torily interpreted in terms of a mechanism involving water as electron donor.

Baxendale and Bridge[3] reported that the quantum yield for disappearance of $Fe(phen)_3^{3+}$ was linear in the first power of the initial concentration of $Fe(phen)_3^{3+}$; they therefore proposed that reactions such as

$$[Fe(phen)_3^{3+}]^* + Fe(phen)_3^{3+} \longrightarrow Fe(phen)_3^{2+} + \text{products}$$

were significant. That such a reaction could occur during the short lifetime of excited $Fe(phen)_3^{3+}$ seems highly improbable, especially since the reaction requires interaction of two tripositive ions. Furthermore, the dependence of Φ upon concentration of $Fe(phen)_3^{3+}$ becomes important only in strongly absorbing solutions (Figure 5). It is therefore probable that the concentration dependence of Φ arises from the secondary reactions described above, which would more significantly affect apparent Φ values in strongly (and inhomogeneously) absorbing solutions. Again, Φ for appearance of product ($Fe(phen)_3^{2+}$) is virtually independent of the initial concentration of reactant, which is consistent with previous discussion. Consequently, no justification emerges for postulating interactions between excited and ground-state molecules of $Fe(phen)_3^{3+}$.

Finally, we consider the unusual wavelength dependence for the photoreduction (Figure 1). It is evident that the low-lying doublet ligand→metal ($\pi \rightarrow t_2$) CT excited state is photochemically inert. The quantum yield data appear to show that spin-allowed intraligand (π, π^*) excited states of $Fe(phen)_3^{3+}$ are photochemically active. This is an unexpected conclusion, especially since phen does not appear to be the electron donor in photoreduction of $Fe(phen)_3^{3+}$. Two alternative explanations for the wavelength dependence of the quantum yield can be offered. First, a higher, spin-allowed, CT band (*e.g.*, $\pi \rightarrow e$) may overlap the phen $\pi \rightarrow \pi^*$ bands. Assuming that a higher energy CT band exhibited a molar absorptivity equal to that of the visible CT transition ($\sim 10^3$), it would not be detected in the ultraviolet region due to the much higher intensities of the intraligand bands. Hence, the validity of this hypothesis is not susceptible to experimental verification, and no theoretical studies of the locations of higher CT states in $Fe(phen)_3^{3+}$ have appeared.

Alternatively, it is possible that, following excitation of a (π, π^*) band in $Fe(phen)_3^{3+}$, radiationless intersystem crossing to a spin-forbidden, reactive, excited state takes place. Intersystem crossing from singlet to triplet states in free phenanthroline is known to occur[18] and its extent is known to be increased by complexation of phen with metal ions.[19] Again, however, it is difficult to understand why a spin-forbidden ligand-localized excited state would exhibit the observed photochemistry. It might be argued that spin-forbidden CT excited states can ultimately be populated by intersystem crossing. There are no spin-forbidden ($\pi \rightarrow t_{2g}$) CT excited states in $Fe(phen)_3^{3+}$, but spin-forbidden ($\pi \rightarrow e_g$) excited states are possible. At present, nothing is known about the energetics of spin-forbidden, or spin-allowed ($\pi \rightarrow e$), CT excited states in $Fe(phen)_3^{3+}$. Hence, the importance of intersystem crossing phenomena in the photochemistry of $Fe(phen)_3^{3+}$ must remain a matter of conjecture, as the usual experimental techniques employed for evaluating the importance of spin-forbidden excited states in photochemical reactions (energy transfer[20] and esr) are not feasible in this system (because both the spin-allowed and spin-forbidden states are paramagnetic).

It is clear that the interesting and unusual wavelength dependence of photoreduction in $Fe(phen)_3^{3+}$ cannot now be satisfactorily interpreted. Further theoretical study of CT states (both spin allowed and spin forbidden) in this complex is needed. Furthermore, extensive mixing of metal and ligand orbitals in $Fe(phen)_3^{3+}$ [5] will render tenuous any attempt to describe the unusual excited-state chemistry of this complex in simple terms.

Acknowledgment.—We thank J. K. Kochi for use of the mercury lamp photolysis apparatus. This work was supported in part by the National Science Foundation (Grant GP-26109) and the Public Health Service (Grant AM 11081).

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Preparation and Studies of Di-μ-nitrogen-decaaquodiruthenium(II) Fluoroborate

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The preparation of salts containing the ion $(H_2O)_5RuN_2Ru(H_2O)_5^{4+}$ is described, as are experiments which were directed toward bringing about cleavage of the N≡N bond in the complex by internal disproportionation. In none of the attempts, which included treating the binuclear complex with oxidizing agents, was evidence found for disproportionation.

