Contribution from the Department of Chemistry,
Worchester Polytechnic Institute, Worcester, Massachusetts 01609

Nickel(II) and Copper(II) Complexes of Linear Pentadentate Ligands Derived from Substituted *o*-Hydroxyaceto- and *o*-Hydroxybenzophenones

JOSEPH W. KOLIS, DOROTHY E. HAMILTON, and NICHOLAS K. KILDAHL*

Received August 4, 1978

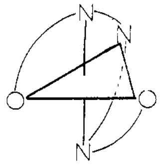
Ni(II) and Cu(II) complexes of an extensive series of potentially pentadentate ligands derived from bis(3-aminopropyl)amine and substituted *o*-hydroxyacetophenones and *o*-hydroxybenzophenones have been synthesized. The complexes are monomeric and five-coordinate, as shown by the results of infrared spectral, electronic spectral, magnetic, and molecular weight measurements, which give results consistent with those obtained for other known five-coordinate complexes of these two metal ions. In addition, EPR spectra have been obtained for the copper complexes, and the relative magnitudes of $g_{\|}$ and $g_{\perp}$ support a tetragonal stereochemistry about Cu(II). The question of the generality of M–X bonding in complexes of this type, where X represents the central donor atom, has been discussed in terms of the available structural and spectral data. It has been concluded that the reported spectroscopic criteria for coordination have *not* been convincingly invalidated by available X-ray data.

Introduction

There has been an escalating interest over the past 10 years in five-coordinate transition-metal complexes containing linear pentadentate ligands. Early interest[1-4] was largely a result of, first, a desire to impose an at-that-time odd coordination number and stereochemistry upon metal ions which ordinarily prefer regular cubic stereochemistries and, second, a hope that these odd surroundings might give rise to unusual magnetic, electronic, and spectroscopic properties in the resulting complexes. Extensive work has since justified these early hopes. More recently, complexes containing linear pentadentate ligands have been studied because of the possible significance of pentacoordination in many biologically active molecules.[5] Complexes of cobalt(II) have been particularly examined in this regard.[6-11] There exists an additional very appealing aspect of metal compounds containing pentadentate ligands. Such complexes contain *only one* acceptor site, which is available for occupation by a potential donor molecule. Interaction with one donor results in coordinative saturation at the metal ion. These systems are thus ideal for systematic investigations of the Lewis acidities of transition-metal ions and the ways in which acidity is affected by electronic and steric constraints imposed by the polydentate ligand. In addition to being ideal for thermodynamic investigations, such systems are excellent for basic mechanistic studies of ligand-exchange and substitution processes at transition-metal ions.[12]

The majority of linear pentadentate ligands which have been studied have been derived from the Schiff base condensation of 2 mol of an appropriate carbonyl compound with 1 mol of an amine containing three donor atoms. Ligands derived from salicylaldehyde and, respectively, bis(3-aminopropyl)amine (DPT) and bis(3-aminopropyl)methylamine (MeDPT) were the first examples of such species to be synthesized.[1-4] They were found to form isolable, monomeric complexes with many of the first-row transition elements. Complexes containing similar ligands derived from substituted salicylaldehydes and diethylenetriamine,[11-13] bis(2-aminoethyl) sulfide,[11,14-16] bis(3-aminopropyl) sulfide,[7,10,17,18] bis(3-aminopropyl) ether,[7,10,17,18] bis(3-aminopropyl)methylphosphine,[17,18] and bis(3-aminopropyl)phenylamine[17,18] have since been studied, primarily by Taylor and co-workers. These investigators have also studied pentadentate ligands derived from 2-pyridinecarboxaldehyde and bis(3-aminopropyl)amine,[19,20] which give rise to cationic and primarily six-coordinate complexes with the first-row transition elements. Presumably the absence of charge on the pentadentate ligand in this case makes it necessary for the metal ion to coordinate a sixth group in order to effect sufficient charge dispersal. Pentadentate ligands derived from *o*-mercaptobenzaldehyde and DPT or MeDPT have been found by Bertini et al.[21] to give cobalt(II) and nickel(II) complexes which behave similarly to the analogous SalDPT and SalMeDPT complexes.

