$[(NH_3)_5Ru]_2N_2^{4+}$ (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.

Acknowledgment.—Financial support for this research by the National Institutes of Health, both for Grant No. GM 13797 and for the predoctoral fellowship for C. Creutz, 1967–1970, is gratefully acknowledged.

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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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spin trimethylene derivative was proposed[8] to have an extensively flattened tetrahedral geometry on the basis of its anomalous electronic spectrum. The insolubility of this series of complexes allowed only solid-state measurements[8] and, although mass spectral results precluded the existence of polynuclear complexes, there remained the possibility of increased coordination number *via* intermolecular bridging in the solid derivatives.

In this paper we report the synthesis and characterization of an analogous series of alkyl-substituted salicylaldimine complexes of cobalt(II). These complexes exhibit solubility in a variety of nondonor and donor solvents and the investigation of their stereochemistry as a function of chelate ring size is extended to solution studies. In addition, the solubility of *N,N'*-bis(3-isopropylsalicylidene)ethylenediaminocobalt(II), $Co(3\text{-}i\text{-prsal})_2N_2(CH_2)_2$, has permitted the characterization of the ligand field spectrum of square-planar Co(II) in the spectral region 4000–7000 cm^{-1}.

The behavior of this series of tetradentate Schiff base Co(II) complexes in pyridine solution is described also. Bis-bidentate salicylaldimine complexes of nickel(II), cobalt(II), and copper(II) generally expand their coordination number in the presence of pyridine to form five- and six-coordinate species.[9] Planar nickel(II) and copper(II) complexes with tetradentate Schiff base ligands exhibit a lesser tendency to increase their coordination number in donor solvents;[9,10] little is known of the behavior of tetradentate Schiff base complexes of cobalt(II) as Lewis acids. The formation of adduct species with additional donors has been shown to be a requirement for the reversible oxygenation of the tetradentate cobalt(II) chelates.[11,12] Whereas the electronic structures of the oxygenated forms have been extensively examined,[11b,c] the unoxygenated adduct species and parent square-planar complexes have received comparatively little attention. The anomalous magnetic behavior of a low-spin monopyridine adduct of $Co(sal)_2en$ has been studied[13] and this species has recently been shown to have a square-pyramidal structure.[14]

Experimental Section

Materials.—3-Isopropylsalicylaldehyde was prepared from 2-isopropylphenol (Aldrich Chemical Co.) by the method of Duff;[15] yield ~30%, bp 60–66° (4 mm); lit. bp[16] 86–94° (7 mm). Reagent grade dichloromethane (Matheson), deaerated at room temperature with nitrogen gas, was the solvent for spectral and magnetic susceptibility measurements. Pyridine was dried by refluxing over anhydrous barium oxide overnight followed by distillation in nitrogen atmosphere.

Preparation of the Ligands.—The ligands were prepared by refluxing 0.02 mol of 3-isopropylsalicylaldehyde and 0.01 mol of the aliphatic diamine in about 30 ml of methanol for 20 min and then cooling the solution in an ice bath. The tetra- and hexamethylene ligands separated out as lemon yellow crystals and were recrystallized from methanol; melting point: tetramethylene ligand, 62°; hexamethylene ligand, 50°. The remaining ligands could be isolated as oils at room temperature.

Preparation of the Cobalt(II) Complexes.—The complexes, in solution, displayed a marked sensitivity to oxidation and accordingly the preparations were performed in a nitrogen atmosphere. The following general method of preparation was used. A 0.01-mol sample of the ligand and 0.01 mol of cobalt(II) acetate tetrahydrate were dissolved in separate portions of boiling absolute methanol (*ca.* 150 ml) and the cobalt(II) solution was added to the hot ligand solution. The crystalline complexes precipitated when the reaction mixtures cooled. The crystals were filtered off and recrystallized from dry, deaerated toluene. The heptamethylene complex is not soluble in noncoordinating solvents and was not recrystallized. The complexes were dried at 135° for 4–6 hr *in vacuo* except for the hexamethylene compound which was dried at 70° owing to its low decomposition point (97°). Galbraith Laboratories, Knoxville, Tenn., provided the analytical data for the solid complexes.

Spectral Measurements.—The electronic spectra of the solid complexes were obtained using a Beckman DK2 recording spectrophotometer equipped with a reflectance attachment. Magnesium oxide served as the reference material. Solution spectra and solid mull spectra were obtained with a Cary Model 14 recording spectrophotometer. All solutions were prepared and handled in a nitrogen atmosphere.

