Metal-Promoted Ligand Synthesis, Preparation, and Characterization of Cobalt(II) and -(III) Complexes with a Highly Unsaturated Tetraaza Macrocyclic Ligand

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We have utilized the facile promotion of oxidative dehydrogenation exhibited by macrocyclic complexes of iron to prepare and characterize macrocyclic complexes of cobalt not available via other synthetic routes. The secondary amine groups of the macrocyclic ligand in the complex [Fe(Me6[14]4,11-dieneN4)(CH3CN)2](SO3CF3)2 are oxidatively dehydrogenated leading to the isolation of [Fe(Me6[14]1,4,8,11-tetraeneN4)(CH3CN)2](PF6)2. In contrast to the corresponding Ni(II) complex, the ligand is readily displaced from iron. The free base readily coordinates with cobalt(II) to produce five-coordinate, low-spin complexes of the type [Co(Me6[14]1,4,8,11-tetraeneN4)X](ClO4)2 where X = Cl−, Br−, ClO4−, H2O, and CH3CN. A series of cobalt(III) complexes has also been prepared and characterized. Analysis of the visible spectra of these complexes permits a comparison of the ligand field strength of the tetraimine with those of a series of similar 14-membered macrocyclic ligands varying in position and degree of unsaturation.

Introduction

Goedken and Busch[1,2] initially reported on the ability of iron to promote the oxidative dehydrogenation of secondary amine groups bound to the metal as part of a macrocyclic ligand. Thus the iron(II) complex [Fe(Me6[14]4,11-dieneN4)-(CH3CN)2]2+ [3,4] reacts smoothly with oxygen, under acidic conditions, to yield, in succession, the iron(II) complexes of Me6[14]1,4,11-trieneN4, Me6[14]1,4,8,11-tetraeneN4, and ultimately, by tautomerization, Me6[14]1,3,8,11-tetraeneN4. The structures of ligands of interest are summarized in Figure 1. The iron(II) complexes of two related macrocycles, Me6[14]4,14-dieneN4[1,2] and Me6[14]aneN4,[5,6] have also been shown to undergo similar oxidations thereby producing a variety of new highly unsaturated iron(II) complexes which differ from the products derived from the 4,11-dieneN4 system in their degree and position of ligand unsaturation. A mechanism, involving the tripositive state of iron, has been proposed to account for the observed changes, the iron(III) complexes being isolated from the reaction mixture.[1] Such intramolecular redox reactions producing oxidized forms of these ligands were first demonstrated with the analogous nickel(II) complexes.[7] Addition of HNO3 to [Ni(Me6-[14]4,11-dieneN4)]2+ or [Ni(Me6[14]aneN4)]2+ yields the same isolated tetraimine complex, [Ni(Me6[14]1,4,8,-1-tetraeneN4)]2+, as the final product and in this case, the unusual tripositive oxidation state of nickel is implicated in the reaction mechanism. More recently, Barefield et al.[8] have demonstrated that the decomposition of the nickel(III) complexes of Me6[14]aneN4 and [14]aneN4 in basic solvents leads to the formation of nickel(II) complexes containing monoimine macrocyclic ligands via a nickel(II) ligand radical species. Such species have previously been suggested for the iron systems. Based on the results for the iron and nickel systems, it is apparent that the oxidative dehydrogenation reactions involving the fully saturated ligand, Me6[14]aneN4, are metal ion specific. Copper(II) complexes do not undergo this reaction with HNO3, whereas copper(III) complexes generated electrochemically do appear to promote dehydrogenation of these ligands.[9] Unfortunately, ligand oxidation reactions are relatively rare among cobalt complexes, but the desired product can be obtained by first generating the required ligand on another metal ion followed by its removal and subsequent reaction with anhydrous cobalt(II) salts.[2,5b,10] In the case of relatively unsaturated ligands, the procedures are nontrivial because of their hydrolytic sensitivity and the tendency of some of these ligands to rearrange. We report here the synthesis and characterization of low-spin five-coordinate cobalt(II) and six-coordinate cobalt(III) complexes of the tetradentate macrocyclic ligand, 5,7,7,12,14,14-hexa-methyl-1,4,8,11-tetraazacyclotetradeca-1,4,8,11-tetraene (abbreviated Me6[14]1,4,8,11-tetraeneN4 or more simply [14]tetraeneN4) (I). The nickel(II)[7] and iron(II) complexes[1] of [14]tetraeneN4 have been studied extensively whereas the copper and cobalt complexes have only received brief mention in earlier reports.[1] These studies not only present interesting new substances but also illustrate the power of using metal-promoted ligand synthesis to obtain other complexes which cannot be prepared otherwise. The proper choice of metal ion for the synthesis is crucial. The element iron is ideal in this instance, because it is both extremely effective at promoting the dehydrogenation and it is relatively easy to remove from the ligand. On the other hand, while nickel is also very effective in promoting ligand dehydrogenation, the ligand Me6[14]1,4,8,11-tetraeneN4 cannot be displaced from that metal. A question with which we are particularly concerned here is the effect of conjugation on ligand field strength given a particular degree of unsaturation and ring size in the macrocyclic ligands to be compared. The bis-α-diimine ligand Me4[14]1,3,8,10-tetraeneN4 (II)[11] provides the basis for comparison. Cobalt(III) complexes are particularly useful for gaining insight into the effects of changes of structural parameters on ligand strengths and on such chemical properties as reduction potentials for these[12-14] and other related complexes.[2-15]

