) forms 1:1 complexes with the chlorides and bromides of Fe(II), Co(II), Ni(II), and Cu(II). Spectral, conductivity, and molecular weight data indicate that these complexes have the discrete molecular structure $\text{M}(\text{Me}_4\text{daeo})\text{X}_2$ both in solution and in the solid state. The crystal field spectra of these complexes strongly suggest a full fivefold coordination of the metal ions. The 1:1 compounds of $\text{Co}(\text{NCS})_2$ and $\text{Ni}(\text{NCS})_2$ with the ligands Me_4daeo and bis(2-dimethylaminoethyl)methylamine have been prepared and studied. All of the above compounds have values of the magnetic moment typical of a high-spin configuration.

Introduction

Recently several papers have dealt with five-coordinated complexes of the bivalent metals of the first transition group. When the ligands contain donor atoms such as nitrogen and oxygen, high-spin complexes are obtained.¹⁻⁴ On the other hand, with ligands containing donor atoms with a low electronegativity, as is the case with phosphines, arsines, isonitriles, and ligands containing sulfur, the compounds are of the low-spin type.⁵

The steric requirements of the ligands and the nature of the donor atoms both appear to be critical factors in determining whether a five-coordinated structure is attained instead of a four- or six-coordinated structure. In order to vary both of these factors systematically we have now prepared a series of compounds formed from the potentially tridentate ligand $\text{O}[\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]_2$, bis(2-dimethylaminoethyl) oxide (Me_4daeo), with the salts MX_2 , where M = the transition ions between Fe and Cu and X = Cl, Br, or NCS. This ligand is structurally similar to $\text{CH}_3\text{N}[\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]_2$, hereafter

abbreviated as Me_5dien , which forms five-coordinated complexes with the metals mentioned above.³ It is also similar to $\text{HN}[\text{CH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2]_2$, hereafter abbreviated as Et_4dien , which, as Dori and Gray have shown, forms five-coordinated complexes with cobalt(II) and four-coordinated planar complexes (one free X^-) with nickel(II) in the solid state.⁴ Compared with Me_5dien and Et_4dien , Me_4daeo appears to be a less bulky ligand. The oxygen of the ether group is not usually a good donor atom but when it is part of chelate ligands it has been shown to coordinate with 3d metal ions.⁶

Experimental Section

Materials.—All solvents were of reagent grade quality. 1,2-Dichloroethane was washed with 5% aqueous sodium hydrogen carbonate, dried for 24 hr over anhydrous calcium chloride, and fractionally distilled.

Preparation of the Compounds.—The preparation of bis(2-dimethylaminoethyl) oxide was accomplished by methylation of bis(2-aminoethyl) oxide with a $\text{HCOOH}-\text{HCHO}$ mixture. After the evolution of carbon dioxide had practically stopped, all of the volatile fractions were removed by vacuum distillation. The solid residue was treated with a saturated solution of sodium hydroxide and the oily layer formed was extracted into ether. The ethereal extract was dried over potassium hydroxide. After removal of the ether the compound bis(2-dimethylaminoethyl) oxide distilled as a colorless oil, bp 42° (1.5 mm). *Anal.* Calcd for $\text{O}[\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]_2$: N, 17.48. Found: N, 17.61. Hot solutions of the appropriate metal salt (0.010 mole) in 1-butanol (60 ml) and bis(2-dimethylaminoethyl) oxide (0.012 mole) in 1-

(1) L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, *Inorg. Chem.*, **4**, 943 (1965); L. Sacconi, M. Ciampolini, and G. P. Speroni, *ibid.*, **4**, 1116 (1965); *J. Am. Chem. Soc.*, **87**, 3102 (1965); L. Sacconi and I. Bertini, *ibid.*, **88**, 1520 (1966).

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(5) A. Sacco and M. Freni, *Gazz. Chim. Ital.*, **89**, 1800 (1959); G. Dyer, J. G. Hartley, and L. M. Venanzi, *J. Chem. Soc.*, 1293 (1965); G. Dyer and D. W. Meek, *Inorg. Chem.*, **4**, 1398 (1965), and previous references cited therein.

