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Macrocycle-Promoted Oxygenation Reactions: Equatorial and Axial Ligand Effects

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Equilibrium data are reported for the complexation of dioxygen by the cobalt(II) complexes of 1,4,8,11-tetraazacyclotetradecane and 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene in the presence of various trans axial donors including pyridine, imidazole, ammonia, cyanide, and coordinated water. A switch in preferred stoichiometry from 2:1 to 1:1 occurs from the saturated to unsaturated systems. Data for these systems are compared with previously investigated systems, and the equilibria are explained in terms of ligand donor properties. Spectroscopic characterization of these oxygenated species and their reactivity are briefly reported.

Introduction

There has been intense interest during the past several years in the properties of metal–dioxygen adducts.[1-3] While a wide variety of transition-metal complexes are known to bind dioxygen,[9] interest has largely centered on iron[2,4] and analogous cobalt[1-3] complexes, the former being of foremost biological interest and the latter appearing to function as excellent general models for metal–dioxygen binding.[1]

It is now widely[1-4] but not universally[5] accepted, largely on the basis of cobalt complex work, that dioxygen adds to metals via an "internal redox" reaction, i.e.

$$\mathrm{LM}^{n+} + \mathrm{O}_2 \underset{}{\overset{K_1}{\rightleftharpoons}} \mathrm{LM}^{(n+1)+}\mathrm{O}_2^- \underset{K_2}{\overset{\mathrm{LM}}{\rightleftharpoons}} \mathrm{LM}^{(n+1)+}\mathrm{O}_2{}^{2-}\text{-}\mathrm{LM}^{(n+1)+}$$

in which the metal is formally oxidized and O_2 formally reduced.

Work from several laboratories, including those of Martell,[1] Basolo,[2] and others, have begun to clarify the structural and electronic effects which govern the position of equilibria K_1 and K_2, but much remains to be accomplished in this respect. To this end, we have begun a systematic study of the bonding of dioxygen by macrocyclic cobalt complexes.

While the potential of synthetic macrocyclic complexes for mimicking the biologically important porphyrin macrocycles has long been recognized,[6] few if any studies of macrocycle-promoted oxygenation reactions exist.[7] These ligands offer a number of advantages in mechanistic studies, including rigid stereochemical control, allowing individual parameterization of axial and equatorial ligand effects. Equatorial effects may be utilized to traverse a series of ligands from a fully saturated nitrogen donor (cyclam) to the fully unsaturated porphyrins and porphyrin analogues,[8] whereas axial effects may probe the sensitivity of oxygenation to direct differences in relative energy and occupancy of the d_{z^2} orbital with which O_2 combines.

The inert character of the equatorial ligand, with corresponding stereochemical control of ligand exchange, used to great advantage by Poon et al. in studies of Co(III) ligand exchange reactions, makes these systems ideal for investigating ligand-exchange reactions at an oxygenated metal center, as well as allowing simplified mechanistic studies of the conversion of CoO_2 to an irreversibly oxidized Co(III) complex. In order to carry out these mechanistic studies, good equilibrium data describing the oxygenated system must be available.

In the present paper, thermodynamic data are reported for the formation of oxygen adducts of cobalt promoted by 1,4,8,11-tetraazacyclotetradecane (abbreviated cyclam or (14)aneN_4) and 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (abbreviated Me_6(14)4,11-dieneN_4), a partially unsaturated analogue, which form two members of such a series.

Axial effects have been probed for the cyclam system utilizing H_2O, CN^-, imidazole, pyridine, and ammonia trans to coordinated O_2.