Results and Discussion

The formation of the macrocyclic ligand, 5,7,7,12,14,-14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene dihydrotrifluoromethanesulfonate, Me6[14]4,11-dieneN4·2HSO3CF3 (III), by the reaction of acetone with the trifluoromethanesulfonate salt of 1,2-diaminoethane is the first step in the synthetic route to the cobalt complexes of [14]-tetraeneN4. The ligand, Me6[14]4,11-dieneN4·2HSO3CF3, reacts readily with [Fe(CH3CN)6](SO3CF3)2 (generated in situ by the action of trifluoromethanesulfonic acid on iron powder in acetonitrile solution) to produce, upon addition of triethylamine to neutralize the excess acid, the iron(II) complex, [Fe(Me6[14]4,11-dieneN4)(CH3CN)2](SO3CF3)2. Oxidative dehydrogenation[1] of this iron(II) complex, followed by the addition of NH4PF6, produces the complex [Fe-(Me6[14]1,4,8,11-tetraeneN4)(CH3CN)2](PF6)2. The use of the analogous perchlorate salts has been avoided due to the extreme hazardous nature of such iron derivatives.[1,4] Addition of 3 mol of 1,10-phenanthroline to the tetraimine complex leads to the isolation of the free ligand in a tautomeric form, Me6[14]2,4,9,11-tetraeneN4. The free base and the ligand complexed to iron, cobalt, and nickel are related by the migration of double bonds from positions 2 and 9 to positions
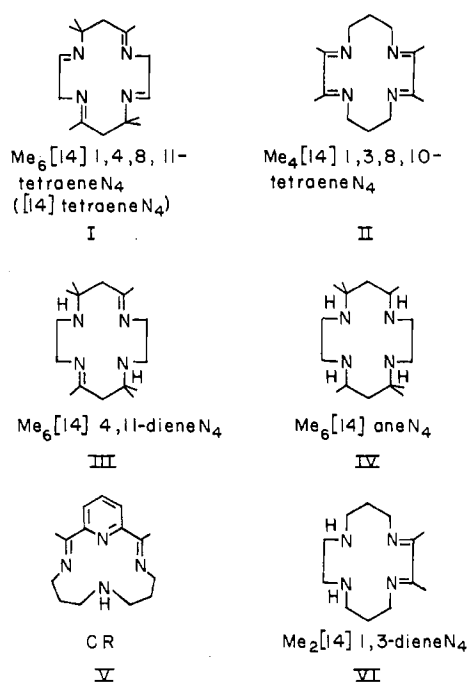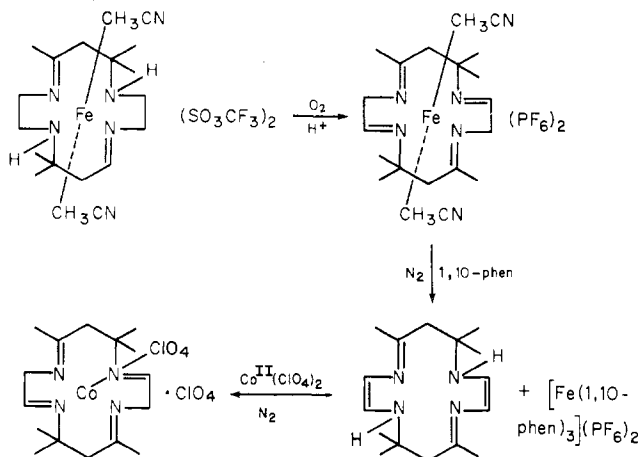
Me$_6$[14] 1,4,8,11-
tetraeneN$_4$
([14] tetraeneN$_4$)

I

Me$_4$[14] 1,3,8,10-
tetraeneN$_4$

II

Me$_6$[14] 4,11-dieneN$_4$

III

Me$_6$[14] oneN$_4$

IV

CR

V

Me$_2$[14] 1,3-dieneN$_4$

VI

Figure 1. Ligand structures. The abbreviations used indicate the number of methyl substituents, the size of the rings in brackets, followed by the number and location of unsaturated groups in the ligand.[5]

Scheme I

1 and 8 as shown in Scheme I. The structure of the coordinated ligand and the free base have been unequivocally assigned from NMR data reported previously.[1,16] The enamine–imine rearranged ligand reacts with anhydrous cobalt perchlorate under an inert atmosphere to produce [Co-(Me$_6$[14]1,4,8,11-tetraeneN$_4$)ClO$_4$]ClO$_4$. The axial site is quite labile and this position can be readily substituted with neutral (H$_2$O, CH$_3$CN, CH$_3$OH) or anionic (Cl$^-$, Br$^-$) ligands. These cobalt(II) complexes join a small but expanding group of complexes with macrocyclic ligands, including those of Me$_4$[14]1,3,8,10-tetraeneN$_4$ (II),[17] Me$_6$[14]4,11-dieneN$_4$ (III),[18] Me$_6$[14]4,14-dieneN$_4$,[10,18] Me$_6$[14]aneN$_4$ (IV),[19] CR (V),[20] and Me$_2$[14]1,3-dieneN$_4$ (VI)[17] which have been formulated as low spin and, commonly, five coordinate. Most low-spin cobalt(II) complexes contain sulfur and phosphorus donor atoms,[21-23] whereas five-coordinate cobalt(II) complexes with saturated or unsaturated nitrogen donor atoms are usually high spin.[24-27]

Oxidation of the cobalt(II)–[14]tetraeneN$_4$ complexes in acidic solutions results in the formation of the cobalt(III) dihalogeno complexes. Many cobalt(III) complexes with

Table I. Physical Properties of the New Complexes

Compd	Color	μ_{eff} β	Λ_m,[a] cm^2/(ohm mol)	Solvent
Co([14]tetraeneN$_4$)- (ClO$_4$)$_2$	Yellow	2.12	180	CH$_3$NO$_2$
[Co([14]tetraeneN$_4$)- (CH$_3$CN)](ClO$_4$)$_2$	Yellow	1.97	307	CH$_3$CN
[Co([14]tetraeneN$_4$)- (H$_2$O)](ClO$_4$)$_2$	Brown	2.03	190	H$_2$O
[Co([14]tetraeneN$_4$)- Cl]ClO$_4$	Brown	2.13	92	CH$_3$NO$_2$
[Co([14]tetraeneN$_4$)- Br]ClO$_4$	Brown	2.02	94	CH$_3$NO$_2$
[Co([14]tetraeneN$_4$)- Cl$_2$]ClO$_4$	Green		156	CH$_3$CN
[Co([14]tetraeneN$_4$)- Br$_2$]ClO$_4$	Green		160	CH$_3$CN
[Co([14]tetraeneN$_4$)- (NO$_2$)$_2$]ClO$_4$	Yellow		134	CH$_3$CN
[Co([14]tetraeneN$_4$)- (CH$_3$CN)$_2$]ClO$_4$)$_3$	Orange		343	CH$_3$CN

[a] Conductivities were run at 25°C with concentrations approximately 1.0×10^{-3} M.

macrocyclic ligands are now well-characterized and most of them have the common six-coordinate and diamagnetic configuration.[12,28-33]

Attempts to produce the free tetraimine ligand by decomposition of [Ni(Me$_6$[14]1,4,8,11-tetraeneN$_4$)]$^{2+}$ with cyanide, 1,10-phenanthroline, or dimethylglyoxime were disappointingly unsuccessful in view of the relative ease of preparation of the nickel(II) complex[7] as opposed to the more arduous synthesis of the analogous iron(II) complex.[1] This emphasizes the dual requirements of ligand synthesis of this class. The nickel complex satisfies the first requirement of ease of ligand formation, but it fails the second, ease of removal of the ligand from the metal ion used during synthesis. It should be noted, however, that other ligands such as Me$_6$-[14]4,14-dieneN$_4$,[10] Me$_6$[14]4,11-dieneN$_4$,[19] and Me$_6$[14]-aneN$_4$[19,34] are more conveniently removed from nickel than from iron.