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TABLE I
 PROPERTIES AND ANALYSES OF THE M(II) COMPLEXES

Compd	Color	Molar conductance, cm ² /ohm M ^c	M _{found} ^d / M _{calcd}	% N		% metal		% halogen	
				Calcd	Found	Calcd	Found	Calcd	Found
Fe(Me ₄ daeo)Br ₂	Pale pink	0.06		7.45	7.30			42.52	42.40
Co(Me ₄ daeo)Cl ₂	Blue	0.03	1.04	9.66	9.79	20.32	20.19	24.44	24.38
Co(Me ₄ daeo)Br ₂	Blue	0.04	1.03	7.39	7.38	15.55	15.29	42.17	42.03
Co(Me ₄ daeo)(NCS) ₂ ^a	Violet	0.05	1.07	16.71	16.62	17.58	17.80		
Co(Me ₃ dien)(NCS) ₂	Violet	0.03	1.04	20.10	20.32	16.92	17.03		
Ni(Me ₄ daeo)Cl ₂	Brick red	0.04	1.06	9.67	9.77	20.25	20.41	24.46	24.40
Ni(Me ₄ daeo)Br ₂	Brick red	0.02	1.07	7.40	7.49	15.49	15.26	42.20	42.05
Ni(Me ₄ daeo)(NCS) ₂ ^b	Turquoise			16.72	16.78	17.51	17.71		
Ni(Me ₃ dien)(NCS) ₂	Green	0.04	1.05	20.12	20.16	16.86	16.75		
Cu(Me ₄ daeo)Cl ₂	Green	0.95	1.04	9.51	9.60	21.57	21.39	24.06	23.80
Cu(Me ₄ daeo)Br ₂	Light green	0.35	1.06	7.30	7.46	16.57	16.65	41.67	41.59

^a Calcd: C, 35.81; H, 6.01. Found: C, 35.83; H, 6.01. ^b Calcd: C, 35.84; H, 6.02. Found: C, 36.00; H, 6.03. ^c For ca. 10⁻³ M solutions in 1,2-dichloroethane at 25°. Reference value in 1,2-dichloroethane is: [(n-C₄H₉)₄N]Br, 17.0. ^d For ca. 2 × 10⁻² M 1,2-dichloroethane solutions at 37°.

butanol (10 ml) were mixed. Concentration by distillation followed by cooling yielded the required complex compound. The crystalline compounds were filtered in a closed system and dried in a moisture-free nitrogen stream. They were recrystallized by dissolving them in chloroform containing a few drops of Me₄daeo and adding petroleum ether to the filtered solution. In the case of the ferrous compound all of the operations were executed in an atmosphere of pure nitrogen.

Physical Measurements.—The absorption spectra were recorded in the range 5000–30,000 cm⁻¹ with a Beckman DK2 spectrophotometer and 1-cm silica cells. The diffuse reflectance spectra were measured using the standard Beckman reflectance attachment and magnesium oxide as the reference.

The conductivity values were measured on a WTW Model LBR/B conductance bridge. Concentrations of the solutions were approximately 10⁻³ M.

Molecular weights were determined in 1,2-dichloroethane at 37° with a Mechrolab Model 301 A vapor pressure osmometer calibrated with benzil. The solutions were approximately 2 × 10⁻² M. The results were reproducible ±1%.

The apparatus and the experimental technique used for the magnetic measurements were described in a previous paper.⁷ The Gouy tube was calibrated with freshly distilled water and nickel chloride solution.⁸ Diamagnetic corrections were calculated from Pascal's constants.⁹

The infrared spectra were recorded on Nujol mulls using a Perkin-Elmer 337 spectrophotometer.

Results

The complexes reported in this paper are very hygroscopic crystalline solids. In the solid state, as well as in solution, the iron(II) complex is oxidized within a few minutes by atmospheric oxygen; the cobalt complexes are indefinitely stable in dry air. The analytical data and some characteristics of these compounds are given in Table I. All of the compounds (except that of Ni(NCS)₂ with Me₄daeo) are readily soluble in nitroalkanes, nitrobenzene, polychloroalkanes, low-boiling alcohols, and 1,4-dioxane, but are generally insoluble in nonpolar solvents.

