ogous terms for the ion-paired species. This equation can be rewritten in terms of the ion-pair formation constant, K_0, as

$$\Delta\nu_{obsd} = \Delta\nu_0 + \left(\frac{K_0[\mathrm{BF_4^-}]}{K_0[\mathrm{BF_4^-}] + 1}\right)\nu' \qquad (5)$$

where ν' is defined as $\Delta\nu' - \Delta\nu_0$. On this basis an explanation for the dependence of $\Delta\nu_{obsd}$ on the free ligand concentration can be made in terms of a change in the solution dielectric constant which in turn changes the value of K_0. Also, model calculations assuming that $\Delta\nu_0 = 400$ Hz and $\nu' = 150$ Hz at 25° show that values of $K_0 \approx 1$ and a heat of formation for the ion pair, ΔH, of ~ -3 kcal/mol or greater produce nonlinearity in a plot of $\Delta\nu_{obsd}$ vs. $1/T$ of the type observed in Figure 2. It is very difficult to estimate values for K_0 and ΔH in the acetone–nitromethane solutions but in view of previous studies[19,20] values of $K_0 \approx 1$ and $\Delta H \approx -3$ kcal/mol do not appear unreasonable.

Thus, it seems that an ion-pairing model can account for the changes in $\Delta\nu_{obsd}$ either by assuming that a dipolar contribution to the isotropic shift is induced in the ion pair or by assuming that the hyperfine coupling constant of the complex is altered in the ion pair.

The ion-pair model can also be used to explain the variation in $1/T_{2M}$ as the composition of the solution is changed in that ion pairing might be expected to alter the electron spin relaxation time. Model calculations with $\Delta H \approx -3$ kcal/mol and $K_0 \approx 1$ and assuming values of the line widths due to the free complex and the ion-paired complex at 25° to be 23 and 33 Hz, respectively, show that a plot of log $(\Delta\nu_{1/2})_{obsd}$ vs. $1/T$ gives good linearity in the temperature region from $10^3/T = 2.5$–5.0. This assumes that $(\Delta\nu_{1/2})_{obsd}$ is given by an expression analogous to eq 5. Thus these calculations support the assumption that $(\Delta\nu_{1/2})_M$ is linear

(19) R. G. Pearson and P. Ellgen, *Inorg. Chem.*, **6**, 1379 (1967).
(20) A. Kowalak, K. Kustin, R. F. Pasternack, and S. Pertrucci, *J. Amer. Chem. Soc.*, **89**, 3126 (1967).

in the temperature range covered in this study. This assumption is further supported by the excellent agreement obtained between rates from the line shape technique and the two line width methods.

Finally, it is possible that the observed dependence of $\Delta\nu$ and $1/T_{2M}$ on the free ligand concentration may result from the presence of small amounts of nonoctahedral species produced by the insertion of nitromethane or tetrafluoroborate into the coordination sphere. However, in view of the results from the spectral studies and the fact that the rates obtained from all solutions agree very well at all temperatures, large amounts of such species (>3–4%) cannot be present. Also the fact that the plot of ln (k/T) vs. $1/T$ shows no apparent curvature over a 110° temperature range is not consistent with any significant decomposition of the octahedral complex. On the other hand, Frankel[3] has observed that the activation enthalpies for exchange of DMSO with $\mathrm{Ni(DMSO)_6^{2+}}$ and $\mathrm{Co(DMSO)_6^{2+}}$ are the same in methylene chloride and nitromethane. He has interpreted this to mean that ion pairing does not significantly affect the $\Delta H^{\ddagger}$ for ligand exchange. On this basis the linear activation enthalpy plot obtained in this work is not inconsistent with the ion-pairing model discussed above.

Further studies on similar systems are now in progress to explore the concentration dependence of $\Delta\nu$ and $1/T_{2M}$ and to determine the significance of the donor strength of the ligand and the importance of solvation energies as contributions to the enthalpy of activation for exchange.