Characterization of the Cobalt(II) Complexes. The complex, Co([14]tetraeneN$_4$)(ClO$_4$)$_2$, precipitates from a degassed alcoholic solution of anhydrous cobalt perchlorate and the free ligand Me$_6$[14]2,4,9,11-tetraeneN$_4$ as a pale yellow microcrystalline solid. Recrystallization of this complex from methanol, acetonitrile, or water produces yellow or brown (aquo) crystals of the complex containing one molecule of the respective solvent coordinated to an axial site. The coordinated solvent molecules are lost on prolonged drying in vacuo to re-form the anhydrous compound containing one coordinated perchlorate group. The infrared spectrum shows the disappearance of those bands characteristic of the coordinated solvent. The addition of lithium bromide or chloride to an alcoholic solution of the perchlorato complex results in the formation of red-brown complexes of the type [Co([14]-tetraeneN$_4$)X]ClO$_4$. Upon exposure to air, the halogeno complexes slowly decompose in the solid state. The acetonitrile complex decomposes within a few days, whereas the aquo and perchlorato complexes are stable under normal laboratory conditions for extended periods of time. All complexes are sparingly soluble in alcohols, but more soluble in nitromethane and in acetonitrile. They can be prepared in the atmosphere without appreciable formation of cobalt(III) species, although the addition of aqueous halo acids does promote oxidation by air. Neutral solutions of these complexes are stable in the presence of air for short periods of time before spectral changes are noted.

The molar conductivities of the complexes are given in Table I. The values in nitromethane for the halo complexes are in
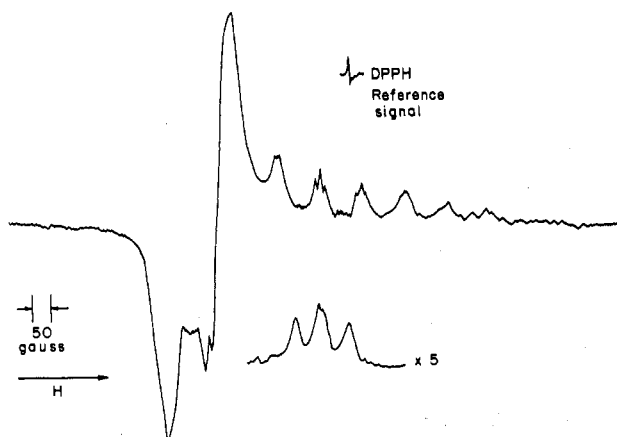
Figure 2. The EPR spectrum of [Co([14]tetraeneN$_4$)CH$_3$CN]-(ClO$_4$)$_2$ in frozen acetonitrile solution containing tetra-*n*-butylammonium tetrafluoroborate at 77 K, using DPPH as a reference standard for spectrum calibration. The spectrum was recorded at a sweep width of 2500 G. The superhyperfine splitting observed for one component of the g_z reaction is shown below the main spectrum, at a sweep width of 500 G.

the proximity of other uni-univalent electrolytes in that solvent[35] while the acetonitrile and aquo complexes behave as di-univalent electrolytes.[35,36] The values found for the perchlorato complex suggest that in nitromethane and in acetonitrile, the coordinated perchlorate anion has been replaced by a solvent molecule. This solvation process is supported by spectrophotometric and EPR data and is discussed below.

The cobalt(II) complexes all have a low-spin d^7 configuration as shown by their effective magnetic moments at room temperature in the solid state, Table I. The values are slightly higher than the spin-only moment for one unpaired electron, falling within the range 1.97–2.13 μ_B, and are consistent with the values reported for low-spin five- and six-coordinate cobalt(II) complexes.[19,37,38] The presumed square-planar cobalt(II) complexes generally exhibit higher magnetic moments.[21,23,38] However, values as low as 1.1 μ_B have been recorded for a few low-spin five-coordinate cobalt(II) complexes of Me$_4$[14]1,3,8,10-tetraeneN$_4$ and Me$_2$[14]1,3-dieneN$_4$ in the solid state[17] possibly arising from coupling interactions of unpaired electrons of two cobalt atoms, via either a weak Co–Co σ bond formation or via bridging ligands such as cyanide or halide. The observed values in Table I closely follow those obtained for the analogous complexes of Me$_4$[14]1,3,8,10-tetraeneN$_4$,[17] Me$_6$[14]4,11-dieneN$_4$,[18] and CR.[20] The general trend in the moments for all four series of these complexes is Cl$^-$ > Br$^-$ ≈ H$_2$O > nitrogen donor axial ligands. A few magnetic moments have been calculated from the EPR data, to be discussed below, and agreement between the two methods is very good.

In order to ascertain whether the cobalt(II) complexes of [14]tetraeneN$_4$ are five or six coordinate we have investigated their EPR spectra. The spectrum of [Co([14]tetraeneN$_4$)-(CH$_3$CN)](ClO$_4$)$_2$ in acetonitrile solution at 77° K containing tetra-*n*-butylammonium tetrafluoroborate is shown in Figure 2. The observation of three distinct g values indicates that the effective symmetry of the complex is no higher than twofold.[37] The interpretation of the EPR spectra of species having the spin-paired d^7 electronic configuration has been discussed by Maki et al.[39] The observed g values for the CH$_3$CN complex are g_x = 2.343, g_y = 2.243, and g_z = 2.017. Hyperfine splitting between the cobalt nucleus (spin$^7/_2$) and the unpaired metal electron is observed in the g_z region, with a hyperfine splitting constant of A_z = 113. Only six components are observed, the remaining two being obscured by the intense signal associated with a second g value. No hy-

perfine splitting is observed in the g_x and g_y region. One component in the g_z region is clearly resolved into three lines with intensity ratios of 1:1:1. Such superhyperfine splitting arises from the coupling between the unpaired electron on cobalt and a nitrogen donor atom in the axial site. Since only three lines are observed, with a superhyperfine splitting constant of A_N = 14.1, only one molecule of CH$_3$CN is coordinated.[39] A six-coordinate complex involving two molecules of CH$_3$CN would show an EPR spectrum with g values similar to that observed, but the superhyperfine splitting pattern in the g_z region would then consist of five lines in the ratio of 1:2:3:2:1.