Electric conductivity measurements on the solutions show that these compounds are essentially non-

electrolytes in 1,2-dichloroethane though they are strongly dissociated in methanol. Measurements of molecular weight at 37° in 1,2-dichloroethane show that a small percentage of associated species is present in solution. The degree of association $\bar{n} = M(\text{found})/M(\text{calcd})$ is 1.03–1.07 (Table I).

The magnetic moments of the complexes at room temperature (Table II) are typical of the high-spin

 TABLE II
 MAGNETIC DATA FOR SOME COMPLEXES
 IN THE SOLID STATE

Compd	t, °C	10 ³ χ _M	10 ³ χ _{M0}	μ _{eff} BM
Fe(Me ₄ daeo)Br ₂	22	30.45	11,631	5.26
Co(Me ₄ daeo)Cl ₂	19	31.71	9363	4.70
Co(Me ₄ daeo)Br ₂	19	29.57	9497	4.73
Co(Me ₄ daeo)(NCS) ₂	20	24.17	8293	4.45
Co(Me ₃ dien)(NCS) ₂	21	24.79	8851	4.58
Ni(Me ₄ daeo)Cl ₂	19	16.32	4895	3.40
Ni(Me ₄ daeo)Br ₂	20	12.40	4893	3.40
Ni(Me ₄ daeo)(NCS) ₂	20	11.61	4074	3.10
Ni(Me ₃ dien)(NCS) ₂	21	13.18	4800	3.38
Cu(Me ₄ daeo)Cl ₂	19	4.01	1347	1.79
Cu(Me ₄ daeo)Br ₂	20	3.56	1551	1.91

configuration of each element. The spectra of the solid compounds and of their solutions in 1,2-dichloroethane and methanol have been recorded at room temperature. The absorption spectra of the solutions in 1,2-dichloroethane have also been recorded at 37 and 70°. No appreciable temperature dependence was detected over this range. The reflectance spectra of a number of representative Me₄daeo compounds are shown in Figures 1–3. The molar absorptivities at the peaks, for the 1,2-dichloroethane solutions, are: Fe-(Me₄daeo)Br₂, ε₇₈₀₀ 9; Co-(Me₄daeo)Cl₂, ε₇₆₀₀ 29, ε_{16,200} 225, ε_{18,000} 151; Ni-(Me₄daeo)Cl₂, ε_{11,500} 38, ε_{12,300} 35, ε_{18,500} 55, ε_{21,500} 117; Cu-(Me₄daeo)Br₂, ε_{11,400} 306.

Infrared spectra of the complexes of Co(NCS)₂ and Ni(NCS)₂ with Me₄daeo and Me₃dien show two ν(CN) stretching vibrations in the range 2130–2066 cm⁻¹ and one or two bands in the region 830–764 cm⁻¹ representing the ν(CS) stretching vibrations (cf. Table III).

(7) L. Sacconi, R. Cini, M. Ciampolini, and F. Maggio, *J. Am. Chem. Soc.*, **82**, 3487 (1960).

(8) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960, p 415 ff.

(9) See ref 8, p 403.