A pentadentate ligand which is in a class by itself is that reported by Wallis and Cummings.[22] The ligand is formed by the Schiff base condensation of 2 mol of trifluoroacetylacetone with 1 mol of DPT. As a result of the rigidity of the acetylacetonimine segments of the ligand, the authors proposed an essentially square-pyramidal stereochemistry which differs somewhat from the structure which prevails among complexes of the more flexible ligands discussed above. This latter structure (I), intermediate between trigonal bipyramidal and square pyramidal, has been verified by several X-ray structural investigations.[23-27,29] Very recently, pentadentate ligands derived from condensation of 5-chloro- and 5-methyl-2-hydroxybenzophenone with DPT and bis(3-aminopropyl) sulfide have been reported.[25-29] X-ray structural investigations of the nickel, copper, and zinc complexes of these ligands substantiate the general qualitative structure indicated in I.[25,26,29]



I

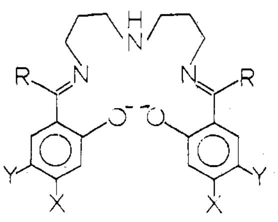
Despite the popularity of the substituted salicylaldehydes as components of pentadentate ligands, substituted acetophenones and benzophenones (with the exceptions cited above) have not been much utilized, although their ligating properties have been adequately explored in other contexts.[30-36] It is surprising that the acetophenones have been particularly ignored, since their pentadentate ligands provide, in a sense, a bridge between the salicylaldehyde- and benzophenone-derived ligands. We are primarily interested in the utilization of five-coordinate metal complexes containing pentadentate ligands as convenient vehicles for systematic thermodynamic and kinetics studies of Lewis acid–base interactions. Toward this end, we report here the synthesis and characterization of the Ni(II) and Cu(II) complexes of a variety of new pentadentate ligands derived from the condensation of substituted *o*-hydroxyaceto- and *o*-hydroxybenzophenones with bis(3-aminopropyl)amine. The ligands are given in structure II. The series extends a family of ligands which has been growing for

0020-1669/79/1318-1826$01.00/0 © 1979 American Chemical Society

Table I. Elemental Analyses

Complex	% C		% H		% N		% M	
	found	calcd	found	calcd	found	calcd	found	calcd
Ni(AcetDPT)							13.9	13.8
Ni(PropDPT)							13.4	13.0
Ni(4-MeOAcetDPT)·$^1/_2$$C_2H_4Cl_2$	56.58	56.26	6.40	6.23	8.01	7.87	11.0	11.0
Ni(4-Me-5ClBenzDPT)							9.3	9.1
Cu(AcetDPT)							14.8	14.8
Cu(5-MeAcetDPT)	63.18	63.07	7.00	6.84	9.12	9.19	13.9	13.9
Cu(PropDPT)							13.7	13.9
Cu(4-MeOAcetDPT)·$^1/_2$$CH_3OH$	58.15	58.26	6.31	6.59	8.10	8.32	12.5	12.6
Cu(5-MeBenzDPT)·H_2O	68.44	68.15	6.08	6.22	6.99	7.01	10.4	10.6
Cu(4-MeOBenzDPT)							10.3	10.4
Cu(4-Me-5-ClBenzDPT)	60.18	62.82	5.48	5.12	6.77	6.46	9.4	9.8

some time and provides fertile ground for thermodynamic and kinetic investigations of the type referred to above.



IIa, R = CH_3, X and Y = H (AcetDPT)
b, R = CH_2CH_3, X and Y = H (PropDPT)
c, R = CH_3, X = H, Y = CH_3 (5-MeAcetDPT)
d, R = CH_3, X = MeO, Y = H (4-MeOAcetDPT)
e, R = Ph, X = H, Y = CH_3 (5-MeBenzDPT)
f, R = Ph, X = MeO, Y = H (4-MeOBenzDPT)
g, R = Ph, X = Me, Y = Cl (4-Me-5-ClBenzDPT)
h, R = 4-ClPh, X = MeO, Y = H (4′-Cl-4-MeOBenzDPT)

Experimental Section

Substituted *o*-hydroxyacetophenones and *o*-hydroxybenzophenones were purchased from the Aldrich Chemical Co., Milwaukee, Wis., and were used as received. Bis(3-aminopropyl)amine was also purchased from Aldrich and used without further purification. All solvents were reagent grade or equivalent.