The EPR spectrum of Co([14]tetraeneN$_4$)(ClO$_4$)$_2$ in nitromethane solution at 77 K containing tetra-*n*-butylammonium tetrafluoroborate is very similar to that for the complex in acetonitrile. The g values observed are 2.328, 2.250, and 2.018 for g_x, g_y, and g_z, respectively, with a hyperfine splitting constant of A_z = 109 in the g_z region. Superhyperfine splitting is again observed with A_N = 16.1 producing three lines of equal intensity. The complex can therefore be formulated as being five coordinate in nitromethane solution with one molecule of nitromethane, or possibly some impurity from the solvent, occupying the axial site. This replacement of the coordinated perchlorate group in both acetonitrile and nitromethane solutions is verified by the conductance values in those solvents. The EPR spectrum of the bromo complex in nitromethane solution at 77 K containing tetra-*n*-pentylammonium bromide was poorly resolved with no discernible superhyperfine splitting. Approximate g values have been estimated to be 2.451, 2.249, and 2.015 for g_x, g_y, and g_z, respectively. Neither of the aquo or chloro complexes gave resolvable spectra.

The EPR spectra recorded here are very similar to those observed for the five-coordinated cobalt(II) cobalamin base-coordinated complexes and to a series of five-coordinate cobaloxime and cobinamide complexes reported previously.[40,41]

The effective magnetic moments for some of the [14]-tetraeneN$_4$ complexes have been calculated from the EPR data using the equation μ_{eff} = $g_{av}[S(S + 1)]^{1/2}$ where g_{av} = $^1/_3(g_x + g_y + g_z)$ and S = $^1/_2$.[37] The values calculated for the acetonitrile (μ_{eff} = 1.91β) and for the bromo complex (μ_{eff} = 1.94β) are slightly lower than those recorded by the Faraday method at room temperature (1.99 and 2.02, respectively). The conditions for the two measurements were substantially different and the direct determination requires diamagnetic corrections so that the slight differences are to be expected. By the same method the complex Co([14]tetraeneN$_4$)(ClO$_4$)$_2$ has a magnetic moment of 1.90β in nitromethane solution.

The infrared spectra of the free and of the coordinated tetraimine ligand have been reported previously[1] and, in conjunction with NMR data, these data have been used to assign the structures shown in Scheme I. Briefly the ir of Me$_6$[14]2,4,9,11-tetraeneN$_4$ indicates the absence of water, but shows a strong sharp band at 3245 cm^{-1} due to the N–H stretching mode and two broad bands in the 1620–1610-cm^{-1} region due to C=C and C=N absorptions. The ir of the cobalt(II) complexes show no absorption due to N–H stretching modes while the imine functions appear at higher energy as a doublet in the 1670–1640-cm^{-1} region. The spectrum of Co([14]tetraeneN$_4$)(ClO$_4$)$_2$ shows bands at 1120, 1060, 930, and 620 cm^{-1} indicative of a coordinated perchlorate group[42] while bands at ~1100 and 615 in the spectra of all of the complexes indicate the presence of ionic perchlorate groups.[43] The aquo complex shows strong absorptions in the ir at 3480 and 3510 cm^{-1} which are assignable to the antisymmetric and symmetric OH stretching modes of the coordinated water.[43] A shoulder at 1625 cm^{-1} and a weak band at 870 cm^{-1} which does not appear in the spectra of the

Table II. Electronic Spectra of the Complexes[a,b]

Complex	Absorption maxima
Co([14]tetraeneN₄)- (ClO₄)₂[c]	7.1 (39), –, 23.8 (257); 28.2 (1836); 34.7 (1440)
[Co([14]tetraeneN₄)- (CH₃CN)](ClO₄)₂[d]	7.8 (76); 17.4 (38); 24.4 (258); 29.6 (2823); 34.5 (2500)
[Co([14]tetraeneN₄)- (H₂O)](ClO₄)₂[e]	7.9 (37); 17.9 (sh), 23.8 (205); 28.6 (2854); 35.1 (2095)
[Co([14]tetraeneN₄)- (H₂O)](ClO₄)₂[f]	~8.7 (br); 18.8 (sh); 23.8 (sh); 28.0; 35.1
[Co([14]tetraeneN₄)- Cl]ClO₄[c]	~7.1 (30); 22.2 (1265); 28.5 (sh); 37.0 (sh); 44.2 (10430)
[Co([14]tetraeneN₄)- Br]ClO₄[c]	6.8 (11); 19.6 (sh); 31.3 (sh); 37.0 (6670); –
[Co([14]tetraeneN₄)- Cl₂]ClO₄[d]	16.7 (52); –; 33.8 (8500)
[Co([14]tetraeneN₄)- Br₂]ClO₄[d]	15.8 (87); 25.6 (3470); 31.1 (25500)
[Co([14]tetraeneN₄)- (NO₂)₂]ClO₄[d]	22.2 (sh); 27.2 (5300); 39.2 (6940)
[Co([14]tetraeneN₄)- (CH₃CN)₂](ClO₄)₃[d]	21.3 (56); 25.6 (118); 30.3 (sh); 40.0 (sh)

[a] Maxima are in kK; numbers in parentheses are extinction coefficients. [b] Abbreviations: sh = shoulder; br = broad. [c] Nitromethane solution. [d] Acetonitrile solution. [e] Aqueous solution. [f] Solid state mull spectrum.

other complexes may be due to the HOH bending and rocking modes of coordinated water, respectively. Upon prolonged drying in vacuo over P₄O₁₀, the brown crystalline aquo complex and the yellow crystalline acetonitrile complex crumble to a yellow powder. The ir spectrum of this powder attests to the absence of solvent and to the presence of a coordinated perchlorate group. The acetonitrile complex shows a weak doublet centered at 2280 cm⁻¹ due to coordinated CH₃CN. Uncoordinated CH₃CN absorbs at ~2230 cm⁻¹.

Electronic Spectra of the Cobalt(II) Complexes. The absorption maxima and molar extinction coefficients of the complexes are listed in Table II. The spectra are similar to those reported for the analogous complexes of Me₄[14]1,3,-8,10-tetraeneN₄,[17] Me₂[14]1,3-dieneN₄,[17] Me₆[14]4,-1-dieneN₄,[18] and Me₆[14]4,14-dieneN₄[18] and are interpretable in terms of square-pyramidal geometry. The spectra can be divided into four regions of absorption: a broad weak band in the 5.0–10.0-kK region which appears asymmetric on the low-energy side, a weak shoulder near 18.0 kK, an absorption in the visible region near 24.0 kK, and two intense bands in the 28.0–36.0-kK region. For the chloro and bromo derivatives, these latter three bands are obscured by more intense charge-transfer bands. For the remaining complexes, the two bands in the 28.0–36.0-kK region may be associated with charge transfer involving the imine functions. The nickel(II),[44] iron(II),[4] and cobalt(II)[18] complexes of Me₆[14]4,11-dieneN₄ and the [Fe(Me₆[14]1,4,8,11-tetraeneN₄)(CH₃CN)₂]²⁺ complex[1] all have an absorption of comparable intensity in this same region. These bands vanish on hydrogenation of the imine functions[19] and also are not present when all of the imine linkages are conjugated.[5b,17]

The spectra have been tentatively interpreted using the energy level diagram derived by Caulton.[45] A more detailed analysis is not possible because of the disparity in the number of observed and predicted bands for low-spin d⁷ square-pyramidal systems. The lowest energy band near 8.0 kK is assigned to the ²E ← ²A₁ transition. Since this involves transitions from the d$_{xz}$ and d$_{yz}$ orbitals to the d$_{z^2}$ orbital, the band is expected to move to higher energy with increasing axial ligand field strength. This is in agreement with the results, the band shifting to higher energy in the order of Br⁻ < Cl⁻ < H₂O ≈ CH₃CN.