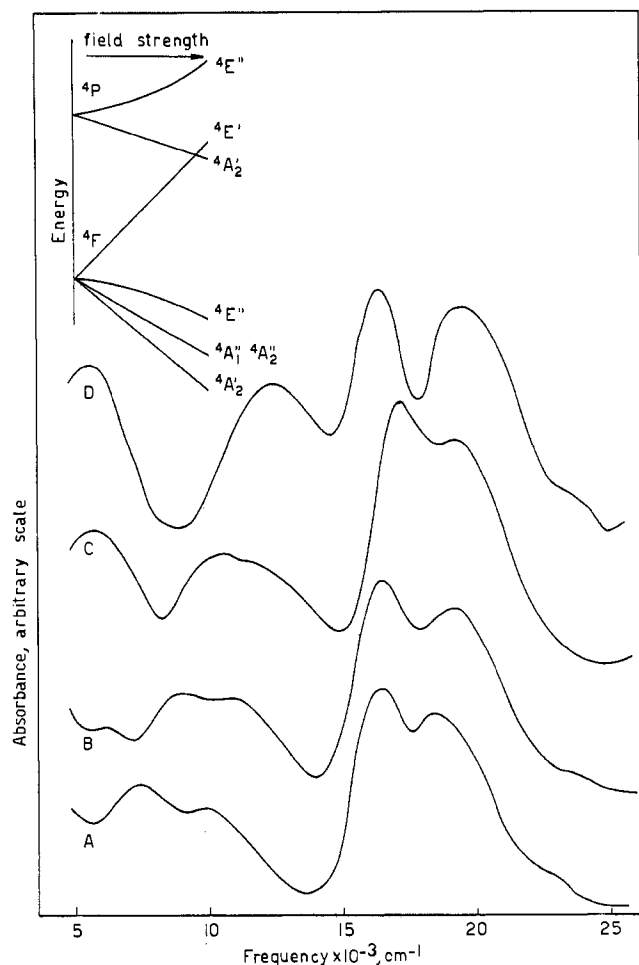


Figure 1.—Diffuse reflectance spectra of some five-coordinated high-spin complexes of cobalt(II): A, $\text{Co}(\text{Me}_4\text{daeo})\text{Cl}_2$; B, $\text{Co}(\text{Me}_3\text{dien})\text{Cl}_2$; C, $\text{Co}(\text{Me}_4\text{daeo})(\text{NCS})_2$; D, $[\text{Co}(\text{Me}_6\text{tren})\text{Br}]\text{Br}$. The structures of the compounds $\text{Co}(\text{Me}_3\text{dien})\text{Cl}_2$ and $[\text{Co}(\text{Me}_6\text{tren})\text{Br}]\text{Br}$ have been determined by X-ray methods.

TABLE III
INFRARED ABSORPTION FREQUENCIES (cm^{-1})
OF THE THIOCYANATE GROUPS^a

Compd	Frequencies, cm^{-1}		
	C-N str		C-S str
$\text{Co}(\text{Me}_4\text{daeo})(\text{NCS})_2$	2066 s, sp	2083 s, sp	828 m
$\text{Co}(\text{Me}_3\text{dien})(\text{NCS})_2$	2070 s, sp	2085 s, sp	818 m, 808 m
$\text{Ni}(\text{Me}_4\text{daeo})(\text{NCS})_2$	2090 s, sp	2130 s, sp	810 m, 764 mw
$\text{Ni}(\text{Me}_3\text{dien})(\text{NCS})_2$	2080 s, sp	2095 s, sp	810 m

^a s, strong; m, medium; mw, medium weak; w, weak; sp, sharp.

X-Ray powder photographs of the complexes formed by the same ligand and anion with different metals are very similar to each other (with the exception of those of the metal thiocyanates with M_4daeo). The relevant X-ray powder data are available through the ASTM file.

Discussion

$\text{M}(\text{Me}_4\text{daeo})\text{Cl}_2$ and $\text{M}(\text{Me}_4\text{daeo})\text{Br}_2$ Complexes.—Analytical, conductivity, and molecular weight data indicate that these complexes must be monomeric entities with the formula $\text{M}(\text{Me}_4\text{daeo})\text{X}_2$. The similarity between the spectra of the solids and of the solutions indicates that the solids also have this struc-