Experimental Section

Cyclam and Me_6(14)diene were obtained from Strem Chemicals, recrystallized from ethanol–water, and purity-checked by potentiometric titration. Spectrophotometric measurements were obtained on a Cary 14 spectrophotometer using matched quartz cells. Oxygenation equilibria were monitored using an oxygen-sensitive (polarographic) electrode (Yellow Springs Instrument Co.). Equilibria were characterized at a constant temperature of 25.0 ± 0.1 °C in the presence of 0.1 M KNO_3 as an electrolyte. In a typical experiment, ligand solution was air saturated, an initial instrument setting made, and a small known volume of air-saturated Co(II) solution added by syringe to the closed system. Typically 40 min was allowed to attain equilibrium (this time reflects the slow macrocycle complex formation with subsequent addition of O_2 being fast[1]). After the Co(II) macrocycle aquo complex had attained equilibrium with O_2, an aliquot of a stock solution of the trans axial ligand of interest was added by

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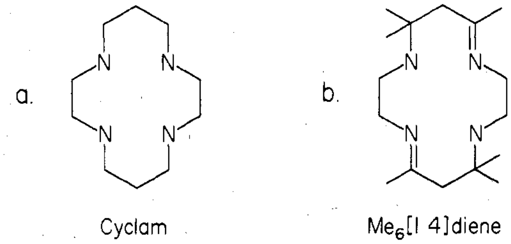

Figure 1. Structures of cyclam and Me_6(14)diene.

syringe. Although rapid decreases in O_2 pressure accompanied the ligand introduction, another 20–30 min was allowed to attain equilibrium. For each equilibrium constant reported at least four measurements were taken under each set of conditions, and conditions were varied to afford four concentrations of metal complex and two concentrations of O_2.

The validity of these equilibria was verified in several ways, including premixing of cobalt and the axial ligand (for pyridine and imidazole, the cobalt complex is not oxygen active) followed by addition of macrocycle. Alternatively, the Co(II) macrocycle complex was synthesized and isolated (for cyclam, great care must be taken to exclude traces of oxygen—prepurified N_2 is *not* sufficient). Isolation as the perchlorate salt is simplest[7] (note: the dry Co(II) cyclam perchlorate complex explodes violently on gentle heating). As a safety measure the chloro complex was generally substituted. Dissolution of the preformed macrocycle in O_2-saturated water results in almost immediate uptake of O_2 in quantitative agreement with results obtained by macrocycle formation in situ.

The complexes of [Co(cyclam)LO_2] and [Co(cyclam)L] were isolated as perchlorate salts by the method of Poon and Tobe.[7a] These materials were used to prepare μ-superoxo complexes, obtained by addition of solid peroxo complexes to cold dilute perchloric acid in the presence of a large excess of peroxodisulfate, giving a green solution which exhibited a standard[1] 15-line cobalt hyperfine spectrum: $A_{\mathrm{iso}} \approx 10$ G, $g_{\mathrm{iso}} = 2.002$ (for the aquo complex).

Analogous isolation of the Me_6(14)diene complexes was not feasible. In situ oxidation by peroxodisulfate resulted in a weak EPR signal at room temperature centered at ~2.0 G presumably due to the μ-superoxo species.

Electrochemical measurements were made on a Beckman electroscan 30, using a platinum working electrode and calomel reference electrode.

Data reduction for the binuclear systems follows directly from the O_2 uptake measurements. The change in % O_2 saturation can be converted to a concentration difference $\Delta(O_2)$ using published solubility values.[15] Since an oxygen originally consumed forms an O_2 adduct, $\Delta(O_2) = (O_2 \text{ complex})$. For a μ-peroxo adduct, $(M)_{\mathrm{tot}} = (ML) + 2(O_2 \text{ complex})$. Thus $(M)_{\mathrm{tot}} = 2(\Delta O_2) + (ML)$ and $\Delta(O_2)/(ML)^2(O_2)_{\mathrm{final}}$. The dependence of K_{O_2} on $(M)_{\mathrm{tot}}$ thus serves as evidence for 2:1 stoichiometry.