The transition ²B₁ ← ²A₁ may produce the observed asymmetry on the low-energy side of the ²E ← ²A₁ band in

the spectra of the aquo and acetonitrile complexes. The spectra of some of the cobalt(II) complexes of Me₆[14]4,11-dieneN₄ show this transition as a shoulder near 5.0 kK.[18] The absorption near 24.0 kK may arise from the ²E ← ²A₁ or ²A₂ ← ²A₁ transitions, both of which should be relatively insensitive to the nature of the axial ligand. Within experimental error, the position of this band maximum is indeed invariant. The weak shoulder in the 17.0–20.0-kK region is probably due to the ⁴A₂ ← ²A₁ and ⁴E ← ²A₁ transitions.

In acetonitrile solution the complex Co([14]tetraeneN₄)-(ClO₄)₂ shows a d–d spectrum identical with the authentic solid acetonitrile complex. This solvation process is supported by the EPR data. The solid state spectra of all of these complexes closely resemble the solution spectra in band positions, although the low-energy transition in the infrared region is broad and diffuse and in some cases is not resolvable. The two bands in the 17.0–24.0-kK region generally appear as shoulders on the more intense higher-energy bands.

Based on the evidence discussed above, the cobalt(II) complexes of Me₆[14]1,4,8,11-tetraeneN₄ are formulated as being five coordinated and low spin with square-pyramidal geometry. There is no evidence in the chemistry of the cobalt(III) complexes (see below) to suggest that the tetraimine ligand coordinates in a folded form thereby supporting the suggested geometry for the Co(II) species. The evidence for five coordination rests heavily on the EPR spectra, where superhyperfine splitting patterns suggest that only one axial (CH₃CN) ligand is coordinated. These data are supported by the conductance values for the halo complexes. The electronic spectra are best interpreted in terms of a low-spin square-pyramidal structure. The low-spin configuration for the cobalt(II) complexes reported here was shown by both susceptibility and EPR studies. The in-plane ligand field strength generated by the four imine nitrogen donors is sufficiently strong to induce spin pairing in the d⁷ system, a condition found common to cobalt(II) complexes of other tetraaza macrocyclic ligands.[17-20]

Characterization of the Cobalt(III) Complexes. Addition of the halo acids to ethanolic solutions of (Co[14]-tetraeneN₄)(ClO₄)₂ produced a rapid color change from yellow through brown to green. Aeration of the solutions overnight produced well-defined crystals of the respective cobalt(III) complexes. The remaining complexes were prepared by metathetical reactions on the dichloro or dibromo derivatives. The complexes are slightly soluble in water and alcohol and more soluble in acetonitrile and nitromethane. The acetonitrile complex behaves as a uni-trivalent electrolyte in acetonitrile, while the remaining complexes exhibit behavior typical of uni-univalent electrolytes in that solvent. The dihalo complexes do solvate slowly if allowed to remain in acetonitrile for extended periods of time.

The ir of these cobalt(III) complexes are similar to those detailed for the analogous cobalt(II) species. The imine stretching modes appear near 1655 and 1645 cm⁻¹, these absorptions appearing in the same region for the analogous complexes of iron(II)[1] and nickel(II)[7] and for complexes of Me₆[14]4,11-dieneN₄ and Me₆[14]4,14-dieneN₄.[4,12,18,44] The infrared spectrum of the *trans*-acetonitrile complex shows a doublet centered at 2305 cm⁻¹ due to coordinated CH₃CN. Strong, well-defined bands at 1415, 1310, 820, and 620 cm⁻¹ in the ir of the dinitro complex are indicative of NO₂ coordination. The positions of these four bands indicate that the NO₂ groups are N bonded.[43]

The NMR spectrum of [Co([14]tetraeneN₄)Br₂]ClO₄ has been reported previously and like those of the complexes [Fe([14]tetraeneN₄)(CH₃CN)₂](ClO₄)₂[1] and [Ni([14]-tetraeneN₄)](ClO₄)₂[16] shows a simple five-line pattern assignable to the geminal dimethyl protons (at 1.45 ppm), the

imine methyl protons (2.48 ppm), the bridgehead methylene protons in the six-membered rings (3.08 ppm), the methylene protons in the five-membered rings (4.90 ppm), and the C–H protons of the imine linkages (8.18 ppm). The NMR spectrum of the complexed ligand differs appreciably from that obtained for the free ligand and the changes have been interpreted in terms of proton and double bond migrations as indicated in Scheme I.[1]

Electronic Spectra of the Cobalt(III) Complexes. The electronic spectra of the $[Co([14]tetraeneN_4)X_2]^{n+}$ complexes are given in Table II and can be interpreted in terms of D_{4h} symmetry. According to the method of Wentworth and Piper,[46] the spectra of tetragonally distorted octahedral complexes can be rationalized in terms of the equations

$$\nu_A = 10Dq^{xy} - C$$

$$Dt = 4/35(10Dq^{xy} - \nu_E - C)$$

$$Dq^z = Dq^{xy} - {}^7/_4Dt$$

where C is the interelectronic repulsion term (insensitive to ligating atoms and usually taken as having a value of 3800 cm^{-1}) and where Dt is a measure of the splitting of the T_{1g} state (O_h symmetry) into its two components, ν_E ($^1E^a_g \leftarrow {}^1A_{1g}$) and ν_A ($^1A_{2g} \leftarrow {}^1A_{1g}$), on lowering the symmetry to D_{4h}. Dq^{xy} and Dq^z are the field strengths of the in-plane and out-of-plane ligands, respectively. The spectra of the dichloro and dibromo complexes show one band (ν_E) near 16.0 kK with the ν_A band partially obscured by the onset of charge-transfer absorptions. Assuming values[11,12] for $Dq^z(Cl^-)$ and $Dq^z(Br^-)$ of 1460 and 1277 cm^{-1}, respectively, the values of Dq^{xy} can be calculated from the equations given above (2640 cm^{-1} for the dichloro derivative and 2663 cm^{-1} for the dibromo derivative). These values are consistent with the observation that Dq^{xy} varies in an inverse manner with Dq^z.[11,12] The consistency of these values can be estimated by comparing the value of ν_A as calculated from ν_E, Dq^z, and C with the observed value of ν_A for each complex. The values calculated are 22.6 and 22.8 kK for the chloro and bromo derivatives, in reasonable agreement with the position of shoulders near 23.0 kK observed in their spectra. The calculated values for Dt are 674 cm^{-1} (Cl$^-$) and 792 cm^{-1} (Br$^-$).