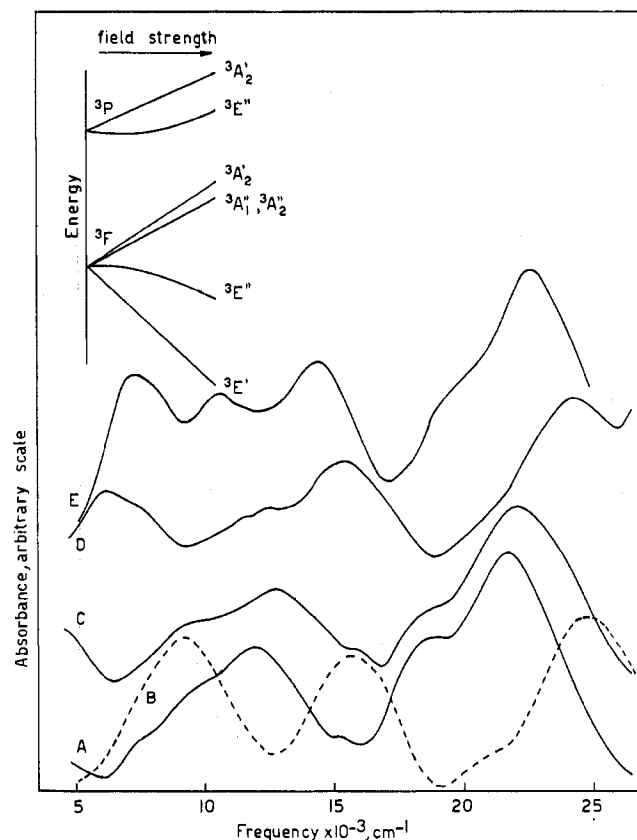


Figure 2.—Diffuse reflectance spectra of some high-spin complexes of nickel(II): A, $\text{Ni}(\text{Me}_4\text{daeo})\text{Cl}_2$; B (dotted line), $\text{Ni}(\text{Me}_4\text{daeo})(\text{NCS})_2$; C, $\text{Ni}(\text{Me}_3\text{dien})\text{Cl}_2$; D, $\text{Ni}(\text{Me}_3\text{dien})(\text{NCS})_2$; E, $[\text{Ni}(\text{Me}_6\text{tren})\text{Br}]\text{Br}$.

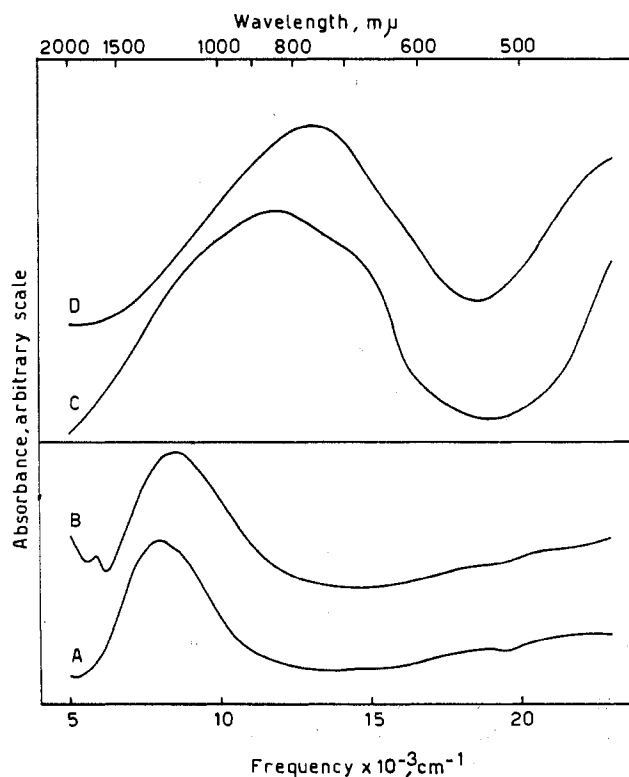


Figure 3.—Diffuse reflectance spectra of some complexes: A, $\text{Fe}(\text{Me}_4\text{daeo})\text{Br}_2$; B, $\text{Fe}(\text{Me}_3\text{dien})\text{Br}_2$; C, $\text{Cu}(\text{Me}_4\text{daeo})\text{Br}_2$; D, $\text{Cu}(\text{Me}_3\text{dien})\text{Br}_2$.

ture. Furthermore, their isomorphism suggests that they must all have essentially the same structure. The coordination number of the metals in these compounds will therefore be four or five according to whether Me_4daeo acts as a bidentate or as a tridentate ligand. This possibility of four-coordination must, however, be excluded because the spectra of the complexes $\text{M}(\text{Me}_4\text{daeo})\text{X}_2$ are interpretable in terms of a five-coordinated structure of low symmetry, but not in terms of a pseudo-tetrahedral structure. These spectra will be discussed in detail later on in this paper. We therefore propose a fully five-coordinated structure for the complexes $\text{M}(\text{Me}_4\text{daeo})\text{Cl}_2$ and $\text{M}(\text{Me}_4\text{daeo})\text{Br}_2$.

