latter exerts a slightly stronger nephelauxetic effect;[59] hence slightly greater electron transmission to the ligand might be expected. A part of this difference may also arise from dihedral angle origins; the six-membered ring axial proton has an Ni-N-C-H angle (70°) more conducive to electron delocalization than that of its Ni(en)$^{2+}$ analog which was found to be 80°. At the same time, the equatorial proton of Ni(tn)$^{2+}$ also has a more favorable orientation for spin transmission. The conformational dependence elucidated for ^{4}A coupling in the six-membered chelate rings in this paper suggests the possibility of another source for some of the large observed difference. By virtue of the ring structure in Ni(en)$^{2+}$ each α proton can be visualized to experience electron delocalization from the nickel atom through each nitrogen atom, *i.e.*, *via* an ^{3}A and an ^{4}A coupling route. Our data indicate that these coupling paths will produce oppositely sensed spins at the proton nucleus and may produce some coupling decrease by a net cancelation effect. The Ni(tn)$^{2+}$ structure, on the other hand, would provide ^{3}A and ^{5}A coupling contributions for its α protons and purely ^{4}A coupling at the β proton nuclei. The α proton shifts would then be virtually fully determined by ^{3}A coupling, the influence of ^{5}A interaction (also negative on spin-polarization grounds) expected to be greatly diminished. Multipath coupling considerations would then predict an α proton in Ni(en)$^{2+}$ to exhibit slightly less contact shift than Ni(tn)$^{2+}$, all other factors being equal. In view of the substantial ^{4}A coupling for Ni(tn)$^{2+}$ demonstrated here, Cramer's recent HMO analysis[60] of Ni(*N*-Meen)$^{2+}$ proton contact shifts which neglected multipath coupling may require further consideration. It is noteworthy that such multipath coupling schemes are supported by theoretical calculations (INDO) for carbon-13 internuclear coupling in cyclic organic systems.[61] The enhanced magnitude of electron-nuclear coupling in these nickel(II) systems makes them extremely attractive as models for such phenomena.

The contact shift information for six-membered ring chelates presented here can prove exceedingly useful in conformational studies. For example, the proton nmr spectrum of the 1:1 nickel(II)-histidine system reported by Milner and Pratt[2] can be reinterpretated. From their spectrum and resonance assignment which seems correct, it appears likely that the ligand is bound in a tridentate fashion requiring the six-membered ring formed between the nitrogen donors to be rigidly maintained. This structure can account for the large shift obtained for the glycinate methine proton and the upfield appearance of two distinct resonances for the methylene group.

Acknowledgments. The authors are greatly indebted to Professor Ernest Eliel for a number of helpful discussions and suggestions, as well as the donation of generous amounts of several diamines used in this study. The financial support of the National Institutes of Health (Grant GM-12598) and the National Science Foundation (Grant GP-30692) is gratefully acknowledged.

Registry No. Ni(tn)$^{2+}$, 24669-45-2; Ni(1,3-Me$_2$tn)$^{2+}$, 50601-08-6; Ni(1-Metn)$^{2+}$, 50601-09-7; Ni(2,2-Me$_2$tn)$^{2+}$, 50601-10-0; Ni(*N*-Metn)$^{2+}$, 50601-11-1; Ni(2-Ettn)$^{2+}$, 50790-64-2; Ni(tn)$_2{}^{2+}$, 45843-82-1; Ni(tn)$_3{}^{2+}$, 18347-71-2; Ni(*rac*-1,3-Me$_2$tn)$_2{}^{2+}$, 50600-58-3.

[59] O. Bostrup and C. K. Jorgensen, *Acta Chem. Scand.*, 11, 1223 (1957).

[60] R. E. Cramer, *Inorg. Chem.*, 11, 1019 (1972).

[61] A. K. Jameson, presented at First Rocky Mountain Regional Meeting of the American Chemical Society, Fort Collins, Colo., July 1972; see Abstracts, No. Physical-17.