The spectrum of the dinitro complex shows only a shoulder at ~22.0 kK on the edge of intense charge-transfer bands. Since Dq^z (NO$_2^-$) is greater than Dq^{xy} ([14]-tetraeneN$_4$), the parameter Dt will be negative and the ν_E band will appear at higher energy than ν_A. Thus the shoulder near 22.0 kK probably represents the ν_A band of the dinitro complex, a conclusion supported by the fact that this agrees with the position of ν_A for the dihalo complexes. Presumably the ν_E band for the NO$_2^-$ complex is masked by the onset of charge-transfer absorptions.

Previous workers[11,12] have shown that the field strengths of macrocyclic ligands increase as their extent of unsaturation increases. Thus, CR and Me$_4$[14]1,3,8,10-tetraeneN$_4$, being highly unsaturated, have the highest values of Dq^{xy} (~2800 cm^{-1}) while the fully saturated ligands, Me$_6$[14]aneN$_4$ and Me$_2$[14]aneN$_4$, have lower values (~2500 cm^{-1}). The values of Dq^{xy} and Dt calculated here for the Me$_6$[14]1,4,8,11-tetraeneN$_4$ ligand (~2640 cm^{-1}) suggest that it is of comparable strength to the ligands Me$_6$[14]4,11-dieneN$_4$ (Dq^{xy} = 2640, Dt = 674 cm^{-1}) and Me$_2$[14]1,3-dieneN$_4$ (Dq^{xy} = 2580, Dt = 640 cm^{-1}) containing two isolated imine functions and a single α-diimine function, respectively, but less than that found for Me$_4$[14]1,3,8,10-tetraeneN$_4$ containing two α-diimine groups.[11] The values of Dq^{xy} and Dt used in the comparison above were all calculated for the respective dichloro complex and a value of Dq^z = 1460 was assumed in each case. Such an assumption automatically restricts the true variation in values of Dq^{xy} since both values are intimately

related. Thus as Dq^{xy} increases with increasing degree of unsaturation, the value of $Dq^z(Cl^-)$ will decrease, often significantly. The only accurate means of determining Dq^{xy} and hence Dq^z is to have both the ν_E and ν_A bands clearly resolved in the spectrum of each complex.

With this restriction in mind the results suggest that replacement of amines by imines increases the ligand field strength, at constant ring size, only when the first one or two replacements are made. This restriction does not apply to α-diimines or conjugated imine systems in related ligand structures. This latter result is parallel to the behavior of unsaturated ligands with the isoelectronic low-spin iron(II) complexes. However, the greater interaction of bis-α-diimines with iron(II) is usually attributed to back-bonding,[6] a factor expected to be much less important in the case of trivalent cobalt.

Experimental Section

Physical Measurements. Infrared spectra were obtained on a Perkin-Elmer Model 457 recording spectrophotometer using Nujol mulls and polystyrene as a calibrant. Visible, near-infrared, and ultraviolet spectra were obtained with a Cary Model 14 recording spectrophotometer. Spectra of solid samples were obtained with Nujol mulls impregnated on filter paper. Magnetic susceptibilities of solid samples were determined at room temperature by the Faraday method on a system equipped with a Cahn Electrobalance. Mercury(II) tetrathiocyanatocobaltate(II) was used as a calibrant and diamagnetic corrections were applied to all measurements. The diamagnetic correction for the ligand Me$_6$[14]1,4,8,11-tetraeneN$_4$ was calculated to be 210 × 10^{-6} g/atom. Solution conductivities were measured at 25°C and 1000 Hz on approximately 10^{-3} M solutions using an Industrial Instruments RC16B conductivity bridge. EPR spectra were obtained on a Varian Associates X-band dual cavity spectrometer, Model No. V4500-10A. The solutions were degassed and then frozen at liquid nitrogen temperature. The NMR spectra were recorded in dimethyl-d_6 sulfoxide using tetramethylsilane as an internal refrence on a JEOL 100-MHz spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc. and Chemalytics, Inc.

Materials. All materials were of reagent grade and used without further purification. Organic solvents were of reagent grade and dried for several weeks with molecular sieves before distillation and/or deoxygenation.

Preparation of Me$_6$[14]4,11-dieneN$_4$·2HSO$_3$CF$_3$. Twenty grams (0.33 mol) of 1,2-diaminoethane was added to 500 ml of methanol in a 1-l. Erlenmeyer flask. Fifty grams (0.33 mol) of trifluoromethanesulfonic acid from a freshly opened glass ampule were added slowly from a dropping funnel (*Caution!* This acid reacts violently with all solvents, with the exception of acetonitrile) over a period of 1 hr. The solution was stirred vigorously during the addition of the acid. The reaction mixture was taken down to dryness with a rotary evaporator and the white product of 1,2-diaminoethane hydrotrifluoromethanesulfonate was further dried in vacuo over P$_4$O$_{10}$. This product was dissolved in 300 ml of acetone and the solution was refluxed for 1.5 to 2 hr before cooling to room temperature. A small amount of a white precipitate may be visible in the red solution. Anhydrous diethyl ether was added with stirring to precipitate the product which was removed by filtration. Initial addition of two much ether tends to produce an oil which can be dispersed by addition of small amounts of tetrahydrofuran. More product was obtained from the filtrate by alternate addition of ether and tetrahydrofuran. The acetone–ether–tetrahydrofuran mixture upon reaching 1 l. in volume was reduced to approximately 200 ml and treated as above to yield more product. This process was repeated several times. The combined product was stirred in a slurry of tetrahydrofuran to remove remnants of the oil, filtered, washed with tetrahydrofuran, and dried in vacuo over P$_4$O$_{10}$: yield, 60–70 g; ir 3150 (N–H), 1660 (C═N), 1540 (NH$_2^+$), 1250, 1149, 1041, 641 cm^{-1} (SO$_3$CF$_3^-$). Anal. Calcd for C$_{18}$H$_{34}$N$_4$S$_2$O$_6$F$_6$: C, 37.23; H, 5.86; N, 9.65; S, 11.05. Found: C, 37.33; H, 5.80; N, 9.41; S, 11.00.