Low-Spin Five-Coordinate Nickel(II) Complexes Containing a Macrocyclic Tetradentate Amine

By E. KENT BAREFIELD and DARYLE H. BUSCH*

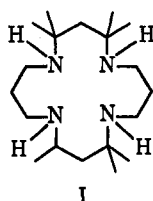Catalytic reduction of the complex (II) prepared by condensation of $\mathrm{Ni(tm)_3(ClO_4)_2}$ (tm $\equiv$ trimethylenediamine) and acetone leads to a low-spin five-coordinate complex containing ligand I and coordinated perchlorate. Nmr evidence indicates that only one ligand stereoisomer is formed in the reduction. Other low-spin five-coordinate complexes with bonded $\mathrm{Cl^-}$, $\mathrm{Br^-}$, and $\mathrm{I^-}$ have been prepared. These represent new examples of low-spin five-coordinate nickel(II) complexes, which are rather rare for ligands containing more than one nitrogen donor. Others are discussed. In donor solvents the equilibrium $\mathrm{NiL(solvent)^{2+}} \rightleftharpoons \mathrm{Ni(L)^{2+}} +$ solvent occurs and the concentration of the five-coordinate species is proportional to the donor strength of the solvent, DMSO $>$ DMF $>$ $\mathrm{CH_3CN}$ $\sim$ $\mathrm{H_2O}$ $>$ $\mathrm{CH_3NO_2}$. These species are also low spin in electronic configuration.
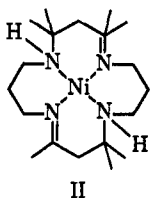
Introduction

Since the first report of five-coordinate nickel(II) in complex molecules there has been a steady increase in the number of established examples. Five-coordinate

nickel(II) complexes approximate either of two distinct geometrical forms, square pyramidal or trigonal bipyramidal. Within these two geometrical types the metal ion may be either high spin ($S = 1$) or low spin ($S = 0$).

Examples of each of the four forms are known.[1] Generally, examples of each of the forms have been prepared with a large number of ligand types. However, low-spin complexes of either geometry with ligands containing more than one nitrogen donor are rather scarce and only a few examples have been reported. While continuing our investigations on macrocyclic complexes derived from acetone and amines,[2,3] we have determined that the Ni(II) complex containing the ligand shown in structure I forms low-spin five-coordinate complexes of stoichiometry [Ni(I)X]X with a number of donor ions. Complexes containing ligands of this

I

homologous series are prepared by reduction of the parent diimine complex obtained by the condensation of acetone with a diamine in the presence of nickel(II) salts.[4] The initial preparation of the parent diene for this complex from acetone and trimethylenediamine was reported by Curtis in 1964.[5] At that time the stereochemistry of the parent diene complex was not known. Our recent investigations have shown[3] that the stereochemical disposition of the two imines is trans, structure II. Reductions of analogous complexes

II

prepared from ethylenediamine and acetone and characterization of the reduced products have been reported;[2,4] however, the reduction of complex II has only been briefly mentioned[4] and no characterization of the products has appeared.

We wish now to report the catalytic reduction of compound II and the preparation of some low-spin five-coordinate complexes containing the fully reduced tetramine ligand.

Experimental Section

2,4,4,10,12,12-Hexamethyl-1,5,9,13-tetraazacyclohexadeca-1,9-dienenickel(II) Perchlorate, [Ni(*trans*[16]diene)](ClO₄)₂.—This complex was prepared by the procedure given by Curtis.[5]

Reduction of [Ni(*trans*[16]diene)](ClO₄)₂.—Six grams of [Ni(*trans*[16]diene)](ClO₄)₂ was dissolved in 2500 ml of reagent grade methanol and was then placed in a high-pressure hydrogenation apparatus with about 0.15 g of platinum oxide (Matheson Coleman and Bell, Adams catalyst). The apparatus was charged with hydrogen at 500 psi pressure and was shaken for 20 hr.