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Synthesis and Reactivity of Five-Coordinate Nickel(II) and Copper(II) Complexes with a Pentadentate Ketoamine Ligand

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A general method for the synthesis of hitherto unreported pentadentate fluorinated Schiff base ligands is presented. Two new five-coordinate metal complexes, Ni(tfacDPT) and Cu(tfacDPT), where H$_2$(tfacDPT) is the pentadentate Schiff base derived from trifluoroacetylacetone and bis(3,3′-aminopropyl)amine, have been prepared and characterized by various physical techniques. Data for the Cu(II) complex indicate that it is square pyramidal while electronic spectra for the high spin Ni(II) complex suggest that it may possess a geometry intermediate between square pyramidal and trigonal bipyramidal. Ni(tfacDPT) coordinates with pyridine to produce a pseudooctahedral adduct, Ni(py)(tfacDPT), which releases pyridine *in vacuo* or on gentle heating of the complex.

Introduction

While numerous five-coordinate transition metal complexes have been described in recent years, only a limited number have contained linear pentadentate ligands.[1,2] The most common ligands of this type are Schiff bases derived from substituted salicylaldehydes[3,4] or 2-pyridinecarboxaldehyde[5] and tridentate polyamines. Until now, no complexes containing pentadentate ketoamine ligands have been reported although many with tetradentate[6] and a few with sexadentate ketoamine ligands[7,8] have been well studied.

[1] L. Sacconi, *Transition Metal Chem.*, 4, 199 (1968).

[2] C. Furlani, *Coord. Chem. Rev.*, 3, 141 (1968).

[3] L. Sacconi and I. Bertini, *J. Amer. Chem. Soc.*, 88, 5180 (1966).

[4] W. M. Coleman and L. T. Taylor, *J. Amer. Chem. Soc.*, 92, 1449 (1970); 93, 5446 (1971); *Inorg. Chem.*, 10, 2195 (1971).

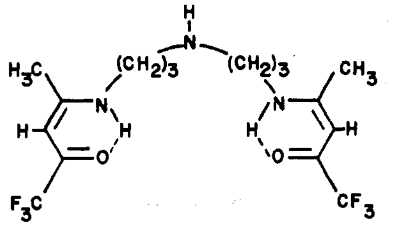
[5] C. T. Spencer and L. T. Taylor, *Inorg. Chem.*, 10, 2407 (1971).

[6] R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, *Progr. Inorg. Chem.*, 7, 83 (1966), and references therein.

[7] F. Lions and K. V. Martin, *J. Amer. Chem. Soc.*, 80, 3858 (1958).

[8] S. C. Cummings and R. E. Sievers, *Inorg. Chem.*, 11, 1483 (1972).

Work in our laboratory has shown that ketoamine ligands and metal complexes derived from fluorinated β-diketones and polyamines are more easily isolated than those with nonfluorinated β-diketones.[8] We now report our studies of neutral five-coordinate nickel(II) and copper(II) complexes containing the doubly condensed linear pentadentate Schiff base (I) derived from trifluoroacetylacetone, tfac, and bis(3,3′-aminopropyl)amine, DPT.[9]



I

Experimental Section

Ligand Synthesis. A solution of 154 g (1.0 mol) of freshly distilled tfac in 300 ml of absolute methanol was chilled to 20° in an ice bath. To this was slowly added with stirring 65.5 g (0.5 mol) of DPT which had been diluted with 200 ml of methanol. Heat was evolved and the solution turned yellow. The solution was heated to ~30° and stirred for 0.5 hr after which it was slowly added to 3 l. of water. The cloudy solution which resulted was concentrated under an air stream and white crystals of H_2(tfacDPT) which formed were collected and recrystallized from 2,2-dimethoxypropane; yield, ~30%. *Anal.* Calcd for $C_{16}H_{23}N_3O_2F_6$: C, 47.63; H, 5.76; N, 10.42; O, 7.93; F, 28.26; mol wt, 403.4. Found: C, 47.89; H, 5.44; N, 10.63; O, 7.87 (diff); F, 28.17; mol wt ($CHCl_3$), 395. This procedure can be adapted to other pentadentate fluorinated Schiff bases by varying the tridentate polyamine. For example, H_2-(tfacdien) has been prepared by substituting dien for DPT. The two ligands are similar in all respects except for the presence of two extra bridging methylene groups in the former.