Introduction

In the work described here we set out to prepare nitrogen complexes derived from $Ru(H_2O)_6^{2+}$.[1] Besides the intrinsic interest which these species held for us, they appeared to us to be especially promising in searching for evidence of reduction of bound nitrogen. For these purposes they have an obvious advantage over ammine complexes in that the combined

[1] The oxygen-ligand-containing complex $RuN_2(H_2O)_2Cl_2THF$ has been described by A. K. Shilova, A. E. Shilov, and Z. N. Vostrokhnutova, *Kinet. Katal.*, **9**, 924 (1968); A. K. Shilova and A. E. Shilov, *ibid.*, **10**, 267 (1969).

dinitrogen is the only source of ammonia which might be formed from the compounds, thus simplifying the analytical problem.

The failure recorded by Harrison[2] in his efforts to reduce nitrogen in $Ru(trien)N_2H_2O^{2+}$, using the most powerful reducing agents compatible with water (including U(IV) and Cr^{2+}) and using prolonged contact times (possible because the trien complex resists reduction to the metal better than does the ammonia complex), persuaded us to forego this approach in our system. Instead, we turned to examine the possibility of reduction by internal disproportionation, as for example, by the reaction

$$12OH^- + (H_2O)_5RuNNRu(H_2O)_5{}^{4+} = 2O_3RuN^{4-} + 16H_2O$$

(For want of definite information, the product Ru(V) species has arbitrarily been assigned a charge of 4−.)

The strategy used in attempting to bring about disproportionation included changing the acidity and treating the binuclear ruthenium complex with oxidizing agents. The rationale for the latter approach is that the internal disproportionation might prove to be more facile for the change Ru(III) → Ru(VI) than it is for the change Ru(II) → Ru(V). The interaction of the ruthenium in the 6+ oxidation state with nitride ion is in fact expected to be stronger than when ruthenium is in the 5+ state.

Experimental Section

Reagents.—Deionized distilled water from the house line was redistilled from a solution 0.04% in potassium hydroxide and 0.02% in potassium permanganate. Water used for ammonia analyses was again redistilled from a solution 0.2 *N* in sulfuric acid. All chemicals used were reagent grade unless otherwise stated. Analytical grade Dowex 50W-X2 resin, 200–400 mesh, hydrogen ion form (purchased from Bio-Rad Laboratories), was cleaned by successive washings with water, acid, base, basic peroxide, acid, water, acetone, and water stored in the absence of light. Trifluoromethylsulfonic acid obtained from 3M Corp. was distilled, the 160° cut being taken. The distillate was stored in a brown bottle and diluted as required. Argon and nitrogen gases were scrubbed successively with $Cr^{2+}(aq)$ and water.

Preparations.—Potassium aquopentachlororuthenium(III) was prepared from soluble Engelhard ruthenium trichloride by the procedure of Mercer and Buckley.[3]

Hexaaquoruthenium(II) in Solution.—Potassium aquopentachlororuthenium(III) (1.00 g, 2.68 mmol) was dissolved in 250 ml of 0.1 *N* trifluoromethylsulfonic acid. A platinum gauze freshly coated with platinum black was added to the Ru(III) solution and hydrogen gas was bubbled into the solution through a coarse glass frit at a moderate rate, care being taken to exclude air from the system. After 5–15 hr the solution changed from red-brown to blue. Analyses of the reducing content of the solution at this stage showed the reduction to be 90–100% complete. (Prolonged treatment of the blue solution with hydrogen gave ruthenium metal under these conditions.)