After this time the solution was filtered and evaporated on a rotary evaporator. About 5.6 g of red-violet material (fraction 1) was obtained when the volume was reduced to about 150 ml. Evaporation of the remaining solution gave about 0.4 g of impure material. This may be purified by recrystallization from fresh methanol (fraction 2). Both fractions were recrystallized from water. *Anal.* Calcd for NiC₁₈H₄₀N₄(ClO₄)₂: C, 37.91; H, 7.02; N, 9.83. Found: C, 38.25; H, 6.64; N, 9.72. Smaller scale reductions were successfully performed at 50–60 psi.

[Ni(*trans*[16]tetramine)Cl]Cl·H₂O and [Ni(*trans*[16]tetramine)-Br]Br·2H₂O.—Each of these complexes was obtained by passing solutions (0.2 g in 50 ml of water) of the perchlorate complex over a 0.5 × 14 in. Dowex 2-X8 anion-exchange column of the appropriate type (10 ml/hr flow rate). The effluent was evaporated to dryness and the red-violet solids were recrystallized from a small amount of methanol by addition of ether. *Anal.* Calcd for NiC₁₈H₄₀N₄Cl₂·H₂O: C, 46.99; H, 9.14; N, 12.18. Found: C, 46.92; H, 9.21; N, 12.08. Calcd for NiC₁₈H₄₀N₄Br₂·2H₂O: C, 38.12; H, 7.76; N, 9.88. Found: C, 37.94; H, 7.63; N, 9.47.

[Ni(*trans*[16]tetramine)I]I.—Two-tenths gram of [Ni(*trans*[16]tetramine)](ClO₄)₂ was dissolved in 150 ml of methanol and to this solution was added 0.3 g of NaI. The solution was refrigerated overnight and red-violet [Ni(*trans*[16]tetramine)I]I separated. *Anal.* Calcd for NiC₁₈H₄₀N₄I₂: C, 34.58; H, 6.40; N, 8.96. Found: C, 35.08; H, 6.44; N, 8.90.

Physical Measurements.—Infrared spectra were obtained on Nujol mulls and KBr pellets with a Perkin-Elmer 337 spectrophotometer. Nmr spectra were obtained on 10–15 wt % DMSO-d₆ and trifluoroacetic acid solutions using a Varian A-60 spectrometer. Chemical shift data are in ppm *vs.* internal TMS. Visible spectra were obtained on a Cary 14 spectrophotometer. Spectra on solid samples were obtained by the diffuse transmittance technique. Solution spectra were obtained using 1-cm quartz cells. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Results and Discussion

Catalytic reduction of the orange complex II over platinum oxide in methanol results in the formation of a red-orange solution from which a highly crystalline red-violet material may be isolated. The infrared spectrum of this product contains a strong band at 3190 cm⁻¹ which is assigned to the N–H stretching vibrations. The absence of absorptions in the range 1550–1650 cm⁻¹ indicates that the complex no longer contains imine bonds. The nmr spectrum in trifluoroacetic acid consists of a singlet at 1.27 ppm, a doublet centered at 1.37 ppm (*J* is about 6 cps), and a singlet at 1.79 ppm downfield from internal TMS. The doublet at 1.37 ppm is assigned to the methyl groups which were attached to the imine carbons before reduction of that linkage and which are now split by the methine hydrogen. The presence of the two singlets indicates that the gem methyl groups are pairwise equivalent with an axial and equatorial distinction between the two methyl groups of a gem pair.[2] The simplicity of the nmr spectrum also indicates that the complex is probably isomerically pure and that only one of the possible diastereoisomers is present. If more than one isomer were present, other methyl resonances should be observed.[2b,c] Since the geometrical disposition of the imine donors in the parent is known, the ligand must have the nominal structure shown in I.