Preparation of Ni(tfacDPT). A 4.03-g sample (0.01 mol) of the ligand dissolved in 50 ml of DMF was added slowly with stirring to 2.48 g (0.01 mol) of $Ni(OAc)_2 \cdot 4H_2O$ dissolved in 200 ml of DMF. The resulting solution was refluxed for 3 hr and then taken to dryness on a rotary evaporator. Ether (about 200 ml) was added and a small amount of insoluble residue was removed by filtration. The ether was evaporated and the green syrup which remained was added slowly to 300 ml of water. The green precipitate which formed was isolated and recrystallized from acetonitrile and then from methanol; yield, ~25%. *Anal.* Calcd for $Ni(C_{16}H_{21}N_3O_2F_6)$: C, 41.77; H, 4.60; N, 9.13; O, 6.95; F, 24.78; Ni, 12.76; mol wt, 460.1. Found: C, 41.93; H, 4.51; N, 9.22; O, 6.94 (diff); F, 24.67; Ni, 12.55; mol wt ($CHCl_3$), 452.

Preparation of Cu(tfacDPT). The copper(II) complex was prepared in the manner reported above except that 1.99 g (0.01 mol) of $Cu(OAc)_2 \cdot H_2O$ was used. The purified complex was obtained as light green crystals. *Anal.* Calcd for $Cu(C_{16}H_{21}N_3O_2F_6)$: C, 41.34; H, 4.55; N, 9.04; O, 6.88; F, 24.52; Cu, 13.67; mol wt, 464.9. Found: C, 41.24; H, 4.55; N, 9.03; O, 6.88 (diff); F, 24.30; Cu, 13.66; mol wt ($CHCl_3$), 455.

Preparation of Ni(py)(tfacDPT). A 0.46-g sample (0.001 mol) of Ni(tfacDPT) was dissolved in 50 ml of pyridine. Water was added to the brown solution until it turned cloudy. The mixture was concentrated under an air stream and the brown precipitate which formed was isolated by filtration and dried on the filter; yield, ~100%. *Anal.* Calcd for $Ni(C_{21}H_{26}N_4O_2F_6)$: C, 46.77; H, 4.87; N, 10.39; O, 5.93; F, 21.14; Ni, 10.89. Found: C, 47.04; H, 4.79; N, 10.58; O, 4.28 (diff); F, 21.97; Ni, 11.34.

Physical Measurements. Infrared spectra were obtained on a Perkin-Elmer Model 457 ir spectrophotometer. Both KBr and Nujol mull techniques were used. Visible and uv spectra were measured with a Cary 14 recording spectrophotometer. Both solution and diffuse transmittance techniques were utilized. Magnetic susceptibility measurements were obtained by the Faraday method. Pascal's constants were used to correct for the diamagnetism of the ligand. Proton nmr spectra were recorded on a Varian A-60 nmr spectrometer in deuteriochloroform with TMS as the internal standard. Chemical analyses and molecular weight data were provided by Alfred Bernhardt, Mikroanalytisches Laboratorium, Elbach, West Germany.

Results and Discussion

Synthesis and Characterization. The synthesis of the pentadentate ligand involves the addition of 1 equiv of DPT to 2 equiv of tfac. The β-diketone is kept in excess throughout the addition to promote formation of the doubly condensed Schiff base. Results of elemental analyses and molecular weight measurements are consistent with this formulation. The 60-MHz pmr spectrum of the free ligand in deuteriochloroform indicates that the methyl groups are equivalent and adjacent to the diamine bridge as reported for the similar sexadentate ligand.[8] Sharp singlets at 2.05, 5.10, and 11.20 ppm with relative intensities of 6:2:1 are assigned to the CH_3, =CH, and backbone NH protons, respectively. The bridging methylene protons give rise to a multiplet at 1.70-3.64 ppm. The presence of a sharp singlet attributable only to the vinylic protons eliminates the possibility of a ketoimine structure while the presence of a broad absorption at 3130 cm^{-1} in the infrared spectrum assigned to a hydrogen-bonded amino group indicates that the best structure for the ligand is the ketoamine form shown in I. Other characteristic bands in the ir spectrum occur at 3340 cm^{-1} (assigned to the backbone NH stretching vibration) and at 1620 and 1585 cm^{-1} (assigned to the C=O and/or C=C stretching modes).

Ni(tfacDPT) and Cu(tfacDPT) are formed when the ligand reacts with the metal acetates in DMF. Isolation is accomplished with some difficulty due to the tendency of the crude products to form a tar, but crystals of each complex can be obtained upon recrystallization from acetonitrile and methanol.