In methanol solution these compounds become strong conductors and their absorption spectra are profoundly different from those of their solution in inert solvents. The conductivity and spectral data indicate that for a given element the solvolysis is more extensive for the bromo complex than for the chloro complex. For the cobalt and nickel complexes the spectra of the solvated species are clearly indicative of an octahedral structure. This is probably formed by dissociation of at least one of the halogen atoms and coordination of two methanol molecules. The spectra of the copper compounds in methanol are not sufficiently characteristic to be clearly explained although they do not conflict with an octahedral structure of the solvated species. The compound $\text{Fe}(\text{Me}_4\text{daeo})\text{Br}_2$ reacts so strongly with methanol that its solutions rapidly become turbid.

Complexes of $\text{Co}(\text{NCS})_2$ and $\text{Ni}(\text{NCS})_2$ with Me_4daeo and Me_3dien .—Both $\text{Co}(\text{NCS})_2$ and $\text{Ni}(\text{NCS})_2$ form 1:1 complexes with Me_4daeo and Me_3dien . The two Me_3dien complexes and the cobalt Me_4daeo complex must be discrete $\text{M}(\text{ligand})(\text{NCS})_2$ entities, where the ligand behaves as a tridentate ligand and the NCS group is coordinated *via* its nitrogen atom. These conclusions are based upon the following evidence: (a) the crystal field spectra, which are completely equivalent both in solution and in the solid state, are interpretable in terms of a five-coordinated and not a pseudo-tetrahedral configuration; (b) the complexes are monomers and nonconductors in 1,2-dichloroethane; (c) the infrared spectra of the solid compounds show CN stretching bands in the region expected for isothiocyanate complexes;¹⁰ the CS stretching is also in the region characteristic of the N-bonded NCS group.¹¹

In contrast to $\text{Co}(\text{Me}_4\text{daeo})(\text{NCS})_2$, the 1:1 compound formed by nickel thiocyanate with Me_4daeo has an octahedral polymeric structure with NCS bridging groups. The evidences in favor of this conclusion are: (a) the crystal field spectrum of the solid compound shows spin-allowed bands at 9300, 15,700, and 25,000 cm^{-1} characteristic of the octahedral complexes of nickel(II) (Figure 2); (b) unlike the three isothiocyanates mentioned above, this compound is insoluble in noncoordinating solvents; (c) the infrared spectrum shows bands which are characteristic of the CN and

CS stretching modes of the isothiocyanate groups, at 2090 and 810 cm^{-1} , respectively. In addition, bands are present at 2130 and 764 cm^{-1} , which may be attributed to bridging NCS groups.^{12,13}

The different stereochemistry of the Me_4daeo complexes of cobalt and nickel thiocyanates constitutes further evidence that nickel has a greater tendency than cobalt to give octahedral complexes rather than five-coordinated complexes.¹⁴ In the $\text{Ni}(\text{Me}_3\text{dien})(\text{NCS})_2$ complex, however, sixfold coordination is not achieved, probably because the steric requirements of the ligand Me_3dien are greater than those of Me_4daeo . These complexes also undergo profound solvolysis in methanol.

Comments on the Spectra of the Five-Coordinated Species.—In order to discuss the crystal field spectra of the Me_4daeo complexes, it is convenient to refer to the spectra of the five-coordinated high-spin complexes having a high symmetry. The complexes of tris(2-dimethylaminoethyl)amine (Me_6tren),¹⁵ $\text{N}[\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]_3$, are suitable for this purpose, since they possess trigonal-bipyramidal microsymmetry (strictly of the point group C_{3v}).¹⁶ In complexes with Me_3dien and Me_4daeo the symmetry of the ligand field is certainly lower owing to the lower number of equivalent atoms and to the geometry of the organic ligands.^{17,18} Though the crystal field spectra of $\text{M}(\text{Me}_3\text{dien})\text{X}_2^3$ and $\text{M}(\text{Me}_4\text{daeo})\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}$) are different from those of the corresponding $[\text{M}(\text{Me}_6\text{tren})\text{X}]\text{X}$ complexes,¹⁵ they can nevertheless be traced back to them. Some symmetrical bands, shown by the Me_6tren complexes, split into various components in the Me_3dien and Me_4daeo complexes and give rise to very broad asymmetrical bands. Fewer variations are noted in the Me_3dien and Me_4daeo complexes when $\text{X} = \text{NCS}$, probably because of the greater equivalence of the donor atoms. These isothiocyanates, therefore, allow the evolution of the spectra from Me_6tren to Me_3dien and Me_4daeo to be traced more clearly.