Magnetic susceptibility measurements show that this red-violet material is diamagnetic. Diamagnetism would be expected for a planar four-coordinate complex but the red-violet color is very unusual for a planar complex with four secondary amine donors. The solid-state diffuse transmittance spectrum for this complex consists of one broad intense band centered at 19,045 cm⁻¹. This absorption is considerably lower in

(1) Review articles covering five-coordination in Ni(II) complexes have recently appeared: (a) C. Furlani, *Coord. Chem. Rev.*, **3**, 141 (1968); (b) L. Sacconi, *Transition Metal Chem.*, **4**, 199 (1968).

(2) (a) L. G. Warner, N. J. Rose, and D. H. Busch, *J. Amer. Chem. Soc.*, **90**, 6938 (1968); (b) L. G. Warner and D. H. Busch, *ibid.*, **91**, 4092 (1969); (c) L. G. Warner and D. H. Busch, "Coordination Chemistry—Papers Presented in Honor of Professor John C. Bailar, Jr.," Plenum Press, New York, N. Y., 1969.

(3) E. K. Barefield and D. H. Busch, submitted for publication.

(4) N. F. Curtis, *Coord. Chem. Rev.*, **3**, 1 (1968).

(5) D. A. House and N. F. Curtis, *J. Amer. Chem. Soc.*, **86**, 223 (1964).

energy than those observed for a large number of planar
diamagnetic tetramine complexes, whose band maxima
normally fall in the range 25,000–20,500 cm^{-1}. From
this it is concluded that the geometry about the metal
ion is nonplanar. Since only the single absorption men-
tioned above is present in the visible spectrum, the
complex cannot be octahedral or tetrahedral. The re-
maining rather common coordination number for
nickel(II) is 5. High-spin five-coordinate complexes
are found to have three to five bands in their electronic
spectra.[1] Low spin five-coordinate nickel(II) com-
plexes, normally found with class B donors, usually
have only one absorption in the visible region, generally
in the range 20,000–16,660 cm^{-1}.[1] The absorption
spectrum for the complex of immediate interest indi-
cates that it might have a low-spin five-coordinate
structure. This would require coordination of a per-
chlorate anion.

Uncoordinated perchlorates have two active absorp-
tions in their infrared spectra, ν_3 and ν_4, which occur at
about 1100 and 620 cm^{-1}, respectively. Hathaway
and Underhill have shown that the infrared spectrum
for monodentate perchlorate, which has C_{3v} symmetry
rather than T_d, should contain two bands in place of
ν_3 and two bands in place of ν_4.[6] In addition the ν_2
band, which is very weak for T_d symmetry, becomes in-
frared active when the perchlorate is strongly bound.

These infrared bands for the proposed monodentate
perchlorate are not clearly shown in the present com-
plex. However, the perchlorate absorption at about
1100 cm^{-1} is very broad and it has been found that
when both ionic and monodentate perchlorate are
present the bands due to coordinated perchlorate may
be obscured. Although the infrared data do not show
explicity that a coordinated perchlorate is present,
neither does it eliminate the possibility.