Elemental analyses, molecular weight measurements, and conductivity studies (both complexes are nonelectrolytes in methanol with Λ_M of 5 ($mhos\ cm^2$)/mol) suggest that the pentadentate Schiff base coordinates as a dinegative ligand on both metal ions. Each of the new complexes is soluble in slightly polar organic solvents including ether, chloroform, and alcohols but insoluble in water. These solubility characteristics are also consistent with a neutral formulation. The infrared spectra of Ni(tfacDPT) and Cu(tfacDPT) are very similar to one another and exhibit strong absorptions at 3290, 1620, and 1545 cm^{-1} which are assigned to the coordinated NH and the C$\overset{...}{=}$N and C$\overset{...}{=}$C stretching vibrations. In addition, very strong bands in the 1200-1100-cm^{-1} region confirm the presence of the CF_3 groups. Ni(tfacDPT) is high spin with μ_{eff} = 3.05 BM, while Cu(tfacDPT) has a moment of 1.77 BM. Although these values are slightly lower than those expected, they are consistent with a five-coordinate environment around the metal ion. Electronic spectral measurements provide the most convincing proof of metal ion geometry. Both the solid state and methanol solution spectra are essentially the same, which indicates no change in coordination geometry due to solvent interactions. The methanol solution spectra are listed in Table I. The spectrum of Cu(tfacDPT) shows a low energy band at 12,422 cm^{-1} which correlates well with that found at 12,700 cm^{-1} (ϵ ~259) for $Cu(dienMe)Cl_2$ which has been described as a distorted square pyramid.[10] Since trigonal bipyramidal Cu(II) characteristically shows two bands, *e.g.*, [Cu(trenMe)Br]Br exhibits bands at 10,400 (ϵ ~49) and 13,300 cm^{-1} (ϵ ~209),[10] the square pyramidal structure

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(9) Taken in part from the M.S. thesis of W. N. Wallis, Wright State University, August 1972.

(10) M. Ciampolini and N. Nardi, *Inorg. Chem.*, 5, 41 (1966).

Table I. Electronic Absorption Spectra of Cu(tfacDPT) and Ni(tfacDPT) in Methanol

Complex	Absorption bands[a] (ϵ)
Cu(tfacDPT)	12,422 (245) 26,490[b] (512) 33,333 (15,250) 35,840[b] (11,700) 42,020 (10,750)
Ni(tfacDPT)	8,928 (14) 10,100[b] (11) 11,834[b] (6) 16,528 (29) 32,520 (11,020) 40,816 (15,850)

[a] Frequencies reported in cm^{-1}. [b] Shoulder.

for Cu(tfacDPT) seems most probable. The spectrum of Ni(tfacDPT) exhibits absorptions which are intermediate between those reported for complexes with the two limiting geometries, *i.e.*, square pyramidal and trigonal bipyramidal, as can be seen from the spectra illustrated in Figure 1. The trend in molar absorptivities agrees best with the spectrum of square pyramidal Ni(II), and molecular models of Ni(tfacDPT) show that ring strain may be somewhat less for the trans square pyramidal model. Change in visible spectrum with pressure has sometimes been useful in distinguishing between different five-coordinate geometries,[11] but the structure can be determined with certainty only from single-crystal X-ray diffraction techniques. The structure of Ni(tfacDPT) may actually be intermediate between the two regular geometries as is the case for Ni(salMeDPT).[12] Indeed, the visible spectrum of Ni(tfacDPT) agrees very closely with that reported for Ni(salMeDPT) which exhibits absorptions at 8,400, 10,000, 12,800, and 16,800 cm^{-1} in the d-d region.[13]

Reactivity. In an earlier study we have shown that the Ni(II) complex which contains the linear sexadentate fluorinated Schiff base derived from tfac and trien rearranges under acidic conditions to yield a complex with a macrocyclic tetradentate ligand, Figure 2.[8] The coordinated pentadentate ligand reported here exhibits no tendency to rearrange in acid over a pH range of 2-7, and no Ni(II) complexes with macrocyclic tridentate ligands have been isolated. This is not too surprising since complexes with planar tetradentate macrocyclic ligands are often more stable than those with ligands of lesser or greater numbers of donor atoms which must adopt higher energy folded configurations on one or more faces of the metal polyhedron.