For nonaqueous mononuclear "superoxo" systems, this polarographic method is inapplicable. Such systems were therefore characterized spectroscopically. A solution of Me_6(14)4,11-dieneN_4 in a 1-cm spectral cell was equilibrated at 25.0 °C with O_2 of a known partial pressure. The cell was then sealed, so that the total concentration of O_2 remained constant throughout the experiments, and placed in a spectral Dewar. Spectra were obtained at room temperature, −78 °C, and −22 °C. The room-temperature spectrum was used to obtain extinction coefficients for the $Co^{II}L$ complex (these were checked with a nitrogen-saturated solution). The dry ice spectrum served as a limiting spectrum so that the O_2 complex could be evaluated directly. Spectra were monitored at 520 nm which appears to be a Co d–d band in these oxygen complexes.[20] This method of data analysis was checked using the Drago–Rose method[16,5] for several partial pressures. Effectively identical results were obtained in all cases except for $CoMe_6(14)dieneClO_4$ for which the "limiting spectrum" condition is apparently not met, even at $p(O_2) = 760$ mm, $T = -76$ °C.

Results and Discussion

Results of oxygenation equilibrium studies are summarized in Table I. In common with many nitrogen donors, the pink high-spin Co(II) macrocyclic complexes[21] react rapidly with O_2 to form a golden-brown species (the color is due to a low energy $O_2 \rightarrow$ Co CT band). As noted in the Introduction, multiple equilibria are possible

Table I. Equilibrium Data for O_2 Adduct Formation[a]

Macrocycle	Axial donor	$\log K_{O_2}$
Cyclam	H_2O	8.1 ± 0.1
Cyclam	Pyridine	9.2 ± 0.2
Cyclam	Imidazole	10.6 ± 0.2
Cyclam	NH_3	12.5 ± 0.5
Cyclam	CN^-	>13[b]
Me_6(14)diene	H_2O	5.6 ± 0.3

[a] 25.0 ± 0.1 °C, $\mu = 0.10$ M (KNO_3). [b] Too large to measure accurately.

$$ML + O_2 \overset{K_1}{\rightleftharpoons} MLO_2$$

$$MLO_2 + ML \overset{K_2}{\rightleftharpoons} MLO_2ML \xrightleftharpoons{K_3;\,H_2O} MLO_2OHML + H^+$$

involving initial complexation of oxygen in a formally "superoxo" complex, followed in some, but not all, cases by rapid "trapping" of the mononuclear dioxygen complex by free ML to give a binuclear formally μ-"peroxo" species. Given an appropriate cis geometry, a second μ-hydroxo bridge may form cis to bridging O_2. In such cases, the oxygenation and olation reactions are intimately linked and may be separated only in very favorable cases. The present complexes, which maintain obligatory trans geometry for the nonmacrocyclic ligands, effectively preclude this olation reaction and uniquely define the position of O_2 relative to the other ligands (a similar situation is obtained for Schiff's base systems,[2] but for aqueous polyamines,[1] nonequivalent positions are available; e.g., for cobalt triethylenetetramine O_2 may be trans to a primary or secondary amine). They thus offer a favorable system for examining axial and equatorial ligand effects. The complexation of O_2 by Co(cyclam) has been reported previously,[7a] the oxygenated species being of interest as a precursor to Co(III) complexes, but no equilibrium data were obtained. The position of overall equilibrium (K_1, K_2) depends markedly on the nature of these ligands, as demonstrated in Table I.

Trans axial ligands can stabilize dioxygen adducts both by σ donation[10] to the formally cobalt(III) center and by π donation to the O_2 π^* orbitals through metal d_{xz} and d_{yz} orbitals.[2] In the binuclear systems, the effect of π donation might be less marked than in the mononuclear cases previously characterized,[2] given the effectively filled O_2 π^* orbitals in formally peroxide O_2. The predominance of σ interactions may be noted in the correlation of pK and K_{O_2} for a number of systems.[10]