The electronic spectrum of the red-violet material in
aqueous solution contains two bands, a predominant
band at 22,220 cm^{-1}, ϵ 100, and a shoulder at about
18,870 cm^{-1}, ϵ 38. The high-energy absorption is
what one might expect for a planar four-coordinate
complex but the low-energy transition is again not
normally found for such complexes. This suggests the
possibility of the coexistence of square-planar and five-
coordinated species in equilibrium. These solutions
obey Beer's law which requires that the solvent be
coordinating if the low-energy band is due to a species
of higher coordination number. Similar behavior was
observed in other solvents for the perchlorate complex.
Spectra obtained for solutions of the complex in a num-
ber of these solvents are given in Figure 1. The in-
tensity of the lower energy band varies as a function of
solvent with the intensity decreasing in the order DM-
SO > DMF > H$_2$O $\sim$ CH$_3$CN > nitromethane. There
is a corresponding increase in the 22,220-cm^{-1} band
as the low-energy band decreases in intensity. Only
the high-energy band is present for nitromethane solu-
tions. No other absorptions are observed in any of the
solvents studied. Although the band intensities vary
considerably, there is little or no change in either band
maximum with a change in solvent. The fact that nor-
mal nmr spectra can be obtained in DMSO indicates
that neither of the species involved in the solvent-
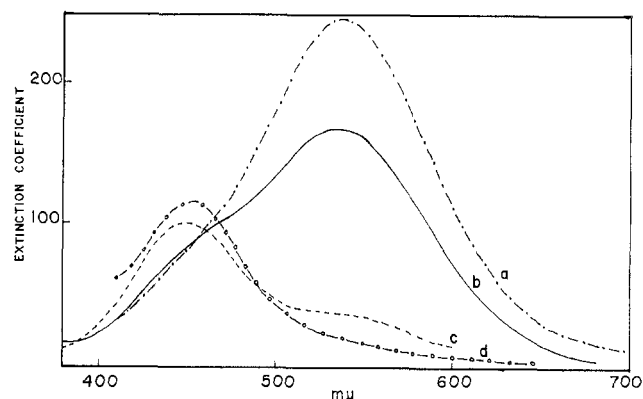dependent equilibrium is paramagnetic. These data

(6) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 309 (1961).

Figure 1.—Absorption spectra of [Ni(*trans*[16]tetramine)](ClO$_4$)$_2$
in (a) DMSO, (b) DMF, (c) water, and (d) nitromethane.

also suggest the presence of a five-coordinate species
which is low spin and whose concentration depends on
the coordinating power of the solvent. That is, the
complex is predominantly five-coordinate in DMSO but
essentially planar in nitromethane.

Metathesis in methanol with sodium iodide to the
iodide salt and conversion to the chloride and bromide
salts by ion exchange result in the formation of new
red-violet complexes. The iodide is an anhydrous salt
while the chloride and bromide are monohydrate and
dihydrate, respectively. Each of these complexes is
diamagnetic and has a broad absorption maximum at a
wavelength at least as great as that of the perchlorate
(Table I). The band maximum moves with the nature

TABLE I
ELECTRONIC SPECTRAL BANDS FOR THE
FIVE-COORDINATE COMPLEXES [Ni(L)X]X

Anion	ν_{max},^{a} cm^{-1}	Anion	ν_{max},^{a} cm^{-1}
ClO$_4$$^-$	19,045	Br$^-$	18,940
I$^-$	19,045,	Cl$^-$	18,690
	31,745^b		

^{a} Spectra obtained in Nujol mulls by the diffuse transmittance
technique. ^{b} Intense charge-transfer band.

of the halide ion in a direction opposite to the usual
spectrochemical series. Spectra for methanol solutions
for all these complexes at low concentrations are identi-
cal with that for the perchlorate salt which indicates
that the anions must be dissociated and that the forma-
tion of the five-coordinated species in solution depends
on solvent coordination alone. Spectra obtained as a
function of temperature indicate that the concentration
of five-coordinate species decreases at higher tempera-
tures while the concentration of planar species decreases
at lower temperature.

