Table VI. Characteristic COO⁻ Frequencies (cm⁻¹)

compd	ν_a^- (COO⁻)	ν_s^- (COO⁻)	Δ
$C_4H_4O_4$	1590	1432	158
$Zr(OH)_3(OOCCH=CHCOOH)$	1565	1441	124
$C_8H_8O_4$	1684	1403	281
$Zr(OH)_3(OOCC_6H_4COOH)$	1546	1415	131

There is a very close similarity in the position of ν_a(COO⁻) and ν_s(COO⁻) in complex I and in the free maleic acid. The position of these bands could indicate that, besides coordinated carboxyl group, also the uncoordinated one is present at the same time. The same was observed with complex II. Further, the separation of ν_a(COO⁻) − ν_s(COO⁻) in this complex is comparable to that in the free ligand (Table VI).

In the case of acetic acid,[18] oxydiacetate,[19,20] and methoxyacetate[21] complexes, it has been found that the same separation is comparable to that existing in the free ligand, when the carboxyl group acts as a bridge between the two metal atoms. If this result can be applied also in the case of complexes with dicarboxylic acids, then it seems reasonable to conclude that the coordinated COO⁻ group in complex I could be a bridge between the two zirconium atoms, raising the coordination number of zirconium and providing the polymeric nature of this complex.

In the absorption spectrum of complex II, in addition to the strong absorption band at 1546 cm⁻¹, there is a nicely resolved band at 1695 cm⁻¹ corresponding very likely to the uncoordinated carboxyl group. The separation between the asymmetric and symmetric stretching frequencies of the coordinated COO⁻ group is smaller than that in the free phthalic acid (Table VI) but greater than 100 cm⁻¹. For the carboxyl group acting as a bidentate ligand toward the same metal atom, this separation was found to be smaller than 100 cm⁻¹.[18] This result suggests the bridging of the COO⁻ group in both complexes: complex I and complex II.

Inspection of the infrared spectra in the region 1050–800 cm⁻¹ shows that these complexes do not exhibit the absorption band corresponding to Zr=O vibrations, which was found earlier in the spectrum of ZrOCl₂ salt prepared from nonaqueous solvents.[22]

Furthermore, infrared spectra are not so explicit in differentiating OH from O bridges between the two metal atoms. In the spectra of these complexes in the region 800–625 cm⁻¹, there is a band of medium intensity that could represent OH bridges in these complexes.

According to physical and infrared spectral data, we are inclined to conclude that (a) both complex I and complex II are polymeric in nature, (b) the polymerization occurs either through a COO⁻ group or through OH bridges or through both of them, and (c) this polymerization is responsible for the amorphous nature and the insolubility as strong as that observed.

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High-Spin, Five-Coordinate Complexes of Cobalt(II), Nickel(II), and Copper(II) with Linear, Pentadentate Keto Iminato Ligands

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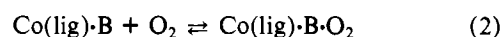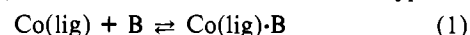
Over 35 transition-metal complexes of Ni(II), Co(II), and Cu(II) with pentadentate Schiff base ligands derived from various β-diketones (Hacac, Htfac, Hbenac, and *p*-XHbenac) and triamines (DPT, MeDPT, and PhDPT) have been isolated and characterized. All of the Ni(II) and Co(II) complexes are high-spin, five-coordinate species with average μ_{eff} values of 3.3 and 4.3 μ_B, respectively. The Cu(II) complexes have experimental μ_{eff} values of ~1.9 μ_B. Visible spectral results on all samples and EPR studies on the Cu(II) complexes indicate that the new compounds are five-coordinate with geometries intermediate between TBP and SP. The Co(II) derivatives bind dioxygen reversibly in solution.

Introduction

Over the past several years, we have been studying the oxygen reactivity of Co(II) complexes containing tetradentate keto iminato and thio iminato ligands.[1-3] Work in our laboratory as well as in several others[4] has shown that bonding of dioxygen by such complexes in low-temperature solutions involves activation of the metal ion with a Lewis base to form a five-coordinate precursor (eq 1) followed by dioxygen coordination (eq 2). One obvious drawback to these types of systems is that the excess Lewis base normally used in the

$$Co(lig) + B \rightleftharpoons Co(lig) \cdot B \qquad (1)$$

$$Co(lig) \cdot B + O_2 \rightleftharpoons Co(lig) \cdot B \cdot O_2 \qquad (2)$$
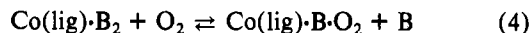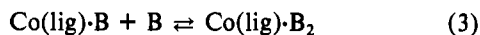
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studies may compete with dioxygen for coordination to the metal ion in the sixth site, thus complicating the equilibria involved, e.g., eq 3 and 4. While reactions 3 and 4 appear

$$Co(lig) \cdot B + B \rightleftharpoons Co(lig) \cdot B_2 \qquad (3)$$

$$Co(lig) \cdot B_2 + O_2 \rightleftharpoons Co(lig) \cdot B \cdot O_2 + B \qquad (4)$$

to be relatively unimportant in most systems,[4] our EPR studies on Co(*p*-Xbenacen) complexes, where X = Cl, Br, CH₃, and CH₃O, indicate the presence in solution of some of the bis-(pyridine) adduct.[5,6]

In order to circumvent these problems and to broaden our understanding of synthetic oxygen carriers, we decided to study the corresponding pentadentate (keto iminato)cobalt(II) systems in which the Lewis base needed is incorporated into the polydentate Schiff base backbone. This paper deals with the synthesis and characterization of the required penta-coordinate Co(II) complexes as well as some Ni(II) and Cu(II) species. A later publication will emphasize the oxygenation work.[7]

Pentacoordinate Schiff base complexes derived from linear tridentate polyamines and salicylaldehydes,[8-11] 2-pyridine-carboxaldehyde,[12] and 2-hydroxyaceto- and 2-hydroxybenzo-phenones[13-15] have been thoroughly investigated. Similar studies with keto amine ligands have been complicated by the fact that these pentadentate ligands tend to undergo metal ion-assisted hydrolysis in the presence of even minute amounts of water. The synthesis of Ni(II) and Cu(II) complexes with fluorinated keto amine ligands was first accomplished in our laboratory and reported in 1974.[16] During the interim we have developed methods for the synthesis of over 35 different five-coordinate complexes of Cu(II), Ni(II), and Co(II). These complexes contain the linear pentadentate keto amine ligands illustrated in structure **I**. Details of the syntheses and physical properties of the complexes are reported herein.[17]