[Fe(Me$_6$[14]4,11-dieneN$_4$)(CH$_3$CN)$_2$](SO$_3$CF$_3$)$_2$. Thirty grams (0.2 mol) of trifluoromethanesulfonic acid from a freshly opened glass ampule was added slowly to 200 ml of dry degassed acetonitrile. This solution was transferred to a screw cap bottle and further deoxygenated by flushing with dry nitrogen. The solution was taken into a nitrogen

atmosphere glove box and transferred to a 1-l. Erlenmeyer flask. Finely divided iron powder, 6 g (slightly in excess of 0.1 mol), was added and the iron powder was agitated by activating the stirring mechanism of a hot stir plate. The solution was warmed gently and the vigorous reaction was allowed to continue for a total of 24 hr. A glass filter funnel, containing a small watch glass, was used as a crude condensor. The mixture was kept in a gentle state of reflux by periodic warming (the reaction is exothermic). The resultant pale yellow solution of [Fe(CH₃CN)₆](SO₃CF₃)₂ was filtered into a 1-l. vacuum flask through filter paper to remove the excess iron powder. Fifty-eight grams (0.1 mol) of Me₆[14]4,11-dieneN₄·2HSO₃CF₃ was added with stirring, followed by 50 ml of dry degassed triethylamine. The volume of the deep red-purple solution was reduced to approximately 100 ml in vacuo and the pale pink material that separated was removed by filtration, washed with a 50:50 mixture of dry acetonitrile–ether and dried. The product was removed from the glove box and further dried in vacuo over P₄O₁₀: yield, 50 g; ir 3225 (N–H), 1645 (C=N), 1265, 1149, 1030, 641 cm⁻¹ (SO₃CF₃⁻). The reaction can be performed wholly on the bench top under nitrogen, but yields are generally smaller because of difficulties in filtration and solution transfers. Anal. Calcd for FeC₂₂H₃₈N₆S₂O₆F₆: C, 36.88; H, 5.31; N, 11.73; S, 8.94. Found: C, 36.91; H, 5.27; N, 11.65; S, 8.90.

[Fe(Me₆[14]1,4,8,11-tetraeneN₄)(CH₃CN)₂](PF₆)₂. Twenty grams of [Fe(Me₆[14]4,11-dieneN₄)(CH₃CN)₂](SO₃CF₃)₂ was dissolved in 300 ml of acetonitrile and acidified with 5 ml of trifluoromethanesulfonic acid and the solution was aerated for approximately 24 hr. The deep red solution was filtered and 200 ml of ethanol saturated with ammonium hexafluorophosphate was added to precipitate the crude product, which was recrystallized several times from acetonitrile by addition of alcoholic ammonium hexafluorophosphate. The red crystalline complex was dried under reduced pressure. Since this oxidative dehydrogenation reaction produces, in turn, iron complexes containing a trien, the desired tetraene, and a rearranged tetraene macrocycle,¹ the solution was monitored periodically by examining the infrared spectrum (to check for unwanted N–H absorptions) and visible spectral properties (to check for the rearranged tetraene complex) of small samples isolated as the PF₆⁻ salt: yield, 13 g; ir 1660 and 1645 (C=N), 830 and 655 cm⁻¹ (PF₆⁻). Anal. Calcd for FeC₂₀H₃₄N₆P₂F₁₂: C, 34.10; H, 4.83; N, 11.93. Found: C, 34.21; H, 4.80; N, 11.91.

Me₆[14]2,4,9,10-tetraeneN₄. The free ligand was removed from [Fe(Me₆[14]1,4,8,11-tetraeneN₄)(CH₃CN)₂](PF₆)₂ with 1,10-phenanthroline after the method of Goedken who used the analogous iron perchlorate complex.¹ Sixteen grams (0.022 mol) of the iron complex and 12.08 g (0.067 mol) of 1,10-phenanthroline were used: yield, 3 g; mp 147°C dec; mol wt. from mass spectrum, (m/e) 276, peak at m/e 261 in mass spectrum corresponds to the loss of one methyl group. Anal. Calcd for C₁₆H₂₈N₄: C, 69.50; H, 10.23; N, 20.27. Found: C, 69.63; H, 10.33; N, 20.01.

[Co(Me₆[14]1,4,8,11-tetraeneN₄)ClO₄]ClO₄. A solution of 2.76 g (0.01 mol) of the free ligand, Me₆[14]2,4,9,11-tetraeneN₄, in absolute ethanol was added dropwise with stirring to a solution of 4 g (>0.01 mol) of cobalt perchlorate hexahydrate dissolved in 80 ml of absolute ethanol and 30 ml of triethyl orthoformate. The addition was performed under a stream of dry nitrogen. The color of the solution changed from pink to yellow as the macrocyclic cobalt(II) complex precipitated. The solution was stoppered and chilled in a refrigerator for several hours. The yellow microcrystalline compound was filtered from the solution, washed several times with an ethanol–ether mixture, and dried in vacuo over P₄O₁₀: yield, 5 g. Anal. Calcd for CoC₁₆H₂₈N₄Cl₂O₈: C, 35.96; H, 5.29; N, 10.49; Cl, 13.27. Found: C, 35.88; H, 5.20; N, 10.60; Cl, 13.34.

[Co(Me₆[14]1,4,8,11-tetraeneN₄)H₂O](ClO₄)₂. This complex was obtained as a brown crystalline material upon recrystallizing the perchlorato–perchlorate complex from water. Anal. Calcd for CoC₁₆H₃₀N₄Cl₂O₉: C, 34.79; H, 5.44; N, 10.15; Cl, 12.85. Found: C, 34.86; H, 5.59; N, 10.00; Cl, 12.05.

[Co(Me₆[14]1,4,8,11-tetraeneN₄)CH₃CN](ClO₄)₂. Yellow needles of this complex were obtained by addition of ether to a 50:50 ethanol–acetonitrile solution of the perchlorato–perchlorate complex. The solution was flushed with nitrogen, stoppered, and chilled overnight. The yellow crystals were removed by filtration, washed with a small amount of cold ethanol, and dried in air. Anal. Calcd for CoC₁₈H₃₁N₅Cl₂O₈: C, 37.58; H, 5.39; N, 12.18; Cl, 12.33. Found: C, 37.62; H, 5.41; N, 12.30; Cl, 12.20.

[Co(Me₆[14]1,4,8,11-tetraeneN₄)X]ClO₄, (X = Cl, Br). Addition

of lithium chloride (or LiBr) in methanol to [Co(Me₆[14]1,4,8,-11-tetraeneN₄)ClO₄]ClO₄ dissolved in the minimum amount of ethanol produced upon chilling under a nitrogen atmosphere a brown product. This was filtered, washed with ethanol, and dried in vacuo. Anal. Calcd for CoC₁₆H₂₈N₄Cl₂O₄: C, 40.89; H, 5.96; N, 11.91; Cl, 15.09. Found: C, 40.96; H, 6.01; N, 11.87; Cl, 15.12. Anal. Calcd for CoC₁₆H₂₈N₄BrClO₄: C, 37.35; H, 5.44; N, 10.88; Br, 15.53. Found: C, 37.40; H, 5.39; N, 10.95; Br, 15.40.