The total "donor ability" of the equatorial ligand is less easy to estimate. It is not clear that pKs offer a good estimate in this case, since the third and fourth pKs must necessarily be quite low (there simply being insufficient "room" for four protons within the ring). Nevertheless, in the absence of a better criterion, the stability of the μ-O_2-[Co(cyclam)H_2O]$_2$ complex may be compared with other monobridged species (only limited data are available at present for such species). Such a comparison is presented in Figure 2. In conjunction with axial ligation studies, it is interesting to note that the cobalt macrocycle complex is fully formed and has reached equilibrium with O_2, addition of the trans axial ligand (e.g., imidazole) results in an *immediate* drop in free O_2 concentration (i.e., less than 30 s is required to reach ~90% of the final reading). This rapid attenuation of the equilibrium implies a great measure of lability for ligand exchange at the formally "cobalt(III)" center. At present, almost nothing is known about ligand-exchange processes in cobalt–dioxygen species. Kinetic studies of these conversions are therefore under way.

Modification of the equatorial ligand results in a dramatic change in oxygen affinity. Substitution of cyclam by Me_6-

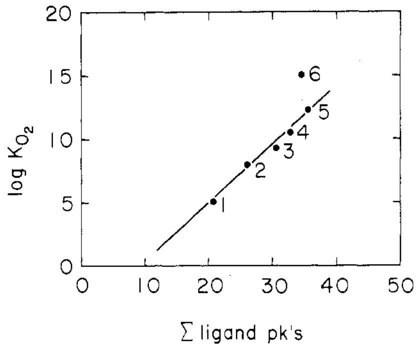

Figure 2. Plot of donor basicity ($\sum$pk) vs. log K_{O_2}: 1 = Me_6(14)diene, p*K* = 10.6, 10.1, <2 (this work); 2 = cyclam(H_2O), p*K* = 10.8 10.2, 3.7, 2.5 (this work); 3 = cyclam(py); 4 = cyclam(imid); 5 = cyclam(NH_3); 6 = tetraethylenepentamine.[10]

(14)diene decreases K_{O_2} by several orders of magnitude. This increasing oxidation in the macrocycle has several effects.[6,8] Increasing the equatorial field strength (i.e., greater tetragonal distortion) serves to lower d_{z^2} toward O_2 π^* and simultaneously decreases the oxidation potential for the Co(II) → Co(III) conversion.[11] Basolo has already noted that for an "internal redox" model, the stability of the complex should be proportional to the Co(II) → Co(III) potential and has demonstrated such a correlation for a wide variety of mononuclear dioxygen systems.[12] This concept has recently been extended with success to binuclear systems.[13] Although the validity of this concept has been questioned,[5] it serves to explain the present data well. As noted above, Busch has demonstrated that increasing oxidation of the macrocycle lowers the Co(II) → Co(III) oxidation potential (effectively making the Co(III) "softer"[14]). Thus as the relative stability of the Co(III) state decreases, the stability of the dioxygen adduct in which a formally Co(III) center is created also decreases. In the present case

$$E^\circ_{ox}(\mathrm{Co(cyclam)}) = -0.40\ \mathrm{V} \qquad \log K_{O_2}(\mathrm{cyclam}) = 8.1$$

$$E^\circ_{ox}(\mathrm{Me_6(14)diene}) = -0.33\ \mathrm{V} \qquad \log K_{O_2}(\mathrm{Me_6(14)diene}) = 5.6$$