I
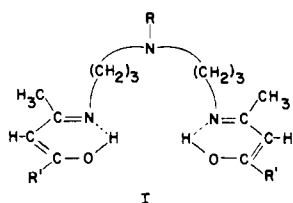
Ia: R = H, R' = CF₃ (H₂(tfacDPT))
 b: R = CH₃, R' = CF₃ (H₂(tfacMeDPT))
 c: R = C₆H₅, R' = CF₃ (H₂(tfacPhDPT))
 d: R = H, R' = CH₃ (H₂(acacDPT))
 e: R = CH₃, R' = CH₃ (H₂(acacMeDPT))
 f: R = C₆H₅, R' = CH₃ (H₂(acacPhDPT))
 g: R = H, R' = C₆H₅ (H₂(benacDPT))
 h: R = CH₃, R' = C₆H₅ (H₂(benacMeDPT))
 i: R = C₆H₅, R' = C₆H₅ (H₂(benacPhDPT))
 j: R = H, R' = *p*-XC₆H₅ (H₂(*p*-XbenacDPT),
   where X = Cl, Br, CH₃, and CH₃O)

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Experimental Section

Materials. Benzoylacetone (Hbenac) and 2,4-pentanedione (Hacac) were purchased from Aldrich Chemical Co., Milwaukee, WI, and used as received. Trifluoroacetylacetone (Htfac) was obtained from Pierce Chemical Co., Rockford, IL, and was freshly distilled before use. The *p*-X-benzoylacetone derivatives were prepared by mixing stoichiometric amounts of the appropriate *p*-X-acetophenone, acetic anhydride, and boron trifluoride etherate according to the modification of Chen and Cummings.[18] *p*-Methylbenzoylacetone was prepared by the procedure of Walker, Sanderson, and Hauser[19] from *p*-methylacetophenone, acetic anhydride, and boron trifluoride.

The triamines 3,3'-iminobis(propylamine) (DPT) and 3,3'-(methylimino)bis(propylamine) (MeDPT) were supplied free of charge by Jefferson Chemical Co., Bellaire, TX, and used as received. The 3,3'-(phenylimino)bis(propylamine), (PhDPT) was prepared by catalytically reducing the corresponding cyano compound.[20]

Spectroquality grade solvents were used in all physical measurements. All other chemicals were reagent grade or equivalent. All solvents used were dried by distillation techniques, stored over molecular sieves, and, in the case of the Co(II) syntheses, deaerated with dry N₂. The tetraethylammonium tetrabromometalate salts were prepared from their respective metal bromides and Et₄NBr by stirring the two reactants in absolute ethanol.[21]

Ligand Syntheses. tfac Series. H₂(tfacDPT) (Ia) was prepared by our previously reported method[16] and was obtained as white crystals, mp 70–71 °C. H₂(tfacMeDPT) (Ib) and H₂(tfacPhDPT) (Ic) were obtained as golden oils. In a typical preparation, 0.048 mol of tfac in 100 mL of methanol was added with stirring to 0.024 mol of the triamine in 100 mL of methanol. The reaction solution was stirred for 3 h at 25 °C, and the methanol was removed with use of a rotary evaporator. The golden oils which remained were dried under dynamic vacuum for 24 h.

acac Series. H₂(acacDPT) (Id), H₂(acacMeDPT) (Ie), and H₂-(acacPhDPT) (If) were obtained as yellow oils by using the following procedure. A solution of 0.25 mol of the required amine in 70 mL of absolute ethanol was added slowly with stirring to a solution of 50 g (0.5 mol) of Hacac in 100 mL of ethanol which had been chilled in an ice bath. The addition rate was adjusted so that the temperature of the reaction mixture never exceeded 40 °C. The golden yellow solution which resulted was stirred at 25 °C for 1 h, and the solvent was then removed with use of a rotary evaporator. The oils were dried under dynamic vacuum for 3–6 h. Note: a hydrated, crystalline form of H₂(acacDPT) could be isolated by recrystallization of the oil from aqueous alcohol, but it proved useless in complexation reactions with the metal ions due to hydrolysis.

benac Series. H₂(benacDPT) (Ig) was prepared by dissolving 16.2 g (0.1 mol) of Hbenac in the minimal amount of diethyl ether and adding to this with stirring 6.6 g (0.05 mol) of DPT in 100 mL of absolute methanol. The solution was stirred for 1 h at room temperature, and the volume then was reduced to one-third with use of a rotary evaporator. The concentrated ligand solution was added slowly to 1200 mL of water with constant stirring. The white crystals which formed were filtered immediately. Additional product was recovered by continued stirring and slow evaporation of the solvent at room temperature over a period of several days. H₂(benacMeDPT) (Ih) and H₂(benacPhDPT) (Ii) were prepared in a similar manner except that the methanolic ligand solution was stirred at room temperature for 3 h and the treatment with water was eliminated. Instead, the solvent was stripped off completely, and the ligand oils were dried under dynamic vacuum for several hours.

***p*-Xbenac Series.** H₂(*p*-XbenacDPT) (Ij), where X = Cl, Br, CH₃, and CH₃O, were each prepared by the same general procedure; i.e., a solution of 0.016 mol of *p*-X-benzoylacetone in 100 mL of methanol was added with stirring to 1.31 g (0.01 mol) of DPT in 100 mL of methanol. The golden solution was stirred for 3 h at room temperature,

(17) Data are taken in part from the M.S. Theses of Y.-Y. Chen (Aug 1979), B. D. McKinney (March 1979) and L. J. Willis (Aug 1977), Wright State University. A portion of the work was presented at the 175th National Meeting of the American Chemical Society, Anaheim, CA, March 1978.
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Table I. Summary of Synthetic Methods Employed and Pertinent Analytical and Physical Data for the New Schiff Base Complexes