From here onward the assignment of the absorption bands of these five-coordinated complexes will always be made in terms of D_{3h} symmetry, whatever the effective symmetry of the complex, which is often unknown. One must realize that the discussion of spectral assignments is only tentative and further studies on the spectra of the five-coordinated complexes are desirable.

Let us first consider the spectra of the five-coordinated complexes of cobalt in trigonal-bipyramidal fields. A crystal field approach led to the levels shown schematically in Figure 1.¹⁹ In accordance with this dia-

(12) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 175.

(13) D. Forster and D. M. L. Goodgame, *Inorg. Chem.*, **4**, 715 (1965).

(14) P. Paoletti and M. Ciampolini, *ibid.*, **6**, 64 (1967).

(15) M. Ciampolini and N. Nardi, *ibid.*, **5**, 41, 1150 (1966).

(16) M. Di Vaira and P. L. Orioli, private communication.

(17) A complete X-ray investigation showed that the coordination polyhedron of the complex $\text{Co}(\text{Me}_3\text{dien})\text{Cl}_2$ is a distorted trigonal bipyramid.¹⁸ The same stereochemistry was also attributed to the other Me_3dien complexes on account of their isomorphism (for a given halogen) and the similarity of their spectra (for a given metal).⁸

(18) M. Di Vaira and P. L. Orioli, *Chem. Commun.*, 590 (1965).

(19) M. Ciampolini, N. Nardi, and G. P. Speroni, *Coord. Chem. Rev.*, **1**, 222 (1966).

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(11) A. Turco and C. Pecile, *Nature*, **191**, 66 (1961); J. Lewis, R. S. Nyholm, and P. W. Smith, *J. Chem. Soc.*, 4590 (1961); A. Sabatini and I. Bertini, *Inorg. Chem.*, **4**, 959 (1965).

gram the four bands found in the spectrum of $[\text{Co}(\text{Me}_6\text{tren})\text{Cl}]\text{Cl}$ at 5900, 12,500, 15,900, and 20,200 cm^{-1} were assigned as transitions from the fundamental state to the states ${}^4\text{E}''(\text{F})$, ${}^4\text{E}'(\text{F})$, ${}^4\text{A}_2'(\text{P})$, and ${}^4\text{E}''(\text{P})$, respectively.¹⁹ The availability of a number of five-coordinated complexes enables us to test this assignment more thoroughly. It can be seen (Figure 1 and ref 3, 15) that all of these complexes give rise to an intense, sharp band at *ca.* 16,000 cm^{-1} almost independently of the nature of the donor atoms and the geometry of the complex. Accordingly, it seems reasonable to assign these transitions to ${}^4\text{A}_2'(\text{F}) \rightarrow {}^4\text{A}_2'(\text{P})$ as the energy curves of the fundamental state and of the excited state against the field strength are approximately parallel. Moreover, because of the orbitally nondegenerate nature of the ${}^4\text{A}_2'(\text{P})$ state it cannot be split in fields with a lower symmetry.

The transition which is present in the spectrum of $[\text{Co}(\text{Me}_6\text{tren})\text{Cl}]\text{Cl}$ at 12,500 cm^{-1} is, on the other hand, very sensitive to the characteristics of the field (in the Me_6tren complexes it is at 13,400 for $\text{X} = \text{ClO}_4$ and at 12,200 cm^{-1} for $\text{X} = \text{I}$).¹⁵ Furthermore, when the symmetry of the complexes decreases, this band splits into two components. These observations are in accordance with the assignment of the excited state of these transitions to the ${}^4\text{E}'(\text{F})$ state, because of the strong field strength dependence expected for this transition and because it is possible to split this orbitally degenerate level as the symmetry of the complex decreases.