Magnetic Susceptibility Measurements.—Magnetic moments of the solid complexes were determined by the Faraday method. There was no evidence of oxidation of the solid complexes after several hours of exposure to air. The susceptibilities of the complexes were found to be independent of field strength and the values for different preparations were in good agreement (±2%). $Hg[Co(NCS)_4]$ was used as the calibrant. Diamagnetic corrections were calculated from tables of Pascal's constants.[17] Solution magnetic moments[18] were determined with a Varian A-60 spectrometer.

Molecular Weight Measurements.—The molecular weights of the complexes in dry, degassed toluene were determined at 35° using a Mechrolab vapor pressure osmometer contained in a glove bag purged with dry nitrogen. The osmometer was calibrated with toluene solutions of benzil.

Results and Discussion

The Schiff base complexes reported here are similar in physical appearance to the unsubstituted complexes, $Co(sal)_2N_2(CH_2)_n$, which have been described previously.[3] The introduction of isopropyl groups on the salicylidene residues imparts sufficient solubility[16] to the present complexes to allow characterization of their properties in solution. The analytical composition of the solid chelates and their osmometric molecular weights in toluene solutions are included in Table I. All of the complexes are monomeric in toluene with the exception of the heptamethylene derivative which did not possess sufficient solubility for the measurement. The complexes all exhibit identical spectra in toluene and dichloromethane solutions and obey Beer's law in the concentration range up to 0.025 *M*. From these results it is concluded that the complexes are behaving as monomeric species for all of the solution measurements reported in this study. The molecular weight studies rule out the possibility of higher coordination numbers achieved *via* intermolecular bridging and the data obtained in nondonor solvents must

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TABLE I

CHARACTERIZATION DATA FOR THE TETRADENTATE COBALT(II) COMPLEXES Co(3-*i*-prsal)$_2$N$_2$(R)

	Analytical data, %							
	C		H		N		Mol wt[a]	
R	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$(CH_2)_2$	64.54	64.77	6.40	6.52	6.84	6.98	409	405
$(CH_2)_3$	65.24	65.20	6.67	6.91	6.62	6.57	423	421
$(CH_2)_4$	65.90	65.85	6.91	6.89	6.40	6.45	437	428
$(CH_2)_5$	66.51	65.45	7.14	7.16	6.21	6.39	451	458
$(CH_2)_6$	67.09	66.91	7.36	7.45	6.02	6.26	465	463
$(CH_2)_7$	67.63	67.72	7.57	7.44	5.84	5.92	...[b]	...[b]

[a] Toluene solutions. [b] Insoluble.

be interpreted on the basis of four-coordinate cobalt(II) species.

Solid-State and Nondonor Solution Properties.—The stereochemistry of a cobalt(II) complex may be assigned in most cases from a consideration of the magnetic properties[19] and ligand field spectrum[9a] of the complex. Solid-state and solution magnetic moments for the present series of cobalt(II) complexes are presented in Table II; electronic spectral data are summarized in Table III and representative spectra are presented in Figures 1–3.

TABLE II

MAGNETIC SUSCEPTIBILITY DATA FOR THE COMPLEXES Co(3-*i*-prsal)$_2$N$_2$(R)

		μ'_{eff},[b] BM	
R	Solid[a]	Dichloromethane soln	Pyridine soln
$(CH_2)_2$	2.35	2.38	5.52
$(CH_2)_3$	4.48	4.54	4.83
$(CH_2)_4$	4.47	4.63	4.78[c]
$(CH_2)_5$	4.42	4.45	4.91
$(CH_2)_6$	4.20	4.30	4.85
$(CH_2)_7$	4.32	...[d]	4.92

[a] Room-temperature Faraday moments. [b] Nmr moments at 42°. [c] Solid derivative—Faraday method. [d] Insoluble in dichloromethane.