compd	color	mp, °C	elemental anal.	synth method (yield, %)	recryst
Co(tfacDPT)	dk green	210–212	C, H, N, M good	A (25)	hot MeOH
Co(tfacMeDPT)	green	250–251	C, H, N, M good	A (7)	hot MeOH
Co(tfacPhDPT)			unacceptable	B	EtOH, ether
Ni(tfacMeDPT)	bright green	211–214	C, H, N, M good	A (2)	MeOH
Ni(tfacPhDPT)			C, H, N marg	B	EtOH, ether, subl
Cu(tfacMeDPT)	lt green	217–218	C, H, N, M good	A (2)	hot MeOH
Cu(tfacPhDPT)	lt green		C, H, N, M good	B	EtOH, ether
Co(acacDPT)	green	207–209	N, H good; C, M marg	B (18)	ether
Co(acacMeDPT)			unacceptable	B	EtOH, ether
Co(acacPhDPT)			not analyzed	B	MeOH, C₆H₆
Ni(acacDPT)	green	211–213	C, H, N, M good	B (28)	EtOH, ether, subl
Ni(acacMeDPT)			C, H good; H, M marg	B	EtOH, subl
Ni(acacPhDPT)			not analyzed	B	EtOH
Cu(acacDPT)	green	209–211	C, H, N, M good	B (28)	ether
Cu(acacMeDPT)	green		C, H, N, M good	B	hot EtOH, ether
Cu(acacPhDPT)	dk green		unacceptable	B	hot EtOH, ether
Co(benacDPT)	brown	242–244	C, H, N, M good	B (45)	hot EtOH
Co(benacMeDPT)	brown	201–203	C, H, N, M good	B (18)	hot EtOH
Co(benacPhDPT)			not analyzed	B	C₆H₆
Ni(benacDPT)	dk olive	242–244	C, H, N, M good	B (45)	hot EtOH
Ni(benacMeDPT)	green	220–221	C, H, N, M good	B (60)	hot EtOH
Ni(benacPhDPT)			unacceptable	B	EtOH, ether, C₆H₆
Cu(benacDPT)	olive green	201–202	C, H, N, M good	B (51)	hot EtOH
Cu(benacMeDPT)	green	205–207	C, H, N, M good	B (55)	hot EtOH
Cu(benacPhDPT)	olive green		C, H, N, M good	B	EtOH, ether
Co(p-Cl-benacDPT)	lt brown	232–234	H, N good; C marg	C (29)	CHCl₃
Ni(p-Cl-benacDPT)	green	202–204	C, H, N, M good	C (31)	CH₃Cl
Cu(p-Cl-benacDPT)	green	210–213	C, H, N, M good	C (48)	CH₃Cl
Co(p-Br-benacDPT)	lt brown	240–243	C, H, N, M good	C (23)	4:1 CH₃Cl/MeOH
Ni(p-Br-benacDPT)	lt green	215–217	C, H, N, M good	C (23)	4:1 CH₃Cl/MeOH
Cu(p-Br-benacDPT)	lt green	223–225	C, H, N, M good	C (16)	4:1 CH₃Cl/MeOH
Co(p-CH₃benacDPT)	red-brown	140–144	unacceptable	C (38)	CH₃Cl
Ni(p-CH₃benacDPT)	olive green	120–123	unacceptable	C (27)	MeOH
Cu(p-CH₃benacDPT)	green	200–205	unacceptable	C (30)	4:1 CH₃Cl/MeOH
Co(p-CH₃ObenacDPT)	brown	179–182	C, H, N good; M marg	C (60)	4:1 CH₃Cl/MeOH
Ni(p-CH₃ObenacDPT)	olive	127–130	unacceptable	C (15)	4:1 CH₃Cl/MeOH
Cu(p-CH₃ObenacDPT)	apple green	188–191	C, H, N, M good	C (55)	4:1 CH₃Cl/MeOH

and then the solvent was stripped off on the rotary evaporator. The oily ligand was taken up in about 20 mL of chloroform, and this solution was added dropwise into 500 mL of hexane. Slow addition and constant stirring resulted in the precipitation of a yellow powder which was isolated by filtration, washed with water (3 × 50 ml) and hexane (3 × 50 ml), and then air-dried.

Synthesis of Metal Complexes. Three basic procedures have been used to prepare the complexes. Each procedure is detailed below for a particular Co(II) complex. Synthetic methods used for the remaining metal complexes and percent yields are listed in Table I, along with selected physical properties and a summary of the analytical results. A complete listing of elemental analyses is available in supplementary Table I.

Method A. Synthesis of 3,3'-Bis(trifluoroacetylacetone iminato)(bis(trimethylene)amine)cobalt(II), Co(tfacDPT). A 4.03-g sample (0.01 mol) of H₂(tfacDPT) and 2.49 g (0.01 mol) of Co(OAc)₂·4H₂O were placed in a 500-mL Schlenk flask, and the flask was deaerated with dry nitrogen. To this was added 150 mL of deaerated DMF. The resulting solution was stirred and refluxed under vacuum for 3 h at which time the solution became dark brown to wine red. DMF was removed by vacuum distillation. The product was extracted from the residue into two 100-mL portions of deaerated diethyl ether, the green ether solutions were filtered and combined, and then the ether was removed under vacuum. The Co(tfacDPT) product was recrystallized from deaerated methanol and appeared as dark green nuggets. Note: this procedure works only for members of the tfac series of complexes which are not very susceptible to ligand hydrolysis.

Method B. Synthesis of 3,3'-Bis(acetylacetone iminato)(bis(trimethylene)amine)cobalt(II), Co(acacDPT). About 300 mL of dry tert-butyl alcohol was distilled onto 14.77 g (0.05 mol) of dried H₂(acacDPT) oil placed in a 500-mL round-bottom flask attached to a Schlenk line. To the resulting yellow solution was added 11.22 g (0.10 mol) of predried potassium tert-butoxide via a powder addition tube. Deprotonation of the ligand resulted in a color change from light yellow to red-orange. The solution was cooled by bubbling dry

N₂ through it. Then 27.51 g (0.05 mol) of (Et₄N)₂(CoBr₄) was added from a powder addition tube. The solution turned green immediately but was stirred for an additional 24 h. The solvent was removed by vacuum distillation, and 300 mL of dry, deaerated benzene was added to extract the complex from the reaction mixture. After 3 h of stirring, the mixture was filtered, and the green filtrate was concentrated to about 50 mL and refrigerated. The green product which precipitated was recrystallized from dry ether and washed with hexane.

Method C. Synthesis of 3,3'-Bis(p-chlorobenzoylacetone iminato)(bis(trimethyleneamine)cobalt(II), Co(p-Cl-benacDPT). A 0.977-g sample (0.002 mol) of H₂(p-Cl-benacDPT) and 0.45 g (0.004 mol) of potassium tert-butoxide were placed in a 200-mL Schlenk flask, and 150 mL of deaerated methanol was added under a N₂ blanket. The solution was stirred for 30 min to allow time for deprotonation of the ligand. Then 0.443 g (0.0025 mol) of predried Co(OAc)₂ was added via a powder addition tube. The solution turned brown immediately, and after a few minutes, a brown solid began to form. The mixture was stirred for 3 h and then concentrated to one-third volume. The light brown powder which precipitated was filtered off and recrystallized from chloroform.