Hexaaquoruthenium(II) was separated from the Ru(III) and other Ru(II) species in the solution by cation-exchange chromatography at 4° under argon. The reduced solution was diluted threefold with oxygen-purged water and loaded onto a 10 in. high, 1-in. diameter column of Dowex 50W-X2 200–400 mesh cation-exchange resin in the hydrogen ion form. The loaded column was washed with 300–400 ml of 0.5 *N* trifluoromethylsulfonic acid to complete removal of the blue species. With this washing, the pink hexaaquoruthenium(II) ion was observed to separate neatly as a salmon-colored band. Subsequent treatment with 100–150 ml of 1 *N* fluoroboric acid removed the $Ru(H_2O)_6{}^{2+}$ band from the column. (Fluoroboric acid was used at this point in the procedure because the fluoroborate salt of the nitrogen complex later prepared from the solution is more insoluble than the trifluoromethylsulfonate salt. Otherwise, use of fluoroboric acid was avoided because hydrofluoric acid in its solutions attacked the glass frits used in the apparatus.) The hexaaquoruthenium(II) solutions were stored under argon at 4°. These solutions were analyzed for ruthenium content by the ruthenate–perruthenate method of Woodhead and Fletcher[4] and for reducing agent by adding aliquots of Ru(II) to deaerated solutions of excess ferric ion and determining the ferrous ion produced by the method of Harvey, Smart, and Amis.[5] By the cation-exchange procedure, solutions up to 0.015 *M* in $Ru(H_2O)_6{}^{2+}$ in 1 *N* acid could be obtained.

Di-μ-nitrogen-decaaquodiruthenium(II) Fluoroborate.—The volume of a solution of hexaaquoruthenium(II) (from above) was reduced on the rotary evaporator, care being taken to exclude air, so that 25–50 ml of a concentrated solution, 0.05–0.1 *M* in Ru(II), resulted. (Occasionally pink crystals, probably $Ru(H_2O)_6(BF_4)_2$, were observed to form at this stage.) The concentrated solution was transferred carefully to an air-purged, nitrogen-filled high-pressure reactor and left with stirring under 5 atm of nitrogen gas in the absence of light. After about 12 hr the gold color of the nitrogen complex could be observed in the solution. At the end of 3 days' time, the solution of nitrogen complex (now gold-brown) was opened to the air, filtered, reduced in volume on the rotary evaporator until crystals appeared (these were also gold-brown), and chilled. The solid nitrogen complex was collected by filtration. The solid was not washed, as it proved exceedingly soluble in water, fluoroboric acid, ether, and alcohol. The solid was dried under vacuum over phosphorus pentoxide at room temperature for 2 days. *Anal.* Calcd for $[(H_2O)_5Ru]_2N_2(BF_4)_4$: Ru, 26.6; N, 3.69; H, 2.64; F, 40.4. Found:[5] Ru, 26.8; N, 3.65; H, 2.68; F, 33.2.[6] Microanalyses were performed by the Stanford Microanalytical Laboratory.

Methods.—The rate of formation of dinitrogenpentaaquoruthenium(II) ion was estimated from the results of a single experiment. A solution 6.8×10^{-3} *M* in $Ru(H_2O)_6{}^{2+}$ and 1 *N* in fluoroboric acid was bubbled with nitrogen at 25° and the increase in absorbance at 218 nm (a maximum for $(H_2O)_5RuN_2{}^{2+}$) was observed. Throughout the experiment the solution was held saturated in nitrogen. In order to calculate the rate of formation of the nitrogen complex, the rate was assumed to be first order in hexaaquoruthenium(II) and nitrogen, as it is when $Ru(NH_3)_5H_2O^{2+}$ is the reactant,[8] and the extinction coefficient of $(H_2O)_5RuN_2{}^{2+}$ was assumed to have the same value at 218 nm as does $(NH_3)_5RuN_2{}^{2+}$ at 221 nm (λ_{max}).[9] The latter assumption is reasonable in view of the fact that the extinction coefficients of $[(H_2O)_5Ru]_2N_2{}^{4+}$ and $[(NH_3)_5Ru]_2N_2{}^{4+}$ [9] at their respective maxima lie within 10% of each other.

The extinction coefficient of di-μ-nitrogen-decaaquodiruthenium(II) fluoroborate was measured for solutions prepared by dissolving weighed (*ca.* 5 mg) samples of the dried salt in oxygen-purged water and ranging in concentration from 4×10^{-6} to 4×10^{-5} *M*.

Reactions of Di-μ-nitrogen-decaaquodiruthenium(II) Fluoroborate. (A) Ammonia Analysis Experiments.—About 20 μmol (15 mg) of solid nitrogen complex was weighed into a 5-ml round-bottom flask containing a Teflon-covered stirring bar. The flask was closed with a serum cap and purged of air by blowing argon through it. The solid was then dissolved in 0.5 ml of air-purged water. The reagent of interest, 1 ml in volume, was added by syringe, and the resulting solution was stirred at room temperature, in the absence of light, overnight, and then subjected to analysis for ammonia.