Factors which control the equilibrium between mononuclear and binuclear oxygenated species are not well understood. For highly oxidized macrocycles (e.g., porphyrins) mononuclear complexes are stable at low temperatures,[2] while the reduced analogues studied here give EPR-quiet binuclear species. Thus as oxidation in the macrocycle increases, a switch from binuclear to mononuclear complexation may be anticipated but does not occur in aqueous solution for the Me_6(14)diene complex. Recent experiments[14,15] suggest that the solvent may play a critical role in influencing the relative positions of K_1 and K_2. We therefore examined the Me_6(14)diene system in DMF. At room temperature, no spectral change is observed on exposing a nitrogen-saturated solution to oxygen. On lowering the temperature (≤−10 °C), however, the light yellow Co(II) solutions became dark red when exposed to dioxygen. These species exhibit well-defined eight-line ESR spectra (A_{iso} ≈ 11 G) indicative of mononuclear "superoxo" adduct formation.[19] Thermodynamic data for several O_2 adducts [CoLL'O_2], L = Me_6(14)4,11-dieneN_4, L' = Br, ClO_4, pyridine, and imidazole, are collected in Table II. The observed stabilities generally parallel ligand basicity, although the correlation is not as strong as for the binuclear adducts. This probably reflects a decreased importance of π bonding in the binuclear systems in which the O_2 π^* orbitals are filled.[18] Further data will be required to attempt any separation of "σ" and "π" effects.

It is interesting to note that the "stoichiometry switch" from binuclear to mononuclear complexation occurs with relatively little change in electronic structure and is solvent dependent.

Table II. Equilibrium Constants for the Formation of [CoLL'O_2][a]

L'	K_{O_2},[b] M^{-1}	L'	K_{O_2},[b] M^{-1}
Cl^-	18.8	Pyridine	26.3
Br^-	21.0	Imidazole	36.1[c]
ClO_4^-	20.3		

[a] L = Me_6(14)4,11-dieneN_4. [b] K_{O_2} ≡ [CoLL'O_2]/[CoLL'][O_2]. [c] Using the more conventional designations, substituting $p(O_2)$ for [O_2] gives $K_{O_2} = 9 \times 10^{-3}$ mM^{-1} for the imidazole complex.

We thus expect that other oxidized macrocyclic cobalt complexes will react with O_2 to give mononuclear superoxo species. Preliminary results with TAAB indicate this indeed occurs, although quantitative data are not yet available. These systems thus offer the possibility of discerning what features (if any) particularly distinguish the binding of O_2 by metalloporphyrins.

Over a long period (>1 day) the peroxo species decay to produce inert Co(III) products. This decomposition may be markedly enhanced by addition of mineral acids (HX) to produce Co^{III}LX complexes. The synthetic utility of this decomposition was reported by Poon,[7] but the precise mechanism of the decomposition remains unknown.

It may be noted, by contrast, that analogous linear-chain amine–cobalt–dioxygen adducts decompose in strong acid to generate cobalt(II), O_2, and protonated ligand[1,3a] and are thus acid reversible. This pathway is not available to the macrocycle; a simple stepwise ligand dissociation is virtually precluded (an effect whimsically dubbed "multiple juxtapositional fixedness" by Busch[6]). The detailed mechanism for Co(III) macrocycle formation is under investigation and will be reported separately.

In summary, the binding of O_2 by 14-membered macrocycles has been studied as a function of axial and equatorial ligand composition. For a fully saturated macrocycle (14aneN_4) a strong correlation has been found between axial ligand basicity and oxygen affinity. On increasing oxidation in the macrocycle, oxygen affinity drops dramatically, and a change to 1:1 stoichiometry occurs. Preliminary experiments indicate that 1:1 adducts may be formed by a wide range of macrocycles. Experiments on the reaction chemistry of such systems are in progress.

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Registry No. [Co(cyclam)H_2O]$^{2+}$, 64784-52-7; [Co(cyclam)-pyridine]$^{2+}$, 64784-53-8; [Co(cyclam)imidazole]$^{2+}$, 64784-54-9; [Co(cyclam)NH_3]$^{2+}$, 64784-55-0; [Co(cyclam)CN]$^+$, 64784-56-1; [CoMe_6(14)diene(H_2O)]$^{2+}$, 61524-01-4; [CoMe_6(14)dieneCl]$^+$, 64784-61-8; [CoMe_6(14)dieneBr]$^+$, 64784-57-2; [CoMe_6(14)diene(ClO_4)]$^+$, 64784-58-3; [CoMe_6(14)diene(pyridine)]$^{2+}$, 64784-59-4; [CoMe_6(14)diene(imidazole)]$^{2+}$, 64784-60-7; O_2, 7782-44-7.