Physical Measurements. Chemical analyses were done by Alfred Bernhardt, Mikroanalytisches Laboratorium, Elbach, West Germany. A Perkin-Elmer Model 457 infrared spectrophotometer was used to record infrared spectra. The spectra were taken as Nujol mulls. A Cary Model 14 recording spectrophotometer was used to record spectra in the near-infrared, visible, and ultraviolet wavelength regions. Methanol was the solvent used for ultraviolet and visible spectra, and carbon tetrachloride and tetrachloroethylene were used in the near-infrared. Spectra were run in 0.1-, 1.0-, and 5.0-cm matched quartz cells with 5 × 10⁻³, 10⁻³, and 5 × 10⁻⁴ M solutions. A Varian Model EM360 spectrometer was used to record NMR spectra, with deuteriochloroform as a solvent and Me₄Si as an internal reference. Magnetic susceptibility data were obtained by the Faraday technique using a Cahn RG recording electrobalance and an Alpha electromagnet with 4-in. constant-force pole caps. Pascal's constants were used to

Table II. 60-MHz ^{1}H NMR Spectra of Ligands in $CDCl_3$

| | | | chem shift $(\delta)^{a,b}$ and assignts | | | | |
compd	$C_6H_4, C_6H_5{}^c$	CH_3O	$CH_3{}^d$	$CH_2{}^{c,d}$	=CH	OH/NH^e	NH^f
H_2(tfacDPT)			2.05 (6)	1.70–3.64 (12)	5.10 (2)	11.20 (3)	2.00 (1)
H_2(tfacMeDPT)^g			2.22 (3), 2.10 (6)	1.38–3.72 (49.5)	5.33 (2)	11.19 (2)	
H_2(tfacPhDPT)	6.20–7.28 (8.6)		1.90 (6)	1.40–3.50 (18)	5.20 (2)	11.12 (1)	
H_2(acacDPT)			1.97 (6), 1.90 (6)	1.33–3.57 (12)	4.93 (2)	10.87 (1.7)	1.50 (1)
H_2(acacMeDPT)			1.93 (9), 1.90 (6)	1.34–3.60 (13.2)	4.90 (2)	10.84 (1.7)	
H_2(acacPhDPT)	6.45–7.35 (7.6)		1.97 (6), 1.83 (6)	1.44–3.60 (13)	4.93 (2)	11.00 (2)	
H_2(benacDPT)	7.17–8.00 (10)		2.01 (6)	1.60–3.57 (12)	5.60 (2)	11.43 (2)	1.37 (1)
H_2(benacMeDPT)	7.00–8.20 (10)		2.08 (3), 1.90 (6)	1.23–3.67 (12.3)	5.62 (2)	11.45 (2)	
H_2(benacPhDPT)	6.54–8.02 (15)		2.00 (6)	1.68–3.60 (12)	5.67 (2)	11.63 (2)	
H_2(p-Cl-benacDPT)	7.10–7.95 (8)		2.05 (6)	1.60–3.62 (12)	5.58 (2)	11.45 (2)	2.37 (1)
H_2(p-Br-benacDPT)	7.20–7.95 (8)		2.08 (6)	1.48–3.66 (12)	5.65 (2)	11.53 (2)	2.34 (1)
H_2(p-CH_3benacDPT)	7.00–7.95 (8)		2.33 (6), 2.05 (6)	1.70–3.63 (12)	5.64 (2)	11.45 (2)	2.30 (1)
H_2(p-CH_3ObenacDPT)	6.65–7.97 (8.4)	3.78 (6.8)	2.02 (6)	1.36–3.55 (13.6)	5.60 (2)	11.40 (2)	2.47 (1)

^{a} Relative to Me_4Si as the internal standard. ^{b} Integrated intensity appears in parentheses after each signal relative to =CH equal two. ^{c} Range of the multiplet region. ^{d} Values for integrated intensities of CH_3 and CH_2 protons were summed together because of overlapping signals. Theoretical values for CH_3 protons were subtracted from this total leaving the value indicated for the CH_2 protons. ^{e} Ionizable protons of the keto amine or enolimine. ^{f} Amine proton of the DPT backbone. ^{g} Contaminated with excess DPT.

calculate ligand susceptibilities. Measurements were taken at approximately 8 and 10 kG. EPR spectral studies using solution and frozen-glass techniques were carried out on a Varian E-104A Century Line EPR spectrometer. All spectra were obtained in the X-band at a frequency range of approximately 9.1 GHz. The magnetic field was calibrated with a Hewlett Packard HX532 B frequency meter and two standards, DPPH and VO(acac)$_2$. Each spectrum was calibrated with DPPH.

Results and Discussion

Ligand Characterization. Infrared and NMR spectral data were used to characterize the ligands and confirm that the doubly condensed Schiff bases had been obtained. No IR vibrations attributable to terminal NH_2 groups were observed in any case; however, strong bands due to C=O, C=N, and/or C=C were present in the 1600–1500-cm^{-1} region for all ligands. Ligands of the DPT series generally showed a weak band at ~3290–3240 cm^{-1} due to the backbone NH stretching mode. Slightly higher energy absorptions in the 3600–3400-cm^{-1} range could be correlated with the keto amine and enolimine ligand forms.

The presence of different tautomeric forms was confirmed by analysis of the ^{1}H NMR spectra of all free ligands. Chemical shifts and peak assignments are given in Table II. In general, signal intensities are close to theoretical values; although overlapping of the CH_3 and CH_2 patterns made analysis of these regions more tentative. Some deviations between calculated and integrated signal intensities were found. These results were expected since over half of the ligands were obtained as oils which may have been contaminated with unreacted triamines.

Prominent in the ligand NMR spectra are signals for the methyl protons of the chelate rings (1.8–2.1 ppm) and of the tertiary nitrogen atom (1.9–2.2 ppm). Additional signals are assigned as follows: backbone CH_2 groups, 1.23–3.72 ppm; =CH of the chelate ring, 4.9–5.7 ppm; backbone NH in DPT ligands only, 1.4–2.5 ppm; NH/OH of chelate ring, 10.8–11.6 ppm.

The acidic protons of the benzoyl and fluorinated ligands are considerably less shielded than those of the acetyl ligands which suggests that the enolimine tautomer may predominate in the first two cases; whereas, the keto amine may be more favored in the latter. The fact that the ring CH_3 and =CH peaks occur as sharp singlets in all cases indicates that the ligands are symmetric and that Schiff base condensation has occurred on the carbonyl carbon adjacent to the CH_3 groups.

Synthesis of Metal Complexes. Three general procedures have been developed to synthesize the new Schiff base com-

plexes. Method A involved refluxing the hydrated metal acetate and ligand in DMF as solvent. This procedure works well only when the ligands are not easily hydrolyzed and when the enolic protons are highly acidic as is the case for the fluorinated ligands and, to a lesser extent, ligands in the benzoyl series.

Method B, an extension of the procedure first reported by Everett and Holm,[22] involved refluxing the ligand which had been deprotonated with strong base with tetrahalometalate salts in dry *tert*-butyl alcohol. This procedure allows for the rigorous exclusion of water at all phases of the complexation reaction and during isolation of the products and is necessary in order to obtain any samples in the acetyl series. The benzoyl derivatives which were somewhat less susceptible to hydrolysis were also prepared by the latter procedure but starting from the anhydrous metal acetate (method C). Use of the metal acetates made purification of the desired complexes via recrystallization and/or sublimation techniques much easier, although obtaining analytically pure samples was always difficult. Complete data on elemental analyses have been made available in supplementary Table I, and the analytical results are summarized in Table I of the text. It will be seen that of the 37 complexes prepared, 21 gave satisfactory C, H, N, and metal analyses. Five gave marginal analyses (±2%), eight were unacceptable (in spite of multiple syntheses and recrystallizations), and three others were deemed too impure by IR inspection to be sent out for elemental characterization. In all cases of poor analyses, the percent carbon found was low while the metal analysis was high. Attempts to eliminate the contaminating metal salts via sublimation, solvent extraction, and chromatographic techniques were unsuccessful in our hands.