Since these new five-coordinate complexes are coordinately unsaturated, they are expected to be very reactive toward adduct formation. Indeed, a change in coordination number of the Ni(II) ion does occur when Ni(tfacDPT) is dissolved in pyridine. This is accompanied by a change in color from green to brown. Elemental analyses on the brown solid which has been isolated from this reaction agree with formation of a 1:1 pyridine adduct, Ni(py)(tfacDPT). Although the higher energy ir active pyridine absorptions are obscured by bands in the spectrum of the parent complex, bands at 755 and 700 cm^{-1}, characteristic of coordinated pyridine, are observed in the infrared spectrum of Ni(py)(tfacDPT). A magnetic moment for the adduct could not be determined accurately because the complex loses pyridine under conditions of reduced pressure used in the measurement; however, the nickel is definitely high spin with a $\mu_{\mathrm{eff}} \simeq 3.1 \pm 0.2$ BM. The pyridine can also be removed by gentle warming of the complex, and weight loss studies confirm the 1:1 ratio of pyridine to metal complex. The electronic spectrum of the complex measured in pyridine gives bands which are typical of pseudooctahedral Ni(II) with absorption maxima at 11,230 (10), 18,115 (14), and 32,000 (13,100) cm^{-1}. The first two bands are assigned to the $^3T_{2g} \leftarrow {}^3A_{2g}$ and $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ transitions. The high intensity of the third band indicates that it must be a charge transfer transition which obscures the third d-d band. The proposed structures of the parent Ni(II) complex (distorted square pyramidal) and pyridine adduct (pseudooctahedral) are shown in II and III.

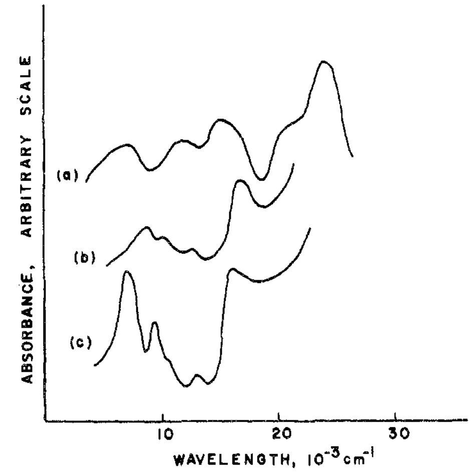


Figure 1. Visible spectrum of (a) $[\mathrm{Ni(Me_6tren)Br}]\mathrm{Br}$, trigonal bipyramidal, and (b) Ni(tfacDPT) and (c) $\mathrm{Ni(salen\text{-}NEt_2)_2}$, square pyramidal. All but b are taken from ref 2, pp 152 and 162.

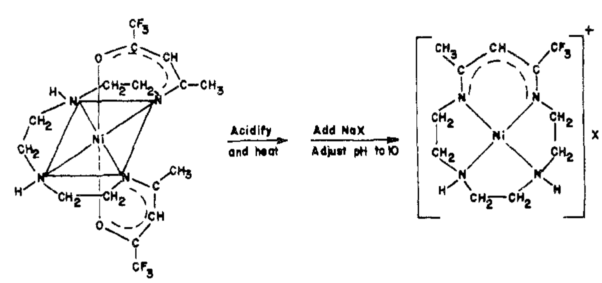
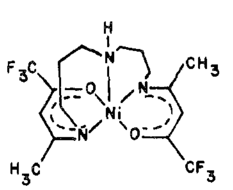
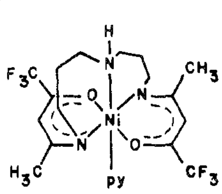


Figure 2. Rearrangement of the pseudooctahedral Ni(II) complex to form the tetradentate macrocycle (the trans isomer is shown arbitrarily).



II



III

We expect Ni(tfacDPT) and its Co(II) analog to form adducts with other small covalent molecules such as oxygen. We favor the trans over the cis structure for II and III due to the similarity of these compounds to Ni(salMeDPT) which has been shown to exist in the trans form.[12]

While five-coordinate Ni(II) and Cu(II) complexes of $\mathrm{H_2(tfacDPT)}$ have been prepared and characterized, no five-coordinate complexes containing the pentadentate ligand derived from tfac and diethylenetriamine could be isolated, although the $\mathrm{H_2(tfacdien)}$ ligand is easily prepared by the

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(11) J. R. Ferraro, D. W. Meek, E. C. Siwiec, and A. Quattrochi, *J. Amer. Chem. Soc.*, **93**, 3862 (1971).

(12) M. Di Vaira, P. L. Orioli, and L. Sacconi, *Inorg. Chem.*, **10**, 553 (1971).