The geometric arrangement of ligands in these five-
coordinate complexes is uncertain. Folding of the
large flexible ligand to approximate a trigonal bipyra-
mid (with a fifth ligand) is perhaps possible with certain
secondary amine configurations, but due to the bulk of
this ligand such arrangements of donor atoms might
cause large steric interactions. In trifluoroacetic acid
where the concentration of five-coordinate species is
very small, the nitrogen donors of the ligand are cer-
tainly planar. This is shown by the pairwise equiva-
lence of the gem methyl groups and the equivalence of
the methyl groups attached to the methine carbons.
The nmr in DMSO is not so easily interpreted and it
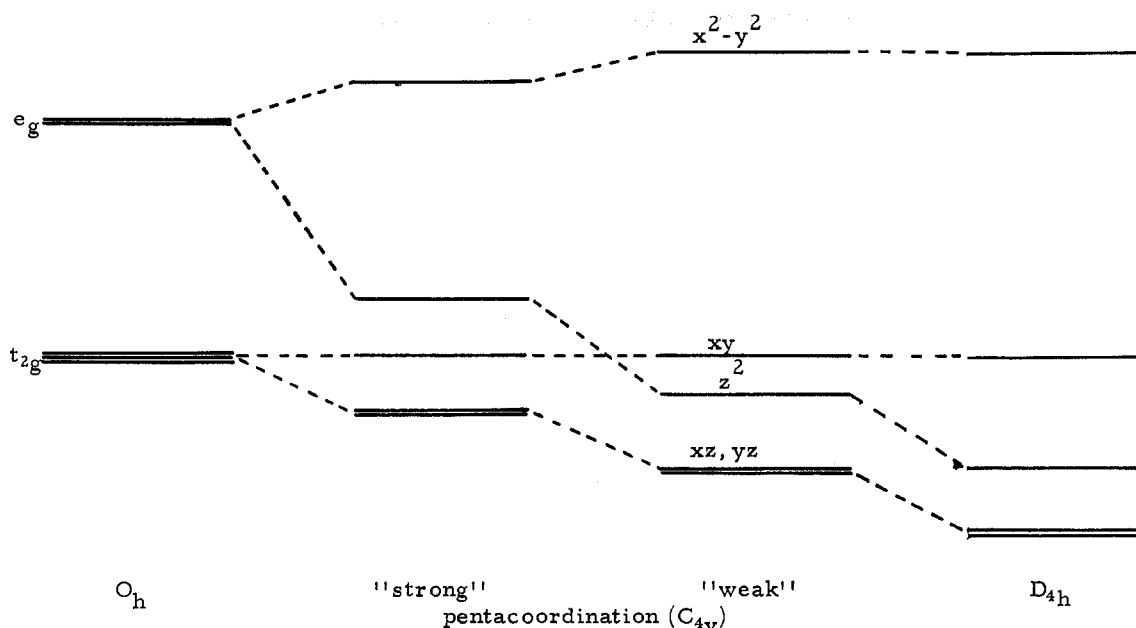appears that an exchange process is occurring. Other

Figure 2.—Energy level diagram for five-coordinate complexes of C_{4v} symmetry.

reported examples of low-spin five-coordinate complexes (with four nitrogen donors) have square-pyramidal structures. These include [Ni(CR)Br]Br·H₂O (CR ≡ structure III) and [*rac*-Ni(CRH)(ClO₄)]ClO₄ (CRH ≡ structure IV).[7,8] Complete X-ray structures[9,10] on these complexes have proven that they contain five-coordinate nickel(II). The electronic spectrum of
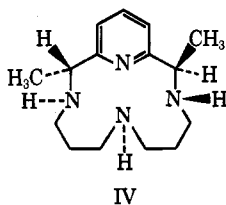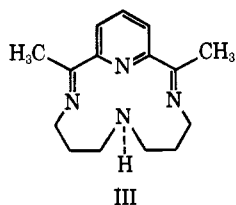
[Ni(CR)Br]Br·H₂O has absorptions at 16,660, 18,180, and 22,220 cm⁻¹. The high-energy bands are very intense and their origin is uncertain. The solid-state diffuse transmittance spectrum for [*rac*-Ni(CRH)-ClO₄]ClO₄ has only one band at 22,225 cm⁻¹ and could be taken as normal for planar Ni(II).[8] The interaction of the perchlorate ion is not clearly shown in the infrared spectrum. The 1100-cm⁻¹ band is rather broad, but as in the present case, the bonded perchlorate absorptions are largely obscured by those of the ionic perchlorate. Other complexes which probably have diamagnetic five-coordinate structures include adducts of complex V. Schrauzer found that pale yellow ace-