Characterization of Metal Complexes. In addition to the results of elemental chemical analyses cited above, the complexes have been characterized by IR, near-IR, visible, and UV spectral studies and magnetic susceptibility measurements.

The IR spectra of all of the complexes are quite similar. Complexes derived from DPT exhibit a weak but sharp band due to the backbone NH stretching vibration at 3290–3242 cm^{-1}. This band is absent in the substituted NR derivatives. All complexes show very strong IR-active bands near 1620–1600 and 1545–1570 cm^{-1} which are attributed to the conjugated C⃛N, C⃛O, and C⃛C stretching vibrations of the chelated keto iminato rings. Additional bands in this same region, i.e., ~1580, 1480, and 1420 cm^{-1} as well as at ~760

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Table III. Magnetic Data[a] and Visible Spectra[b] of Pentacoordinate (Keto iminato)nickel(II) Complexes

compd	μ_{eff}, μ_B	major abs bands × 10³ cm⁻¹ (ϵ)
Ni(tfacDPT)[c]	3.05	8.9 (14), 10.1, 11.8 sh, 16.5 (29), 32.5 (11 000), 40.8 (15 800)
Ni(tfacMeDPT)	3.38 ± 0.2	8.0 (27), 16.7 (39), 27.5 sh (660), 32.8 (13 000), 40.4 (6900)
Ni(tfacPhDPT)	3.52 ± 0.2	7.2, 9.2 sh, 16.0 (60), 26.5 sh (800), 32.8 (14 400), 39.4 (9000)
Ni(acacDPT)	3.25 ± 0.2	8.2 (17), 10.0 sh, 16.1 (40), 26.2 sh (800), 32.4 (22 000)
Ni(acacMeDPT)	3.25 ± 0.2	7.6 (20), 10.2 sh, 16.1 (60), 26.0 (1200), 32.3 (30 000)
Ni(benacDPT)	3.17 ± 0.01	8.1 (18), 10.2 sh, 16.6 (32), 29.0 (14 000), 43.9 (19 000)
Ni(benacMeDPT)	3.62 ± 0.1	8.0 (27), 16.9 (61), 29.2 (22 000), 43.0
Ni(p-Cl-benacDPT)[d]	3.18 ± 0.2	8.2, 11.7, 13.7 sh, 16.7, 25.3, 28.7 (6950), 44.4 (12 300)
Ni(p-Br-benacDPT)[d]	3.30 ± 0.2	8.3, 11.7, 13.5 sh, 16.7, 25.0, 28.7 (9750), 42.7 (26 000)
Ni(p-CH₃benacDPT)[d]	3.18 ± 0.2	8.3, 13.1, 16.6, 25.6, 29.1 (6900), 37.0 (5900)
Ni(p-CH₃ObenacDPT)[d]	3.42 ± 0.2	8.3, 12.8, 16.7, 29.1 (6100), 40.7 (18 500)

[a] Diamagnetic corrections were made with use of Pascal's constants. Errors represent average deviation from room-temperature measurements at two field strengths. [b] Low-energy bands were obtained in CHCl₃ or C₂Cl₄; high-energy bands were obtained in MeOH. [c] Reference 16. [d] Low-energy bands by diffuse transmittance technique.
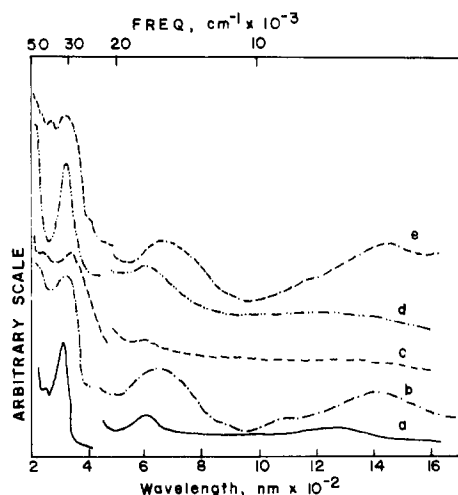
Table IV. Magnetic Data[a] and Visible Spectra[b] of Pentacoordinate (Keto iminato)cobalt(II) Complexes

compd	μ_{eff}, μ_B	major abs bands × 10³ cm⁻¹ (ϵ)
Co(tfacDPT)	4.33 ± 0.1	5.7 (8), 13.5 (16), 15.0 sp (16), 17.9 sh (28), 33.9 (13 000)
Co(tfacMeDPT)	4.24 ± 0.1	5.7 (10), 13.0 (25), 15.0 sp (21), 34.0 (14 000)
Co(tfacPhDPT)	4.32 ± 0.2	6.0 (7), 12.9 (18), 16.9 (22), 19.2 (30), 32.1 (14 000)
Co(acacDPT)	4.28 ± 0.2	5.9 (9), 12.8 (25), 17.7 (100), 21.9 (520), 32.6 (10 600)
Co(acacMeDPT)	4.32 ± 0.2	5.9 (28), 12.5 (46), 15.1 (38), 23.2 (220), 32.4 (49 000)
Co(acacPhDPT)[c]	4.30 ± 0.2	..., 38.8
Co(benacDPT)[d]	4.29 ± 0.1	..., 13.0 sh, 18.5 (155), 29.2 (19 200), 37.0 (16 800)
Co(benacMeDPT)	4.67 ± 0.1	5.9 (5), 12.5 (25), 14.9 sp (20), 17.5 (85), 29.9 (22 000), 42.1 (21 000)
Co(benacPhDPT)[c]	3.50 ± 0.2	..., 39.5
Co(p-Cl-benacDPT)	4.31 ± 0.2	5.8, 8.3, 12.7, 28.4, 41.7
Co(p-Br-benacDPT)[d]	4.26 ± 0.2	..., 8.2, 12.9, 28.4 (8500), 42.4 (27 000)
Co(p-CH₃benacDPT)[d]	4.42 ± 0.2	..., 8.3, 13.5, 29.1 (5700), 40.1 (15 500)
Co(p-CH₃ObenacDPT)	4.42 ± 0.2	5.8, 8.3, 13.7, 17.5, 28.7 (10 000), 35.7 (27 000)