TABLE III

ABSORPTION SPECTRA OF THE COMPLEXES Co(3-*i*-prsal)$_2$N$_2$(R) IN A NONDONOR SOLVENT[a]

R	$\bar{\nu}$, cm^{-1} ($\epsilon_{\max}$)
$(CH_2)_2$	4260 (93),[b] 4700 sh[c] (53),[b] 5800 (23),[b] 8130 (26), 18,250 sh (750), 20,800 (3540), 24,100 (15,200), 28,170 (12,550), 40,820 (41,850)
$(CH_2)_3$	6200 (8), 13,500 (25), 17,240 sh (45), 27,000 (8300), 28,170 (9000), 43,480 (39,000)
$(CH_2)_4$	6250 (27), 11,240 (55), 17,240 sh (42), 18,760 sh (123), 27,600 (14,280), 31,600 (8300), 36,600 (23,500), 42,000 (42,600)
$(CH_2)_5$	7690 (53), 11,110 (38), 17,090 (42), 27,170 (11,200), 30,300 (9100), 34,480 (10,250), 37,040 (22,800), 43,480 (41,400)
$(CH_2)_6$	7580 (57), 11,100 (34), 17,990 (47), 27,000 (9900), 30,300 (8800), 33,900 (11,620), 37,000 (22,000), 44,400 (39,700)
$(CH_2)_7$[d]	7500, 11,360, 17,350, 22,700

[a] Dichloromethane was the solvent unless noted otherwise. [b] Tetrachloroethylene solution. [c] Shoulder. [d] Reflectance spectrum of solid complex.

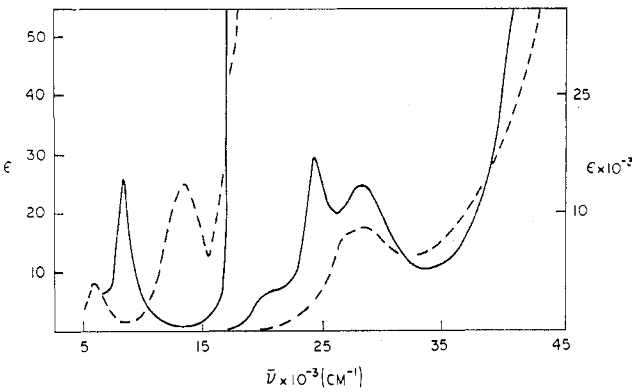

Figure 1.—Electronic absorption spectra of Co(3-*i*-prsal)$_2$N$_2$(CH$_2$)$_2$ (——) and Co(3-*i*-prsal)$_2$N$_2$(CH$_2$)$_3$ (- - -) in dichloromethane.

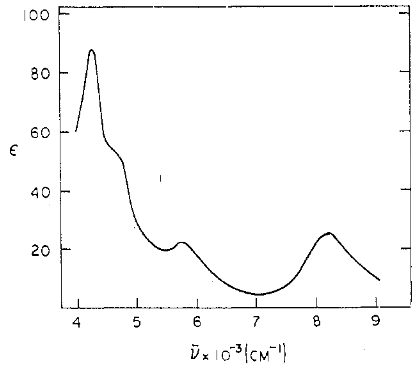

Figure 2.—Electronic absorption spectrum, in tetrachloroethylene, of Co(3-*i*-prsal)$_2$N$_2$(CH$_2$)$_2$ in the range 4000–9000 cm^{-1}.

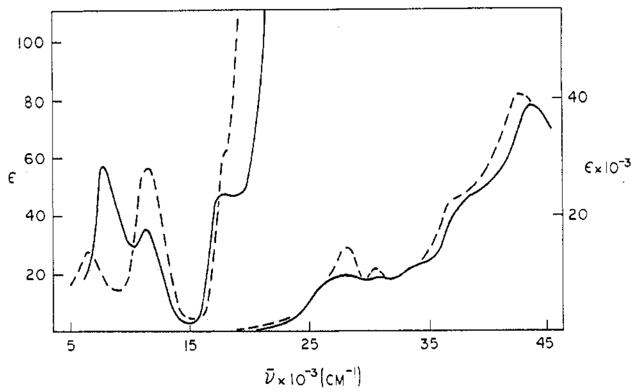

Figure 3.—Electronic absorption spectra of Co(3-*i*-prsal)$_2$N$_2$(CH$_2$)$_4$ (- - -) and Co(3-*i*-prsal)$_2$N$_2$(CH$_2$)$_6$ (——) in dichloromethane.