V
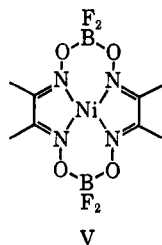
tone solutions of this complex become deep red or purple when they are treated with pyridine, ammonia, or piperidine.[11] Diamagnetic adducts could be isolated. Complexes containing 1 mol of phosphine could also be isolated. It seems likely these are square-pyramidal complexes of the low-spin variety. A low-spin five-coordinate species has also been claimed for the nickel complex shown as structure VI with iodide ion.[12] The proposed five-coordinate complex was not isolated but from spectral, magnetic, and conductivity data was postulated to exist in equilibrium with four- and six-coordinate species. The spectral band assigned to the five-coordinate species occurs at 18,520 cm⁻¹. The

VI
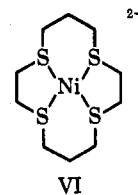
sulfur donors in this example are probably much closer to P and As in their nephelauxetic effect and probably should not be compared with the other cases under discussion here.

The five-coordinate complexes of present interest, as well as the example cited above, agree with the theoretical predictions made by Ciampolini and by Furlani[1a] on the basis of crystal field calculations.[13] When a planar complex adds a fifth, loosely bound, axial ligand there will be a slight shift of the d_{z^2} orbital to higher energy, but the band maximum may change little from that of the ML_4^{2+} planar species so long as the d_{z^2} orbital remains lower in energy than the d_{xy}. This is shown qualitatively in Figure 2. As the fifth ligand becomes more strongly bound the energy of the d_{z^2} orbital becomes higher in energy than d_{xy} and the band maximum undergoes a *red* shift, *i.e.*, to lower energy.

(7) J. L. Karn and D. H. Busch, *Nature (London)*, **211**, 160 (1966).
(8) J. L. Karn, Ph.D. Dissertation, The Ohio State University, 1966.
(9) E. B. Fleischer and S. W. Hawkinson, *Inorg. Chem.*, **7**, 2312 (1968).
(10) E. B. Fleischer and R. Dewar, *Nature (London)*, **222**, 372 (1969).

(11) G. N. Schrauzer, *Chem. Ber.*, **95**, 1438 (1962).
(12) W. Rosen and D. H. Busch, *J. Amer. Chem. Soc.*, **91**, 4694 (1969).
(13) M. Ciampolini, *Inorg. Chem.*, **5**, 35 (1966).

The stronger the fifth ligand the higher the energy of the d_{z^2} orbital becomes. This model requires that the shift in energy be inversely proportional to the axial donor strength.

For the complexes reported here (Table I) the differences in band positions are small; however, it appears that nickel may respond to changes in axial donor strength as predicted. The band maxima are in the order $I^- \sim ClO_4^- > Br^- > Cl^-$, which is, of course, opposite to the spectrochemical series. As previously stated, the chloride and bromide exist as hydrates and data available on these complexes are not sufficient to

tell whether the water molecules or halide ions are coordinated. The fact that there is a light shift in absorption maximum between the Cl^- and Br^- complexes indicates that the fifth ligand is probably not the same for the two. The halide ions are assumed to be coordinated.

Cobalt(III) Complexes Containing the Macrocyclic, Tetradentate, Schiff Base Ligand Tetrabenzo[b,f,j,n][1,5,9,13]tetraazacyclohexadecine
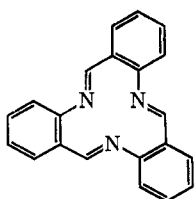
BY SUE C. CUMMINGS AND DARYLE H. BUSCH*

Cobalt(III) compounds of the stoichiometries $Co(TAAB)X_3$ and $Co(TAAB)XY_2$, where TAAB is tetrabenzo[b,f,j,n]-[1,5,9,13]tetraazacyclohexadecine, X^- is Br^-, Cl^-, NO_3^-, NCS^-, or N_3^-, and Y^- is ClO_4^- or NO_2^-, have been prepared *via* the metal ion directed self-condensation of *o*-aminobenzaldehyde. By means of a variety of physical methods the compounds have been characterized as pseudooctahedral cobalt(III) complexes. The geometry of the complexes is discussed with respect to the usual stereochemistry of the cobalt ion and its role as a template in the ring-forming reaction.
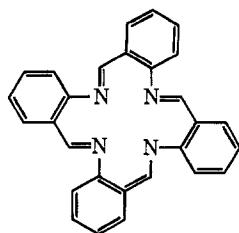
Introduction