[a] Diamagnetic corrections were made with use of Pascal's constants. Errors represent average deviation from room-temperature measurements at two field strengths. [b] Low-energy bands were obtained in CHCl₃ or C₂Cl₄; high-energy bands were obtained in MeOH. [c] Insoluble in all solvents tried; diffuse transmittance technique used. [d] Lowest energy band not discernible at concentrations available.
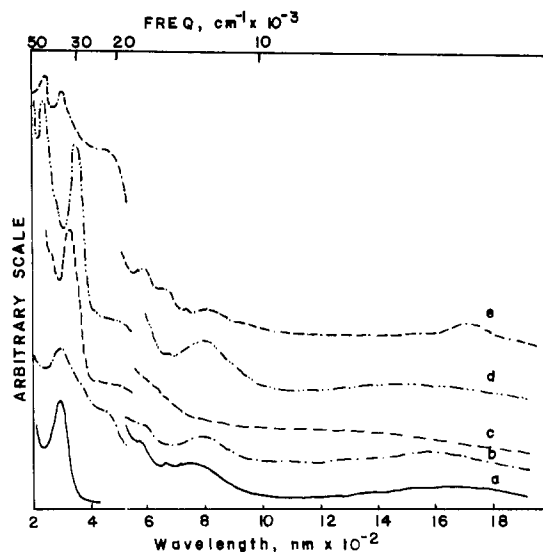

Figure 1. Electronic spectra of (a) Ni(tfacMeDPT), (b) Ni(acac-MeDPT), (c) Ni(benacMeDPT), (d) Ni(benacDPT), and (e) Ni-(tfacPhDPT) 10⁻³ M in C₂Cl₄ (low-energy region) and 10⁻⁴ M in CH₃OH (high-energy region)).

Figure 2. Electronic spectra of (a) Co(tfacDPT), (b) Co(acacDPT), (c) Co(benacDPT), (d) Co(benacMeDPT), and (e) Co(tfacPhDPT) 10⁻³ M in C₂Cl₄ (low-energy region) and 10⁻⁴ M in CH₃OH (high-energy region)).

cm⁻¹, are attributed to phenyl stretching and bending modes, respectively, in the benac and N–Ph series. In addition, all complexes with fluorinated ligands show very strong IR bands at 1300–1100 cm⁻¹ due to the CF₃ stretching modes. The fact that the bands assigned to NH, C=O/C=N, and C=C in the free ligands are shifted to lower energy in the complexes strongly suggests that all five donor atoms are coordinating to the metal ions. The actual geometries of the penta-

coordinate complexes are more difficult to determine, although magnetic measurements and visible spectral data provide some insight in the case of each metal complex series. Calculated magnetic moments and major visible spectral bands for the Ni(II), Co(II), and Cu(II) complexes are presented in Tables III–V. Typical spectra are illustrated in Figures 1–3 for the three different metal ion series.

From the data presented in Table III, it can be shown that the average μ_{eff} of the Ni(II) complexes prepared in this study
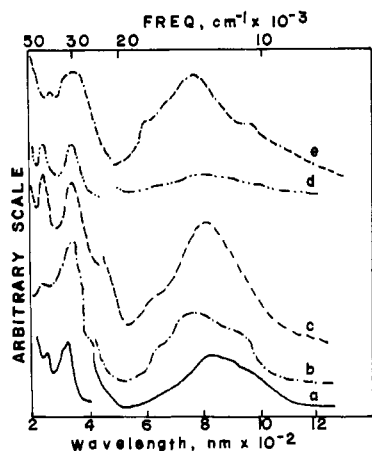
Figure 3. Electronic spectra of (a) Cu(tfacMeDPT), (b) Cu(acac-MeDPT), (c) Cu(benacMeDPT), (d) Cu(benacDPT), and (e) Cu-(tfacPhDPT) 10^{-3} M in C_2Cl_4 (low-energy region) and 10^{-4} M in CH_3OH (high-energy region)).

is 3.3 μ_B which falls within the range (3.2–3.5 μ_B)[8,14,23] normally observed for high-spin, five-coordinate Ni(II). As can be seen from Figure 1, spectra of the Ni(II) species exhibit three important and well-defined bands at $\sim$8.0 × 10^3, (16.5–17.0) × 10^3, and (25.0–27.5) × 10^3 cm^{-1}. Shoulders consistently appear at ($\sim$9.2–10.2) × 10^3 and (11.7–13.7) × 10^3 cm^{-1}. In general appearance, these spectra match closely those reported for Ni(salDPT), Ni(salMeDPT), and various substituted XsalDPT and salDIPA species.[8,24] Ni(sal-MeDPT), for example, exhibits bands at <5.0 × 10^3, 8.5 (39) × 10^3, 10.0 × 10^3 (sh), 11.8 (13) × 10^3, and 16.7 (69.5) × 10^3 cm^{-1} and has a magnetic moment of 3.34 μ_B. An X-ray structure determination has shown that its geometry is close to TBP with some distortion toward SP.[25] Schiff base complexes derived from phenones, on the other hand, tend more toward SP structures. Two such compounds are Ni(cbpN), incorporating 2-hydroxy-5-chlorobenzophenone, and Ni-(AcetDPT), derived from o-hydroxyacetophenone. Spectra of these compounds exhibit absorptions at 8.5 (12.5) × 10^3, 10.5 (6.5) × 10^3 and 16.7 (30.2) × 10^3 cm^{-1} (Ni(cbpN))[13] and 5.4 × 10^3 (br), 8.0 (19) × 10^3, 10.4 (5.2) × 10^3, and 16.5 (5.0) × 10^3 cm^{-1} (Ni(AcetDPT)).[15] In general the molar absorptivities are less than in the TBP cases, although band energies are very close. Without a crystal structure it is impossible to determine the actual geometry of the (keto iminato)nickel(II) complexes prepared in this study although they are likely to have a structure intermediate between the TBP and SP extremes.

From the data presented in Table IV for the (keto iminato)cobalt(II) complexes, an average μ_{eff} of 4.3 μ_B can be calculated. High-spin, five-coordinate Co(II) complexes normally exhibit magnetic moments in the range 4.2–4.4 μ_B and produce two major visible spectral bands at (5.0–6.5) × 10^3 and (14.0–16.0) × 10^3 cm^{-1}.[8,14] Complexes with SP Co(II) rather than TBP, e.g., Co(cbpN), typically have their lowest energy band shifted to the high end of the low range. Most of the Co(II) complexes prepared in this study exhibit a low-intensity and very broad band at $\sim$5.9 × 10^3 cm^{-1} which suggests that the TBP structure is most likely. Other bands at 12.5 × 10^3 and (15–19) × 10^3 cm^{-1} are also observed as illustrated in Figure 2. Taylor and Niswander[26] have noted