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procedure reported here. This may be attributed to the short length of the bridging groups in the amine backbone which precludes wrapping of the ligand around all five coordination sites. Similar behavior has been noted for pentadentate Schiff bases derived from salicylaldehyde.[4] Instead, square-planar Ni(II) and Cu(II) complexes which contain singly condensed, unsymmetrical Schiff base ligands have been obtained from H_2(tfacdien) as a result of partial hydrolysis of the pentadentate ligand. This unusual reaction and others are discussed in the paper which follows.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Registry No. H_2(tfacDPT), 50599-75-2; Ni(tfacDPT), 50600-59-4; Cu(tfacDPT), 50600-60-7; Ni(py)(tfacDPT), 50600-61-8; tfac, 367-57-7; DPT, 56-18-8.

Contribution from the Department of Chemistry,
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Square-Planar Nickel(II) and Copper(II) Complexes with Unsymmetrical Anionic Tetradentate Schiff Base Ligands

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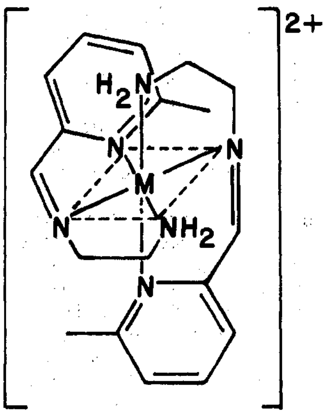
Received July 30, 1973

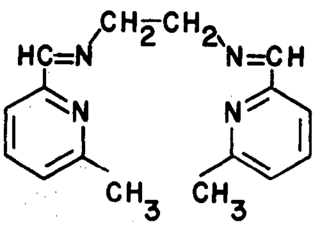
Eight new square-planar Ni(II) and Cu(II) complexes with unsymmetrical anionic singly condensed Schiff base ligands derived from acac, tfac, and dien have been prepared and characterized as I^- and PF_6^- salts. Formation of the complexes has been achieved by reaction of the metal hydroxides with singly condensed ligand salts or with doubly condensed pentadentate Schiff bases. The latter method involves a most unusual partial hydrolysis of the Schiff base ligand. While the mechanism of this reaction is unclear, the role of the metal ion may be to sequester the tetradentate ligand and render it inactive to further hydrolysis.

Introduction

Over the past 100 years, numerous transition metal complexes with β-ketoamine and salicylaldimine ligands have been prepared,[1] but only a very few of the ligands reported have been derived from carbonyl compounds and linear polyamines which have undergone condensation at only one end of the amine. This can be attributed to the difficulties encountered in preparing these types of unsymmetrical ligands by the usual condensation procedures. For example, addition of 1 equiv of acetylacetone to 1 equiv of ethylenediamine in an appropriate solvent followed by the usual method of isolation[2] produces lower yields of *N,N'*-ethylenebis(acetylacetonimine) instead of the singly condensed product. For this reason, workers interested in preparing the unsymmetrical monosubstituted Schiff base ligand have used N-substituted alkyl- or arylethylenediamines whose structures preclude reaction at the secondary or tertiary amine end of the molecule.[3,4] Most ligands which have been reported are tridentate chelating agents which have been prepared by condensation of various substituted salicylaldehydes with the aforementioned diamines. Complexes containing these uninegative ligands are of interest since they can exhibit four, five, or six coordination depending upon the nature of the nitrogen and salicylaldehyde substituents.[3-6] No singly condensed Schiff base ligands prepared from β-diketones appear to have been studied, although one very interesting complex has been reported (I), where M(II) is Cu or Fe and the neutral tridentate ligand results from partial hydrolysis of the tetradentate Schiff base derived from 6-methylpyridine-2-aldehyde and ethylenediamine (II) in the presence of the metal ions.[7]



I



II

While the presence of metal ions is known to catalyze the hydrolytic cleavage of some Schiff bases, a partial hydrolysis of this type must be considered unusual.[8-10]

During our investigations of complexes with pentadentate Schiff base ligands derived from various β-diketones and tridentate polyamines,[11] we have discovered that partial hydrolysis of the pentadentate ligands occurs with ease. We have improved the procedure involved in this unusual reaction so that it now provides a convenient method for the synthesis of unsymmetrical, singly condensed tetradentate ketoamines.

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(1) R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, *Progr. Inorg. Chem.*, 7, 83 (1966), and references therein.

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