In recent years the synthesis of many new macrocyclic ligands has been facilitated by the use of transition metal ions serving as templates.[1] Extensive studies of *o*-aminobenzaldehyde in the presence of a variety of metal ions have demonstrated that this reaction is governed by template effects.[2-9]

Depending upon the particular metal ion used, this reaction yields two types of macrocyclic Schiff base ligands which can be isolated only in the form of their metal complexes. These are a closed tridentate, tribenzo[b,f,j][1,5,9]triazacycloduodecine, abbreviated TRI, structure I, and a closed tetradentate, tetrabenzo-[b,f,j,n][1,5,9,13]tetraazacyclohexadecine, abbreviated TAAB, structure II.

I   II

Because two ligands of different multidentate character can be formed and since a variety of metal ions can be used in this condensation reaction, this system affords a unique opportunity for studying the stereoselectivity of the metal ion acting as a template in the ring-forming reaction. To illustrate, in the presence of nickel(II) ions, both TRI and TAAB are formed and complexes of either square-planar geometry, $Ni(TAAB)^{2+}$, or pseudooctahedral geometry, $Ni(TAAB)X_2$, $Ni(TRI)X_2 \cdot H_2O$, and $Ni(TRI)_2^{2+}$, have been isolated and characterized.[2-7] However, in the presence of copper(II) ions, only TAAB is formed and only complexes of square-planar geometry, $Cu(TAAB)^{2+}$, have been isolated.[6]

In view of the usual stereochemistry of cobalt ions, the self-condensation of *o*-aminobenzaldehyde in the presence of cobalt(II), with subsequent oxidation of the metal ion to cobalt(III), is expected to result in the template synthesis of both ligands which could then be isolated as the pseudooctahedral cobalt(III) complexes. Investigations of the cobalt reactions have confirmed these expectations.[10,11]

In an earlier paper, the synthesis and characterization of two diastereoisomers of the bis-tridentate complex, $Co(TRI)_2^{3+}$, structure III, were reported.[12] No evidence for a complex containing only 1 mol of TRI per cobalt(III) ion was found. The structure of $Co(TRI)_2^{3+}$ was first established by a single-crystal X-ray structure determination.[13]

(1) D. H. Busch, *Helv. Chim. Acta, Fasciculus Extraordinarius, Alfred Werner,* 174 (1967).
(2) G. A. Melson and D. H. Busch, *Proc. Chem. Soc., London,* 223 (1963).
(3) G. A. Melson and D. H. Busch, *J. Amer. Chem. Soc.,* **86,** 4830 (1964).
(4) G. A. Melson and D. H. Busch, *ibid.,* **86,** 4834 (1964).
(5) G. A. Melson and D. H. Busch, *ibid.,* **87,** 1706 (1965).
(6) L. T. Taylor, S. C. Vergez, and D. H. Busch, *ibid.,* **88,** 3170 (1966).
(7) L. T. Taylor and D. H. Busch, *ibid.,* **89,** 5372 (1967).
(8) V. Katović and D. H. Busch, Abstracts, Second Central Regional Meeting of the American Chemical Society, Columbus, Ohio, June 1970.
(9) V. Katović, S. C. Vergez, and D. H. Busch, unpublished results.

(10) S. C. Cummings, Ph.D. Dissertation, The Ohio State University, 1968.
(11) K. Farmery and D. H. Busch, unpublished results.
(12) S. C. Cummings and D. H. Busch, *J. Amer. Chem. Soc.,* **92,** 1924 (1970).
(13) R. W. Wing and R. Eiss, *ibid.,* **92,** 1929 (1970).