Table V. Magnetic Data[a] and Visible Spectra[b] of Pentacoordinate (Keto iminato)copper(II) Complexes

compd	μ_{eff}, μ_B	major abs bands × 10^3 cm^{-1} (ϵ)
Cu(tfacDPT)[c]	1.77	12.4 (245), 26.5 (512), 33.3 (15 300), 35.8 sh (11 900), 42.0 (10 800)
Cu(tfacMeDPT)[d]	1.96 ± 0.1	11.4 (sh), 12.3 (254), 14.9 (sh), 23.6 sh (143), 32.3 (14 600), 33.6 sh (13 400), 42.0 (11 600)
Cu(tfacPhDPT)	1.84 ± 0.2	10.5 sh (30), 13.2 (144), 16.1 (120), 23.6 (280), 26.7 (520), 32.9 (15 200), 42.2 (11 600)
Cu(acacDPT)	1.83 ± 0.2	10.7 sh (86), 12.8 (162), 16.6 (110), 23.3 (330), 26.3 (160), 31.7 (24 500), 40.8 (14 000)
Cu(acacMeDPT)	1.86 ± 0.2	10.5 sh (54), 13.0 (180), 16.7 (82), 23.5 (380), 26.1 (460), 31.8 (22 000), 41.8 (15 000)
Cu(acacPhDPT)	1.95 ± 0.2	10.4 sh (50), 13.8 (120), 16.6 (70), 23.5 (440), 26.1 (420), 32.2 (17 600), 41.5 (11 600)
Cu(benacDPT)[d]	1.90 ± 0.02	10.9 sh, 12.3 (45), 14.7 (26), 21.7 sh, 29.0 (25 800), 41.0 (25 600)
Cu(benacMeDPT)[d]	2.04 ± 0.02	12.0 sh (250), 12.5 (271), 15.1 (113), 20.4 (96), 28.8 (25 400), 33.3 (10 800), 41.1 (28 100)
Cu(benacPhDPT)	1.88 ± 0.2	10.7 sh (62), 13.8 (118), 16.5 (62), 20.7 (230), 28.8 (12 400), 40.2 (12 400)
Cu(p-Cl-benacDPT)[e]	1.85 ± 0.2	10.3, 12.6 (198), 28.4 (22 300), 40.7 (26 000)
Cu(p-Br-benacDPT)[e]	1.83 ± 0.2	10.8, 12.6 (200), 28.4 (21 000), 40.2 (14 200)
Cu(p-CH$_3$benacDPT)[e]	1.89 ± 0.2	10.3, 12.6 (190), 28.7 (20 300), 40.7 (29 000)
Cu(p-CH$_3$ObenacDPT)[e]	1.82 ± 0.2	10.6, 12.7 (176), 28.7 (20 500), 38.2 (21 000)

[a] Diamagnetic corrections were made with use of Pascal's constants. Errors represent average deviation from room-temperature measurements at two field strengths. [b] Low-energy bands were obtained in CHCl$_3$ or C$_2$Cl$_4$; high-energy bands were obtained in MeOH. [c] Reference 16. [d] All bands obtained in MeOH. [e] Lowest energy band observed only in solid state.

that tetrahedral species can also be isolated when strongly electron-donating groups are substituted on the salicylaldimine rings. The Td Co(II) complexes typically show spectral absorptions at 8.0 × 10^3, (11.0–12.0) × 10^3, and (17.0–19.0) × 10^3 cm^{-1} in the solid state, whereas most revert to five-coordination in CHCl$_3$ solutions. The appearance of bands at 8.2 × 10^3, (12.7–13.7) × 10^3, and 17.5 × 10^3 cm^{-1} in the solid-state spectra of the Co(p-XbenacDPT) complexes, where X is either an electron-donating or electron-withdrawing group, may indicate the presence of some tetrahedral Co(II) in these systems. Unfortunately, the low solubilities of these derivatives precluded observation of low-energy bands in any solvent.

The range of magnetic moments calculated for the Cu(II) complexes as reported in Table V confirms the presence of Cu(II), precludes any metal–metal interactions, and agrees well with values reported for five-coordinate Cu(II), i.e., 1.7–2.2 μ_B.[15] The (keto iminato)copper(II) complexes reported here exhibit an intense visible spectral absorption at (12.3–13.8) × 10^3 cm^{-1} (ϵ $\sim$200) with both high- and low-energy shoulders in all but the Cu(p-XbenacDPT) series. These spectra are fairly Gaussian in shape and are centered

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Table VI. EPR Spectral Parameters for (Keto iminato)copper(II) Complexes

compd	g_{iso} (±0.005)	a_{iso} (±1), G	$g_\parallel$ (±0.005)	$a_\parallel$ (±2), G	$g_\perp{}^b$ (±0.005)	$a_\perp{}^b$ (±2), G
Cu(benacPhDPT)	2.112	120	2.241	131	2.047	115
Cu(benacPhDPT) + py			2.240	130		
Cu(acacPhDPT)	2.117	118	2.241	123	2.055	116
Cu(acacPhDPT) + py			2.230	127		
Cu(tfacPhDPT)	2.121	100	2.248	116	2.058	92
Cu(tfacPhDPT) + py			2.249	116		
Cu(benacMeDPT)	2.118	107	2.236	110	2.059	106
Cu(benacMeDPT) + py			2.234	111		
Cu(acacMeDPT)	2.118	92	2.234	96	2.060	90
Cu(acacMeDPT) + py			2.231	95		
Cu(benacDPT)	2.123	100	2.224	88	2.073	106
Cu(acacDPT)	2.124	80	2.222	82	2.075	99
Cu(acacDPT) + py			2.222	80		

^{a} Isotropic values were obtained in 2:1 toluene/methylene chloride solutions at 295 K. Anisotropic data were obtained by freezing the same samples to 77 K. ^{b} Values of $g_\perp$ and $a_\perp$ were calculated as follows: $g_\perp = \frac{1}{2}(3g_{iso} - g_\parallel)$ and $a_\perp = \frac{1}{2}(3a_{iso} - a_\parallel)$.
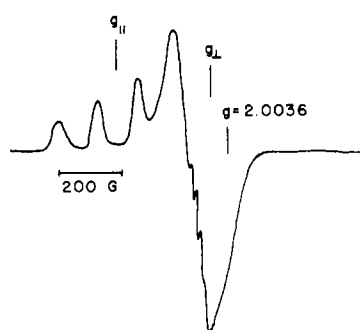

Figure 4. EPR spectrum of Cu(benacPhDPT) in 2:1 toluene/methylene chloride frozen glass at 77 K.

at $\sim12.6 \times 10^3$ cm^{-1} ($\epsilon \sim 180$). Typical spectra are shown in Figure 3. Electronic spectra of Cu(II) complexes are generally poor indicators of geometry; however, it has been suggested[27,28] that TBP Cu(II) will absorb in the range $(11.8–12.5) \times 10^3$ cm^{-1}, whereas SP Cu(II) will absorb between $(14.9–18.2) \times 10^3$ cm^{-1}. Certainly, Cu(salDPT) which shows a prominent band at 12.4×10^3 cm^{-1} is known to be distorted TBP, whereas Cu(cbpN) and Cu(AcetDPT), best described as intermediate structures, exhibit major bands at 13.4×10^3 and 14.6×10^3 cm^{-1}, respectively. Comparison of these results with the spectral data of Table V and Figure 3 leads us to conclude that the new Cu(II) complexes are more similar in structure to the phenone complexes than to the salicylaldimines.