Ammonia Analysis.—The distillation procedure used was adapted from that described by Harrison.[10] A volume of 0.5 ml of 0.2 *M* NaH_2PO_2 and the solution to be analyzed for ammonia were added to a distilling flask containing 20 ml of 40% sodium hydroxide *via* a side arm closed by a serum cap. The mixture was heated to boiling with a Bunsen burner until 5–8 ml of distillate was collected in 15 ml of saturated boric acid as the receiving solution. During the distillation, air prescrubbed by saturated boric acid solution was bubbled through the sodium

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(2) D. E. Harrison, Ph.D. Thesis, Stanford University, 1969.

(3) E. E. Mercer and R. R. Buckley, *Inorg. Chem.*, **4**, 1692 (1965).

(4) J. L. Woodhead and J. M. Fletcher, *J. Chem. Soc.*, 1961 (5039).

(5) A. E. Harvey, Jr., J. A. Smart, and E. S. Amis, *Anal. Chem.*, **27**, 26 (1965).

(6) D. Harrison and J. N. Armor also found fluoroborate salts of ruthenium(II)–nitrogen complexes (in that case, of ammines) to give low and erratic fluorine analyses.[7]

(7) J. N. Armor, private communication.

(8) I. J. Itzkovich and J. A. Page, *Can. J. Chem.*, **46**, 2743 (1968).

(9) D. E. Harrison, H. Taube, and E. Weissberger, *Science*, **159**, 320 (1968).

(10) P. R. Jones, private communication.

hydroxide solution in order to help sweep the ammonia into the receiving trap. When the distillate had cooled, the boric acid trap was washed with water into a 50-ml volumetric flask. The ammonia content of this solution was analyzed according to the spectrophotometric indophenol method.[11]

(B) **Nitrogen Evolution Experiments.**—In a 5-ml roundbottom flask containing a glass-covered 0.5-in. magnetic stirring bar was placed 0.5 ml of a solution containing di-μ-nitrogen-decaaquodiruthenium(II) fluoroborate (10–20 μmol). The reagent solution to be added (0.5–1.0 ml) was placed in an attached side arm. The apparatus was attached to the vacuum line[12] and the solutions were degassed using a freeze–pump–thaw cycle (repeated three times). After the final thaw, the side arm was tilted and its contents were allowed to mix with the ruthenium solution, with stirring.

After 1–18 hr, depending on the reagent, the solution was cooled to 77°K and all gases contained in the apparatus were transferred by a Toepler pump method to a gas buret. To ensure quantitative transfer of dissolved gases, a freeze–pump–thaw cycle was again used. The amount of collected gas was calculated from gas buret and temperature readings.

Gas samples were analyzed for N_2, O_2, and NO by mass spectrometer, and the total amount of N_2 produced in an experiment was calculated from this and the data on total gas yield. The presence of H_2 in the gas from the 40% sodium hydroxide experiment was verified by gas chromatography on a 10-ft 5A Molecular Sieve column installed in a Varian Aerograph 90P gas chromatograph using argon as carrier gas. As these measurements were not quantitative, exact N_2 yields could not be determined for this experiment.

In the experiments in which the nitrogen-containing complex was treated with oxidizing agent, no effort was made to identify the ruthenium-containing product.

Results

Spectra.—The visible–ultraviolet spectrum of di-μ-nitrogen-decaaquodiruthenium(II) fluoroborate shows a very intense band (λ_{max} 255 nm, ϵ_{255} (5.6 ± 0.7) × 10^4 M^{-1} cm^{-1}) in the ultraviolet region and a weaker band (λ_{max} 400 nm, ϵ_{400} *ca.* 4500) in the visible. An infrared spectrum of the solid in a potassium bromide pellet shows a very weak band at 2080 cm^{-1} characteristic of the N≡N stretch.

Rate of Formation of $(H_2O)_5RuN_2^{2+}$.—Using the assumptions noted earlier, the second-order rate constant for the reaction

$$Ru(H_2O)_6^{2+} + N_2 \longrightarrow Ru(H_2O)_5N_2^{2+} + H_2O$$

at 25° in 1 *N* fluoroboric acid was found to be *ca.* 2 × 10^{-3} M^{-1} sec^{-1}.

Attempts to Reduce Nitrogen in $(H_2O)_5RuN{\equiv}NRu(H_2O)_5^{4+}$.—In an effort to detect small amounts of nitrogen which might be produced in the 3− oxidation state, two analytical approaches were used. In the first experiments, solutions after reaction were analyzed for ammonia. In these experiments, the yield of ammonia (mol of NH_3/mol of N in ruthenium complex × 100) did not exceed 2% (the accuracy of the analytical procedure) when 1 ml of any of the following reagents reacted with 20 μmol of nitrogen complex as described earlier: 0.022 *M* sodium peroxydisulfate in 0.1 *M* sodium carbonate–bicarbonate buffer at pH 10, 40% sodium hydroxide, or 0.5 *M* ferric nitrate in 3 *N* hydrochloric acid.