[Co(Me₆[14]1,4,8,11-tetraeneN₄)X₂]ClO₄ (X = Cl, Br). One gram of [Co(Me₆[14]1,4,8,11-tetraeneN₄)ClO₄]ClO₄ was dissolved in 10 ml of ethanol and the solution was acidified with a few drops of aqueous hydrochloric acid (or HBr). The solution was aerated for 24 hr, allowing the solution to evaporate to a few milliliters, and the product was removed by filtration. Small blue-green needles of the complex formed on recrystallization from absolute ethanol, yield, 0.8 g (X = Cl) or 1.0 g (X = Br). Anal. Calcd for CoC₁₆H₂₈N₄Cl₃O₄: C, 38.00; H, 5.54; N, 11.08; Cl, 21.05. Found: C, 38.08; H, 5.50; N, 11.45; Cl, 20.91.

Anal. Calcd for CoC₁₆H₂₈N₄Br₂ClO₄: C, 32.31; H, 4.71; N, 9.42; Br, 26.90. Found: C, 32.72; H, 4.68; N, 9.25; Br, 26.70.

[Co(Me₆[14]1,4,8,11-tetraeneN₄)(CH₃CN)₂](ClO₄)₃. This complex was prepared by the same method as that used for the chloro complex but using acetonitrile as solvent and perchloric acid instead of hydrochloric acid. The complex was also prepared from [Co(Me₆-[14]1,4,8,11-tetraeneN₄)X₂]ClO₄, X = Cl⁻ and Br⁻, in acetonitrile by addition of anhydrous silver perchlorate in a one-to-two molar ratio. The solution was stirred for several hours and filtered to remove the precipitated silver halide, and the complex was isolated by reduction of the volume. The complex was obtained as orange crystals upon recrystallization from the minimum amount of dry acetonitrile. The crystals were washed with alcohol and dried in vacuo. Anal. Calcd for CoC₂₀H₃₄N₆Cl₃O₁₂: C, 33.55; H, 4.75; N, 11.74; Cl, 14.86. Found: C, 33.54; H, 4.42; N, 11.51; Cl, 14.85.

[Co(Me₆[14]1,4,8,11-tetraeneN₄)(NO₂)₂]ClO₄. An aqueous solution of sodium nitrite was added to the dibromo or dichloro derivative in methanol. The color of the solution changed from green to yellow and the product precipitated. This was collected by filtration, washed with a small amount of cold water, and dried in vacuo. Anal. Calcd for CoC₁₆H₂₈N₆ClO₈: C, 36.47; H, 5.37; N, 15.95; Cl, 6.73. Found: C, 36.41; H, 5.31; N, 16.02; Cl, 6.53.

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Single Crystal Electronic Spectra and Ligand Field Parameters of Some Nickel(II) Amine–Isothiocyanato and Amine–Nitrito Complexes

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The single crystal linearly polarized electronic spectra of tetragonal $Ni(en)_2(NCS)_2$ and $Ni(en)_2(NO_2)_2$ over the 8000–30000 cm^{-1} range have been reported and assigned. Ligand field parameters, Dq, Ds, and Dt, and angular overlap parameters, e_σ' and e_π' were derived from the assigned d–d spectra. These parameters have been compared with those of the respective tetragonal amine nickel complexes with known structure whose spectra were reliably assigned. The strong dependence of Dq on the metal–donor distance has been found for en and amine nickel complexes. The possibility of transferring the e_σ' and e_π' parameters of the donor atoms, corrected for the appropriate distance, is also discussed.

Introduction

The electronic spectra of tetragonal metal complexes have been extensively studied[1] largely because the number of ligand field parameters required by symmetry for the nonadditivity model corresponds to the number of independent monoelectronic d–d transitions,[2] as in the case of cubic complexes. Particular attention has been devoted to nickel(II) complexes, which have an orbitally nondegenerate ground state and show spectra with at least three spin-allowed d–d bands.[3] These spectra, however, often revealed small splittings of the transitions of the parent octahedral symmetry[1,4] thus providing the best justification for the rule of the average environment.[5] Even single crystal polarized electronic spectra often failed to show the tetragonal components well resolved.[6–9] For instance the spectra of $Ni(NH_3)_4(NCS)_2$ were practically unpolarized, while those of $Ni(NH_3)_4(NO_2)_2$ did show some polarizations,[9] but the splittings were evaluated from the maxima of broad bands recorded at room temperature.

In the last few years there has been a revival of ligand field calculations for low-symmetry complexes,[9–13] and again tetragonal nickel complexes have been the subject of several studies in order to check the validity of ligand field parameterizations. In particular the possibility of transferring the ligand field parameters in the additivity scheme has been investigated.[10] In this scheme, the number of parameters required to fit the experimental data is larger than the number of independent d–d transitions so that significant values of the parameters cannot be obtained from the electronic spectra. The angular overlap model[14] (AOM), however, has been

shown[10,15–17] to be quite promising in overcoming this problem because it seems to have a more sound physical basis than conventional crystal field models and the values of some parameters can, in principle, be transferred from other similar complexes. It seems necessary therefore to study sets of closely related chromophores which can allow the determination of significant values of the AOM parameters in order to check the validity of the basic assumptions of the model.

With these considerations in mind we have looked for tetragonal nickel(II) amine complexes with the aim of determining the dependence of the best fitting angular overlap parameters on the metal–nitrogen distances. Such a dependence has been compared with that which can be calculated through the diatomic nickel–nitrogen overlap. The choice of amine ligands allows for the reasonable assumption[1,15] of the AOM–π bonding parameter, e_π', equal to zero for sp^3 nitrogen atoms. The complex $Ni(en)_2(NCS)_2$ (I), whose x-ray structure has been reported,[18] shows a large tetragonal splitting and appears to fit well the above requirements. We wish to report the single crystal electronic spectra of I, as well as those of $Ni(en)_2(NO_2)_2$[18] (II), for comparison purposes. Literature data on spectral assignments of complexes with known structure are also taken into consideration.

Experimental Section

Crystal Data. The x-ray crystal structure of $Ni(en)_2(NCS)_2$ (I) has been determined by Brown and Lingafelter.[18] The compound is monoclinic, space group $P2_1/a$, $Z = 2$, $a = 10.28$ Å, $b = 8.26$ Å, $c = 8.88$ Å, $\beta = 121°\ 3'$ with the nickel ion lying on a C_i site symmetry. The Ni–NCS distance is 2.15 Å, whereas the Ni–N in-plane distances