The electronic spectrum (Figure 1) and magnetic moment of the ethylene ($n = 2$) derivative in both the solid state and the nondonor solvents indicate that this complex contains low-spin cobalt(II) in a square-planar environment. The weak (ϵ 26) asymmetric absorption band at 8130 cm^{-1} is characteristic of a square-planar cobalt(II) species.[6,7,20] In addition to this distinctive near-infrared absorption band, the

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(20) G. W. Everett, Jr., and R. H. Holm, *J. Amer. Chem. Soc.*, **88**, 2442 (1966).

spectrum of Co(3-*i*-prsal)$_2$N$_2$(CH$_2$)$_2$ in tetrachloroethylene solution (Figure 2) and in the solid state (Fluorolube mull) reveals well-defined bands between 4000 and 7000 cm^{-1} which have not been reported previously for square-planar cobalt(II) complexes. The low intensities and narrow band widths of these bands suggest that they are spin-allowed d–d transitions. The corresponding nickel(II) complex, Ni(3-*i*-prsal)$_2$N$_2$(CH$_2$)$_2$, does not exhibit any absorption in this spectral region which precludes the assignment of these bands to overtones of ligand vibrational transitions. This observation of new low-energy bands suggests that an extensive revision of previous d–d transition assignments for square-planar cobalt(II)[6,7] is necessary. A proper assignment of these ligand field transitions cannot be made until the uncertainty regarding their ground-state electronic configuration[20] is resolved.

In contrast to Co(sal)$_2$N$_2$(CH$_2$)$_2$, the corresponding 3-isopropyl derivative exhibits an identical electronic spectrum in the solid state and in nondonor solvents. The significant differences in the solid-state (reflectance) spectrum and the nondonor solution spectrum of Co(sal)$_2$N$_2$(CH$_2$)$_2$ can be attributed to the fact that in the solid state the cobalt(II) ion is actually five-coordinate *via* intermolecular bridging.[21] In the case of Co(3-*i*-prsal)$_2$N$_2$(CH$_2$)$_2$, intermolecular bridging is effectively blocked by the presence of the bulky isopropyl groups ortho to the phenolic oxygens and the complex retains its square-planar geometry in the solid state. The alkyl substituents apparently prevent intermolecular association but do not interfere with axial coordination of solvent molecules which possess donor ability, *e.g.*, pyridine (*vide infra*).

The magnetic moment (2.35 BM) of Co(3-*i*-prsal)$_2$N$_2$(CH$_2$)$_2$ provides further evidence of its square-planar geometry. The magnetic moments of square-planar cobalt(II) complexes generally lie in the range 2.1–2.9 BM[19] and are attributed to the presence of one unpaired electron plus some orbital contribution. The essentially identical moments obtained for the $n = 2$ derivative in the solid state and in dichloromethane provide additional evidence for the unperturbed nature of this complex in both environments.

The higher members of the series ($n = 3$–7) are all high spin, with solid-state and solution magnetic moments within the generally accepted range for tetrahedral cobalt(II) complexes. The tetramethylene through the heptamethylene derivatives exhibit solid-state and nondonor solution spectra which are characteristic of pseudotetrahedral cobalt(II) complexes with salicylaldimine ligands.[8] The two bands observed between 6000 and 11,000 cm^{-1}, with ϵ 25–60, are assigned to low-symmetry components of the $^4A_2 \rightarrow {}^4T_1(F)$ tetrahedral d^7 transition. An additional band at $\sim$17,500 cm^{-1} is assigned to the $^4A_2 \rightarrow {}^4T_1(P)$ transition. The ligands with four to seven methylene groups in the central chelate ring apparently have sufficient flexibility to occupy essentially tetrahedral coordination positions about the cobalt(II) ion.