In other experiments the amount of N_2 gas produced upon complete destruction of the nitrogen complex by the reagent of choice was measured. This type of analysis was undertaken, after results of the ammonia analysis experiments proved negative, to circumvent the possibility that reduced nitrogen might not be converted to (and hence analyzed as) ammonia. Analyses of the N_2 produced would, nevertheless, enable us to detect reduced nitrogen by the deficiency in the N_2 analysis. Below are reported the per cent yields of N_2 based on the weight of solid nitrogen complex taken when the following reagents were allowed to react with nitrogen complex: 1 ml of 0.5 *M* $Ce(SO_4)_2$ in 2 *N* sulfuric acid, 91.6 ± 5.9%;[13] sodium peroxydisulfate[14] in 0.1 *M* sodium carbonate–bicarbonate buffer at pH 10, 92.1 ± 3.4%;[13] sodium hypochlorite, 99.5%;[14] 40% sodium hydroxide, 110 ± 3% (the gas was shown to contain also H_2); 30% fuming sulfuric acid (the acid was added to the *dry* solid), 98.5%. In these experiments we had difficulty obtaining reproducible nitrogen yields. The large range in the results for ceric sulfate and sodium peroxydisulfate is due in part to the fact that different batches of solid were used for experiments with a given reagent. Another important factor is the age of a particular solid batch. When not being sampled, the solid was stored in a vacuum desiccator over phosphorus pentoxide. A set of N_2 yields for a given reagent for experiments done on the same solid preparation but at different times (for example, 2 days after preparation or 2 weeks after preparation) indicates that the per cent N_2 produced per weight of solid rises gradually for about the first 10 days of aging and then decreases slowly for the next few days. Because of the operation of these two kinds of difficulties, we do not attach great significance to the low values for ceric sulfate and sodium peroxydisulfate *overall* nitrogen yields. We feel that the results of the comparison experiments reported below are more meaningful and show that no significant loss of N_2 to reduced nitrogen occurs in our experiments. In one experiment a solution of nitrogen complex was prepared from the solid and 0.5-ml portions of the solution were treated as described earlier with ceric sulfate and sodium peroxydisulfate; both portions gave 86.2% N_2 yields. In another set of experiments, determinations done on another batch of nitrogen complex within several days of each other gave 96.1, 94.8, and 98.6% N_2 when the complex was treated with ceric sulfate and 96.4% when treated with sodium peroxydisulfate. Since it is unlikely that two different oxidants would produce identical defects, we conclude from the similarity of the above sets of N_2 yields that oxidation of the complex either by Ce(IV) or by $S_2O_8^{2-}$ in base does not produce detectable amounts of reduced nitrogen.

Discussion

The high-energy spectra of the aquoruthenium(II)–nitrogen complexes $(H_2O)_5RuN_2^{2+}$ (λ_{max} 218 nm) and $[(H_2O)_5Ru]_2N_2^{4+}$ (λ_{max} 255 nm) are similar to those recorded for ruthenium(II)–nitrogen complexes containing ammine ligands. For the aquo ions, the band maxima are shifted slightly to higher energy compared, for example, to $(NH_3)_5RuN_2^{2+}$ (λ_{max} 221 nm)[15] and

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(11) W. T. Bolleter, C. J. Bushman, and P. W. Tidwell, *Anal. Chem.*, **33**, 592 (1961).

(12) We acknowledge with thanks the assistance by P. R. Jones in the vacuum-line experiments.

(13) The *average* per cent deviation is given; for $Na_2S_2O_8$, over six experiments, and for $Ce(SO_4)_2$, over nine experiments.

(14) One mole of oxidizing agent per each mole of nitrogen complex was taken. After the reactant mixture had been left with stirring for 18 hr, a tenfold molar excess of sodium peroxydisulfate dissolved in 0.5 ml of 0.1 *M* carbonate buffer at pH 10 was added to the solution to destroy any nitrogen complex still left unreacted.

(15) D. E. Harrison and H. Taube, *J. Amer. Chem. Soc.*, **89**, 5706 (1967).