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(20) It should be noted that the position and intensity ($\epsilon \sim 750$ at 80 K) are not inconsistent with an MCCT assignment.
(21) The $[CoMe_6(14)diene]^{2+}$ complex is a yellow low-spin species before oxygenation.

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Crystal and Molecular Structure of Tris(ethylenediamine)nickel(II) Tetraphenylborate–Tris(dimethyl sulfoxide), $[Ni(NH_2CH_2CH_2NH_2)_3][B(C_6H_5)_4]_2 \cdot 3(CH_3)_2SO$. Factors Influencing the Ring Conformations in Tris(ethylenediamine) Metal Complexes

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The crystal structure of tris(ethylenediamine)nickel(II) tetraphenylborate–tris(dimethyl sulfoxide), $[Ni(en)_3][B(C_6H_5)_4]_2 \cdot 3(CH_3)_2SO$, has been determined by single-crystal x-ray diffraction techniques. Data complete to $2\theta = 45°$ (Mo $K\bar{\alpha}$ radiation) were collected with a Syntex $P\bar{1}$ automated diffractometer. After least-squares refinement using anisotropic thermal parameters only for the cation and solvates, the conventional R index converged at 0.092. The purple crystals form in the monoclinic space group $P2_1/a$ with $a = 23.51$ (4) Å, $b = 30.14$ (7) Å, $c = 9.910$ (8) Å, $\beta = 120.2$ (1)°, and $Z = 4$. The divalent nickel ion is hexacoordinated and exhibits the usual distortion from octahedral symmetry found in tris(ethylenediamine) complexes with an average twist angle of 50.7 ± 1.5° between the trigonal planes formed by the coordinated nitrogen atoms. The centric cell contains complex cations in both the $\Delta\lambda\lambda\delta$ and $\Lambda\delta\delta\lambda$ configurations. The tetraphenylborate anions are distorted in that the boron centers are found to deviate as much as 0.24 Å from atomic planes defined by the phenyl rings. A limited network of hydrogen bonding exists between the cation and the dimethyl sulfoxide solvate molecules. Inversion disorder at one of the sulfur atoms is observed. The $\Lambda\delta\delta\lambda$ mixed ring conformation found for the tris(ethylenediamine)nickel(II) complex in this structure confirms a previous spectroscopic characterization of the compound. An extensive analysis of other crystal structures of $[M(en)_3]^{m+}$ complexes is presented. The ring geometry observed in each compound is correlated with such parameters as intermolecular hydrogen bonding and anion size. It is suggested that the $\Lambda\delta\delta\lambda$ configuration is the lowest energy isomer for these complex cations.

Introduction

Five-membered ethylenediamine chelate rings have two possible conformations known as δ and λ. When three such chelates form a tris complex, the metal center is chiral and will have two possible enantiomeric configurations known as Δ and Λ. Combining all the structural possibilities there results, even for the simple, symmetrical chelate ethylenediamine (en), a total of eight isomers:[2] $\Lambda\delta\delta\delta$, $\Lambda\delta\delta\lambda$, $\Lambda\delta\lambda\lambda$, $\Lambda\lambda\lambda\lambda$, $\Delta\delta\delta\delta$, $\Delta\delta\delta\lambda$, $\Delta\delta\lambda\lambda$, $\Delta\lambda\lambda\lambda$. In a nonchiral medium the discussion can be limited to the first four of these isomers with the realization that all arguments apply equally well to their appropriate mirror images.