The trimethylene complex, Co(3-*i*-prsal)$_2$N$_2$(CH$_2$)$_3$, exhibits the same ligand field spectrum in the solid state and in dichloromethane. This spectrum is not in agreement with other pseudotetrahedral Schiff base cobalt(II) complexes but is identical with the solid-state spectrum reported[8] previously for *N,N'*-bis(salicylidene)trimethylenediaminocobalt(II). These identical electronic spectra indicate that the same stereochemistry prevails in the solid state for both the isopropyl and unsubstituted trimethylene derivatives. In the present study the monomeric nature (*vide supra*) of the isopropyl-substituted trimethylene derivative in nondonor solution rules out the production of a high-spin nature by intermolecular association. The stereochemistry of the trimethylene complexes must be rationalized on the basis of a four-coordinate cobalt(II) structure and two possibilities may be considered: a high-spin, square-planar geometry or a strongly distorted tetrahedral geometry. Although the high-spin, square-planar structure cannot be ruled out by the present study, the nature of the electronic spectrum and the increased flexibility of the trimethylene derivative, *vis à vis* the ethylene analog, favor a distorted tetrahedral stereochemistry. Whereas the ethylene derivative constrains the cobalt(II) ion within a square-planar array, the additional methylene group in the central chelate ring of the trimethylene derivative should allow sufficient flexibility so that the dihedral angle between the terminal chelate rings would be great enough to produce a quartet ground term. The dichloromethane solution spectra for the series of complexes with three to six methylene groups exhibit greater detail than the corresponding solid-state spectra and reveal a trend in the spectra as the size of the central chelate ring is increased. The separation of the two bands assigned to the low-symmetry components of the $^4A_2 \rightarrow {}^4T_1(F)$ transition decreases systematically from 6000 to 1500 cm^{-1} upon expanding the central chelate ring from three to six methylene groups. This decreased splitting indicates a diminishing distortion from tetrahedral symmetry for this series of complexes. The trimethylene derivative, which is strongly distorted toward a planar geometry, exhibits significantly lower ϵ_{max} values for the d–d transitions than the higher homologs in which any inversion center is effectively removed *via* the pseudotetrahedral geometry.

The alternative possibility for the trimethylene derivative, *i.e.*, a high-spin planar geometry, represents a less likely explanation for the high-spin nature of this complex. For this explanation to be valid, the donor atoms of the trimethylene ligand must occupy essentially coplanar positions about the cobalt(II) ion and the ligand field must be weak enough to permit a decoupling of the electron spins. The decrease in ligand field strength of tetradentate Schiff bases upon lengthening the central chelate ring is consistent with the above requirements, but the increased flexibility of the ligand weakens this possibility.

The presence of an equilibrium between quartet and doublet ground terms depending on either a structural interconversion between high-spin tetrahedral and low-spin planar forms or a simple spin-state equilibrium between high- and low-spin forms of the same geometry has been excluded by temperature-dependent magnetic moment studies. Neither the trimethylene or tetramethylene derivatives show any significant decrease in their magnetic moments down to −80° in dichloromethane solution.

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TABLE IV

ELECTRONIC SPECTRA OF THE CHELATES $Co(3\text{-}i\text{-}prsal)_2N_2(R)$ IN PYRIDINE

R	$\bar{\nu}_{max}$, cm^{-1} (ϵ_{max})
$(CH_2)_2$	7400 (20),[a] 13,700 (20),[a] 16,950 (810),[a] 21,000 (4000), 28,000 (10,500)
$(CH_2)_3$	7580 (12), 10,150 (13), 15,150 (10), 27,000 (10,000)
$(CH_2)_4$[b]	9800, 17,600, 27,400
$(CH_2)_5$	10,000 (12), 17,860 (28), 27,800 (15,400)
$(CH_2)_6$	10,000 (10), 17,500 (20), 28,000 (10,900)
$(CH_2)_7$	10,000 (10), 16,800 (16), 27,200 (18,000)

[a] Shoulder. [b] Reflectance spectra data for a solid derivative.

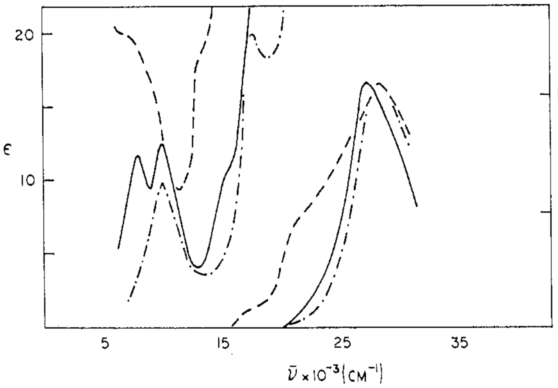

Figure 4.—Electronic absorption of spectra of $Co(3\text{-}i\text{-}prsal)_2N_2(CH_2)_2$ (– – –) in pyridine–dichloromethane and $Co(3\text{-}i\text{-}prsal)_2N_2(CH_2)_3$ (——) and $Co(3\text{-}i\text{-}prsal)_2N_2(CH_2)_6$ (-·-·-·-) in pyridine. Solvent cutoff is more apparent for the $Co(3\text{-}i\text{-}prsal)_2N_2(CH_2)_2$ derivative since a 10-cm cell was used.