$[(NH_3)_5Ru]_2N_2^{4+}$ (λ_{max} 262 nm)[9] as is expected if these bands are due to a metal-to-ligand charge-transfer process;[16] the $(H_2O)_5Ru^{2+}$ moiety is a weaker reducing agent than $(NH_3)_5Ru^{2+}$. No band analogous to the 400-nm band found in the spectrum of the μ-nitrogen-decaaquo ion has been reported for the other ruthenium(II)–nitrogen complexes, however.

The rate of reaction of $(H_2O)_6Ru^{2+}$ with N_2 at room temperature in 1 N fluoroboric acid is about 35 times slower than that of $(NH_3)_5RuOH_2^{2+}$ under similar conditions.[8,17] When the rate of reaction per reacting coordination site is taken into account, the reaction of the hexaaquo ion takes place about 200 times more slowly than that of the aquopentaammine. This contrast in reactivity is similar to that found for Rh(III).[18,19]

Finally, we discuss the experiments directed to bringing about disproportionation of di-μ-nitrogen-decaaquodiruthenium(II) to yield nitrogen in the 3− oxidation state. In one experiment the nitrogen complex was treated with fuming sulfuric acid, a dehydrating agent. In that experiment we hoped that when water was removed from the coordination sphere of the Ru(II) ion, reducing its coordination number, its tendency to form multiple bonds to nitrogen (as in $Ru^{V}\equiv N^{3-}$) would increase. The quantitative yield of N_2 observed on complete destruction of the nitrogen complex indicates the failure of this particular reagent to induce disproportionation.

Since the high oxidation states of Ru(VI), -(VII), and -(VIII) are stabilized by complexation to oxide and formed only in strongly basic solution (RuO_4^- and RuO_4^{2-}), we hoped to promote the oxidation of Ru(II) by N(0) by employing strongly basic conditions (mixing the nitrogen complex with 40% sodium hydroxide).

Both ammonia and nitrogen analyses of the solutions indicate that this approach also failed to induce the desired disproportionation reaction.

It is clear from the data that treating the ruthenium complex with enough oxidant to generate Ru(III) also failed to produce significant disproportionation. This approach has a serious limitation, which is that the Ru^{III}–N_2 bond is quite labile. This disproportionation would need to be very rapid to compete with dissociation of the complex.

The outcome of our experiments on the disproportionation of the binuclear complex, though disappointing, should not discourage others from attempting a similar approach in related systems. We are engaged in an attempt to prepare an analogous binuclear Os complex to exploit the dual advantages which Os offers in being more readily oxidized (at least in an equilibrium sense) and in being more resistant to substitution.

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The Stereochemistry of *N,N'*-Bis(3-isopropylsalicylidene)polymethylenediaminocobalt(II) Complexes in Donor and Nondonor Solvents and in the Solid State[1]

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Cobalt(II) complexes with the homologous series of *N,N'*-bis(3-isopropylsalicylidene)polymethylenediamine ligands, $HO(3\text{-}i\text{-}C_3H_7)C_6H_3CH{=}N(CH_2)_nN{=}CHC_6H_3(3\text{-}i\text{-}C_3H_7)OH$, where $n = 2$–7, have been prepared and characterized in the solid state and in dichloromethane and pyridine solutions. Spectral and magnetic measurements reveal that the $n = 2$ derivative is a low-spin planar complex in the solid state and in dichloromethane. The higher homologs are all high spin and the $n = 4$–7 complexes exhibit pseudotetrahedral spectra in the solid state and in nondonor solvents. The trimethylene derivative does not exhibit a characteristic pseudotetrahedral spectrum and it is postulated that this derivative possesses an extensively flattened tetrahedral geometry. All of the complexes are monomeric in nondonor solvents ruling out higher coordination numbers produced *via* intermolecular association. In pyridine, all of the complexes expand their coordination number to achieve pseudooctahedral structures as deduced from spectral and magnetic measurements.

Introduction

Previous investigations[2–4] have described the stereochemistry of cobalt(II) complexes with tetradentate Schiff base ligands as a function of the central chelate ring size. In contrast to *N,N'*-bis(salicylidene)ethylenediaminocobalt(II), which possesses a low-spin, square-planar geometry[2,5–7] in solution, the derivatives containing four to ten bridging methylene groups are high spin and exhibit properties characteristic of pseudotetrahedral cobalt(II) complexes.[2,3] The high-

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(1) Presented at the 2nd Central Regional Meeting of the American Chemical Society, Columbus, Ohio, 1970; see Abstract 83.

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