Finally, the two bands at 5000–6000 and 18,000–21,000 cm^{-1} also show the expected field strength dependence. Though it is possible that the former band may be split, this was not detectable because it falls near the limit (4000 cm^{-1}) to which our spectrophotometer can measure. The latter band is rather broad and asymmetric even in the Me_6tren complexes.

The energy level scheme for the nickel ion in ligand fields with D_{3h} symmetry has been reported in detail in ref 20 and is given, in a simplified form, in Figure 2. When the nickel atom is displaced, from the plane of the three base atoms, along the threefold axis (as in the case for Me_6tren complexes)¹⁸ the accidental degeneracy of the states A_1'' and A_2'' (in D_{3h}) is removed and they also move toward lower energies.²¹ The spectrum of $[\text{Ni}(\text{Me}_6\text{tren})\text{Cl}]\text{Cl}$ has therefore been tentatively assigned as:¹⁹ the two bands of medium intensity at 7200 and 15,000 cm^{-1} , to ${}^3\text{E}'(\text{F}) \rightarrow {}^3\text{E}''(\text{F})$ and ${}^3\text{A}_2'(\text{F})$ transitions, respectively; the more intense bands above 20,000

cm^{-1} , to transitions derived from the ${}^3\text{P}$ term of the free ion; and the less intense bands between 10,000 and 12,000 cm^{-1} , to transitions to the states ${}^3\text{A}_1''(\text{F})$ and ${}^3\text{A}_2''(\text{F})$. There is moreover a very weak and sharp band at *ca.* 12,000 cm^{-1} , which is probably a spin-forbidden band ${}^3\text{E}'(\text{F}) \rightarrow {}^1\text{E}'(\text{D})$. In the other complexes, all the more intense bands show the expected marked dependence on field strength. In the $[\text{Ni}(\text{Me}_6\text{tren})\text{X}]\text{X}$ complexes, for instance, the bands at 7700, 15,200, and 23,400 cm^{-1} when $\text{X} = \text{ClO}_4$ shift to 7200, 13,800, and 22,300 cm^{-1} when $\text{X} = \text{I}$.¹⁵ In the case of $\text{Ni}(\text{Me}_3\text{dien})(\text{NCS})_2$ the first band is split and in the halogen complexes with Me_3dien ⁸ and Me_4daeo they probably extend below 5000 cm^{-1} . Figure 2 shows that, as the symmetry of the compounds decreases, a very broad band with several components progressively develops around 6000–15,000 cm^{-1} . This complicated system of bands is not surprising, considering the great number of transitions which may be expected in this region for complexes with low symmetry.

In conclusion, it appears that the spectra of the Me_4daeo complexes with both cobalt and nickel can be assigned consistently on the basis of a five-coordinated structure. On the other hand, pseudo-tetrahedral complexes of cobalt and nickel show different spectral features. An indicative comparison can be made with the spectra of pseudo-tetrahedral complexes of the type $\text{M}(\text{ligand})\text{X}_2$ —where $\text{M} = \text{Co}, \text{Ni}$; $\text{X} = \text{Cl}, \text{Br}, \text{NCS}$; ligand = $(\text{CH}_3)_2\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_3)_2$, $(\text{CH}_3)_2\text{N}(\text{CH}_2)_3\text{N}(\text{CH}_3)_2$.²² These last compounds show a greater number of peaks situated at lower frequencies and having molar absorptivities higher than the corresponding Me_4daeo complexes.

Finally, Figure 3 shows that the spectra of the Me_4daeo complexes of iron and copper are very similar to those of the five-coordinated Me_3dien analogs. The peaks of the former compounds are slightly shifted toward the lower frequencies as expected on the basis of the relative positions of the oxygen and of the nitrogen in the spectrochemical series. A five-coordinated structure is thus proposed also for the iron and copper complexes with Me_4daeo .

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