Pyridine Solution Properties.—In pyridine solution, the entire series of complexes exhibits high-spin behavior with magnetic moments (Table II) within the expected range for pseudooctahedral cobalt(II) species.[22] The pyridine solution spectra (Table IV, Figure 4) provide additional evidence for the existence of six-coordinate Co(II) species in this solvent. The higher homologs, $n = 4$–7, exhibit pyridine spectra identical with the corresponding spectra obtained for certain bis-bidentate salicylaldiminocobalt(II) chelates which have been reported to yield high-spin octahedral species in donor solvents.[9a,23] The two low-energy bands observed in these spectra at ~10,000 and ~17,000 cm^{-1} may be assigned to the $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions, respectively. These data are consistent with the addition of pyridine donors to the vacant coordination sites of the tetradentate chelates with no displacement of the Schiff base ligands. Esr evidence for the formation of adducts with several Co(II) chelates (*vide infra*) and the isolation of a pyridine adduct of the tetramethylene derivative of the present series support the conclusion that the tetradentate coordination of the Schiff base is maintained in pyridine solution.

The electronic spectrum of the trimethylene derivative in pyridine (Table IV and Figure 3) is also similar to pseudooctahedral Co(II) spectra, except that the lowest energy transition consists of two components separated by ~2600 cm^{-1}. It is likely that the trimethylene complex only allows the coordination of pyridine in trans positions, and the observed splitting is attributed to the pronounced tetragonal nature of this species similar to that suggested for $Co(sal)_2N_2(CH_2)_3 \cdot 2H_2O$.[3] The d–d spectrum of the high-spin species present in pyridine solutions of $Co(3\text{-}i\text{-}prsal)_2N_2(CH_2)_2$ is partially obscured by solvent (pyridine–dichloromethane) absorption at <6000 cm^{-1} and the presence of an intense band at ~17,000 cm^{-1}. Two weak shoulders are observed (Figure 4) and are tentatively assigned as tetragonal components of the $^4T_{1g} \rightarrow {}^4T_{2g}(F)$ transition. This proposed tetragonal splitting for the $n = 2$ derivative (~6000 cm^{-1}) is considerably larger than that observed for the trimethylene complex but may be reconciled by the greater disparity between the in-plane ligand field strength of the ethylene ligand and the axial pyridine donors.

The nature of the ethylene derivative in pyridine solution is in marked contrast to the behavior exhibited by other low-spin, square-planar Co(II) chelates in donor solvents. Cobalt(II) phthalocyanine,[24] cobalt(II) porphyrin,[25] $Co(acac)_2en$,[11c,26] $Co(aba)_2en$,[26,27] and $Co(dmg)_2$[26,28] all maintain low-spin character in donor solvents. Esr studies[11c] reveal that only one pyridine interacts with the complex $Co(acac)_2en$ in frozen toluene solutions to produce a low-spin, square-pyramidal species. For cobalt(II) phthalocyanine,[24] cobalt(II) porphyrin,[25] and $Co(dmg)_2$,[28] the multiplicity of the nitrogen superhyperfine splittings in frozen glasses containing pyridine reveal that two pyridine donors are axially coordinated, producing spin-paired, six-coordinate Co(II) complexes. The proposed formation of a high-spin, bis-pyridine adduct with the ethylene derivative is also at variance with the low-spin, square-pyramidal species $Co(sal)_2N_2(CH_2)py$.[13,14]

The observed behavior of the ethylene derivative in pyridine cannot be rationalized on the basis of steric interactions. All of the Co(II) chelates which maintain a low-spin nature in donor solvents present less steric inhibition to axial coordination than does the 3-isopropylsalicylaldehyde derivative. The anomalous high-spin behavior of $Co(3\text{-}i\text{-}prsal)_2N_2(CH_2)_2$ in pyridine solution apparently arises from electronic factors. The ligand $(3\text{-}i\text{-}prsal)_2N_2(CH_2)_2$ is presumably a weaker donor than the other ligands which have been studied and cannot stabilize a spin-paired configuration as effectively as stronger in-plane ligands. Weak axial interaction with additional donors is able to produce a high-spin species more readily with $Co(3\text{-}i\text{-}prsal)_2N_2(CH_2)_2$.

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[26] Abbreviations used: $(Hacac)_2en$, *N,N'*-bis(2-pent-2-en-4-ono)ethylenediamine; $(Haba)_2en$, *N,N'*-bis(*o*-aminobenzylidene)ethylenediamine; Hdmg, dimethylglyoxime.

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