Examples of each isomer have been reported as a result of x-ray crystallographic investigations. In agreement with theoretical energy calculations,[3] the $\Lambda\delta\delta\delta$ isomer has been found to be the most abundant. More recently, however, it has been argued that hydrogen bonding[4] or crystal packing forces[5] may cause any of the four isomers to be the most stable. It has also been argued that entropy effects would cause the $\Lambda\delta\delta\lambda$ isomer to have the lowest free energy.[6] In order to test this latter contention it would be necessary to determine the structure of a $[M(en)_3]^{m+}$ complex ion in the presence of a large, nonhydrogen bonding counterion. The tetraphenylborate anion fulfills these criteria, and infrared spectroscopy had indicated that the ring conformations in $[Ni(en)_3][B(C_6H_5)_4]_2$ were mixed.[7] We have therefore determined the structure of this compound by x-ray methods and in this paper we report the results of that investigation.

Experimental Section

Preparation of $[Ni(en)_3][B(C_6H_5)_4]_2$. Tris(ethylenediamine)nickel(II) chloride, $[Ni(en)_3]Cl_2$, was prepared by adding excess ethylenediamine to an aqueous solution of nickel chloride. When the product precipitated from solution upon addition of acetone, it was immediately filtered and dried. The $B(C_6H_5)_4^-$ salt was prepared by dissolving $[Ni(en)_3]Cl_2$ in H_2O and adding a $NaB(C_6H_5)_4$ solution. The product precipitated as a light purple powder which was filtered, washed, and dried. Chemical analyses were in close agreement with the expected values and the vibrational spectrum of $[Ni(en)_3][B(C_6H_5)_4]_2$ has been well characterized.[7] Electronic spectra obtained on Cary Model 14 showed absorption maxima for $[Ni(en)_3][B(C_6H_5)_4]_2$ in Me_2SO at 1.87, 1.27, and 1.14 μm^{-1}. $[Ni(en)_3]Cl_2$ in water gave bands at 1.85, 1.28, and 1.13 μm^{-1}. The literature values for solid $[Ni(en)_3](ClO_4)$ are 1.83, 1.27, and 1.12 μm^{-1}.[8]

Collection and Reduction of X-Ray Intensity Data Long, dark purple crystals of $[Ni(en)_3][B(C_6H_5)_4]_2 \cdot 3(CH_3)_2SO$ were obtained after a second slow recrystallization from a dimethyl sulfoxide solution at 23 °C. A well-formed crystal of original dimensions 0.06 × 0.21 × 3.25 mm was selected under a microscope and cleaved at both ends with a blade to give final dimensions of 0.06 × 0.21 × 0.33 mm. The six-sided, rectangular crystal was cemented using epoxy resin to the end of glass filament in such a way that the long edges of the crystal were nearly parallel to the filament.

A Syntex four-circle computer-controlled diffractometer with graphite monochromatized Mo $K\bar{\alpha}$ radiation ($K\alpha_1$, λ 0.70926 Å; $K\alpha_2$, λ 0.71354 Å) and with a pulse height analyzer was used for preliminary experiments and for the measurement of diffraction intensities. The cell constants and their standard deviations were determined by a least-squares treatment of the angular coordinates of 15 independent reflections with 2θ values up to 21°. The cell constants at 20 °C for $[Ni(en)_3][B(C_6H_5)_4]_2 \cdot 3(CH_3)_2SO$ are $a = 23.51$ (4) Å, $b = 30.14$ (7) Å, $c = 9.910$ (8) Å, $\beta = 120.2$ (1)°, and $V = 6070$ (20) Å^3. The compound crystallizes in a monoclinic lattice with $P2_1/a$ symmetry and four molecules per unit cell. The calculated density $\rho_c = 1.216$ (7) g cm^{-3} is in good agreement with the density measured by flotation in a carbon tetrachloride–hexane solution of $\rho_m = 1.215$ (2) g cm^{-3}.

Diffraction intensities were collected by the θ–2θ scan technique at a scan rate varying from 2°/min in 2θ to 24°/min. A time equal to half the scan time for each reflection was spent counting the

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