In order to further elucidate the structure of the Cu(II) complexes, we have measured both solution and frozen-glass EPR spectra for representative samples. The spectrum of Cu(benacPhDPT), illustrated in Figure 4, is typical of complexes in the PhDPT series. Spectra of complexes derived from the other amines, i.e., MeDPT and DPT, are similar except there is considerably more overlap between the parallel and perpendicular regions. Calculated EPR spectral parameters for selected complexes are listed in Table VI. In all cases, $g_\parallel > g_\perp$ which is consistent with tetragonally distorted Cu(II).[15,29] Since purely TBP Cu(II) is expected to have $g_\perp > g_\parallel$, those cases where $g_\parallel$ and $g_\perp$ are closer in magnitude may possess intermediate geometries. The absence of any observed superhyperfine splitting due to the coordinated central N may

also reflect an intermediate rather than pure SP geometry.

Addition of pyridine to the Cu(II) samples produced no change in either $g_\parallel$ or $a_\parallel$ values. Increases in g values and decreases in a values are commonly observed when planar Cu(II) chelates form 1:1 adducts with neutral molecules;[30,31] therefore, we conclude that all five donors of the pentadentate ligands are indeed coordinated to the Cu(II) ion.

The strength of the axial interaction, i.e., the bond to the central N donor appears to be a function of the keto iminato ring substituents. Thus, for the series Cu(benacPhDPT), Cu(acacPhDPT), and Cu(tfacPhDPT), $A_\parallel$ decreases from 120 to 118 to 100 G. The ability of electron-withdrawing substituents to enhance the tendency for central donor bonding has been well documented for Co(XsalPhDPT) complexes by Taylor and co-workers[32] and seems to be applicable here. Presumably, the electron-withdrawing substituents deplete electron density around the metal ion, thus making it easier for the metal ion to accept a fifth electron pair in its coordination sphere.

Conclusions

From the data presented herein, it may be concluded that pentacoordinate keto iminato complexes of Ni(II), Co(II), and Cu(II) can be prepared as long as reasonable precautions to prevent hydrolysis are taken. The complexes which have been isolated possess properties similar to those reported for pentacoordinate Schiff base complexes derived from salicylaldehydes and phenones. Their structures are most likely intermediate between TBP and SP geometries. The Co(II) complexes do react with dioxygen in low-temperature solution to form 1:1 adducts. A detailed study of the oxygenated Co(II) species has been completed and results will be forthcoming.[7]

Registry No. Ia, 50599-75-2; Ib, 77080-93-4; Ic, 77080-94-5; Id, 77080-95-6; Ie, 77080-96-7; If, 77080-97-8; Ig, 77080-98-9; Ih, 77080-99-0; Ii, 77081-00-6; Ij, X = Cl, 77081-01-7; Ij, X = Br, 77081-02-8; Ij, X = CH₃, 77081-03-9; Ij, X = OCH₃, 77097-74-6; Co(tfacDPT), 77097-11-1; Co(tfacMeDPT), 77097-12-2; Co(tfacPhDPT), 77097-13-3; Ni(tfacMeDPT), 77097-14-4; Ni(tfacPhDPT), 77097-15-5; Cu(tfacMeDPT), 77097-16-6; Cu(tfacPhDPT), 77097-17-7; Co(acacDPT), 77097-18-8; Co(acacMeDPT), 77097-19-9; Co(acacPhDPT), 77097-20-2; Ni(acacDPT),

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Metal Complexes Containing Diastereoisomers and Enantiomers of o-Phenylenebis(methylphenylarsine) and Its Phosphorus Analogue. 1. Stereochemistry and Dynamic Behavior of Square-Planar and Square-Pyramidal Complexes of Bivalent Nickel[1]

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A comparative investigation of the properties of square-planar and square-pyramidal bis(bidentate)nickel(II) complexes containing the internal diastereoisomers and optically active forms of o-phenylenebis(methylphenylarsine) and its phosphorus analogue has been undertaken. The di(tertiary arsine) yields stable complexes which are labile with respect to bidentate ligand redistribution between different metal centers, but the di(tertiary phosphine) derivatives are inert in this respect. The square-pyramidal chloro complexes of both ligands undergo rapid site exchange of their axial chloro ligands under ambient conditions. Variable-temperature ¹H NMR studies on suitable derivatives indicate that this proceeds by internal isomerization of the chelate rings and by intermolecular exchange of the chloro ligand between sterically compatible complex ions.

Introduction

Although bis(di(tertiary arsine)) and bis(di(tertiary phosphine)) derivatives of group 8 metals are among the most widely studied coordination compounds, there is nevertheless a paucity of information in the literature concerning the dynamic processes of complexes of this type in solution. The extensive and pioneering work of Nyholm and Co-workers[2] led to the view that the stereochemistry of o-phenylenebis-(dimethylarsine) (diars) derivatives was essentially static. More recent work concerning the coordination chemistry of o-phenylenebis(dimethylphosphine) reinforced this impression.[3] Whereas the phenomenon of axial-halogeno lability in the square-pyramidal cations [MX(diars)₂]⁺ (where M = Ni, Pd, or Pt and X = Cl, Br, I, etc.) was realized at an early stage, following conductimetric and spectrophotometric studies,[4] it is evident that dynamic processes involving the nature of the metal chelate interaction could not be detected by these means. Furthermore, although DNMR spectroscopy could have, in principle, provided an insight into the mechanism of axial-halogeno–metal exchange in these five-coordinate complexes,[5] the inherent difficulty in investigating the phenomena of intramolecular isomerization of chelate rings and intermolecular bidentate ligand exchange (redistribution) in complexes containing symmetrical ligands resides in the centrosymmetry of the square-planar bis(bidentate)metal moiety (vide infra). It will be readily appreciated that a detailed knowledge of the dynamic properties in solution of a particular coordination

complex must necessarily precede the rational planning of a successful asymmetric synthesis based upon the stereochemistry of that species.

Accordingly, we present our findings concerning the stereochemistry and dynamic properties of bivalent nickel complexes containing the diastereoisomers and enantiomers of o-phenylenebis(methylphenylarsine)[6] and its phosphorus[7] analogue.

Results and Discussion

Stereochemical Considerations. The ditertiary chelating ligands o-phenylenebis(methylphenylarsine)[6] and its phosphorus analogue[7] have been separated into dissymmetric racemic (RR,SS) and internally compensated meso (RS) diastereoisomers, and the former subsequently resolved by fractionally crystallizing internally diastereoisomeric palladium(II) complexes containing the chiral ditertiary species and an optically active ortho-metalated dimethyl(α-methylbenzyl)amine.

The various forms of both ligands are air-stable crystalline solids whose identities have been unambiguously established in previous work (Figure 1).[8,9]

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