Syntheses. Nickel Complexes. The following general procedure was used for the syntheses of the nickel complexes. DPT (0.131 g, 1 mmol) and 0.272 g (2 mmol) of the appropriate phenone were dissolved in 50 mL of ethanol and, the yellow solution was heated at reflux for 30 min. At the end of this time, the solvent was removed by rotary evaporation and to the resulting viscous yellow oil was added a solution of 0.298 g (1 mmol) of nickel acetate tetrahydrate in 30 mL of ethanol. The resulting brown-green solution was refluxed for an additional 0.5 h. The volume of the solution was then reduced by a factor of 2 and a fivefold excess of sodium ethoxide in a minimum of ethanol was added. In most cases, green crystals of product formed immediately. If immediate formation did not occur, crystals were obtained on standing. These were isolated by filtration, washed with water, dried, and recrystallized from hot 1,2-dichloroethane or 1/1 (v/v) 1,2-dichloroethane/hexane.

In the case of the complex Ni(4-MeOAcetDPT) the volume of the ligand solution was not reduced prior to addition of the methanol solution of nickel acetate tetrahydrate. In addition, the complex was obtained from dichloroethane as the hemisolvate, as indicated by elemental analysis.

The complex Ni(AcetDPT) could be prepared by an alternate method, involving direct reaction of H_2AcetDPT and nickel acetate tetrahydrate in ethanol or methanol, followed by treatment with the appropriate alkoxide. H_2AcetDPT was synthesized by slowly adding a stoichiometric amount of DPT to neat 2-hydroxyacetophenone, with stirring. The reaction mixture slowly solidified as reaction proceeded. When reaction was complete, the yellow solid was slurried with hexane and isolated by suction filtration. The nickel complex obtained by this route was identical in every respect with that obtained by the general procedure above.

Copper Complexes. The following general procedure was used. A solution of 1 mmol of copper acetate hydrate in 20 mL of methanol was added to a concentrated methanol solution of the preformed ligand, followed by addition of a slight excess of sodium methoxide in methanol. A color change from green-brown to green was observed upon addition of methoxide. Refluxing for 0.5 h, followed by volume reduction to about 10 mL, generally afforded green crystals. If solid did not form upon volume reduction, the addition of a small quantity of sodium methoxide in methanol usually caused precipitation of the green product. This was then isolated by filtration and recrystallized from hot 1/1 (v/v) 1,2-dichloroethane/hexane. (In the case of Cu(4-Me-5Cl-BenzDPT), green crystals formed immediately upon mixing of the metal acetate and ligand solutions.)

Alternately, the complex Cu(AcetDPT) could be prepared by direct reaction of H_2AcetDPT and $Cu(C_2H_3O_2)_2 \cdot H_2O$ in methanol, followed by treatment with methoxide, as in the alternate procedure for Ni(AcetDPT). Elemental analyses for the new compounds are reported in Table I.

Physical Measurements. Analyses. Metal analyses were performed in these laboratories by using a Perkin-Elmer Model 370 atomic absorption spectrophotometer. Standard solutions for the nickel analyses were standardized by EDTA titration according to the method of Schwarzenbach.[37] Standard Cu solutions were prepared by dissolving a known weight of copper in concentrated nitric acid, followed by dilution in water. Aqueous solutions of the complexes were prepared by digesting a weighed quantity of complex (usually about 0.02 g) with 2 mL of hot concentrated nitric acid for 0.5–1 h, followed by dilution to 50 mL with distilled water. C, H, and N analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Infrared Spectra. IR spectra in the region 4000–250 cm^{-1} were obtained from Nujol mulls and/or KBr pellets by using a Perkin-Elmer Model 457 grating IR spectrometer.

Visible–Near-Infrared Spectra. Electronic spectra in the region 340–2400 nm were obtained in chloroform solution with a Perkin-Elmer Model 323 recording spectrophotometer, using matched 1-cm cells by Precision Cells, Inc., Hicksville, N.Y.

Solution Magnetic Measurements. Magnetic susceptibilities in chloroform solution were obtained by the Evans NMR method[38] by using a Hitachi Perkin-Elmer Model R-24B high-resolution NMR spectrometer. The Me_4Si resonance was used to measure the bulk susceptibility shifts in the majority of cases (vide infra). Diamagnetic corrections were estimated by using Pascal's constants.

Molecular Weight Measurements. Molecular weights in chloroform solution were determined by vapor pressure osmometry using a Mechrolab Model 301 vapor pressure osmometer. Standard resistance–concentration curves were prepared using benzil as the standard.

EPR Spectra. Spectra of chloroform solutions and chloroform glasses of the copper complexes were recorded on a Varian E-9 spectrometer operating at X-band frequencies. Magnetic field strength was measured with a Magnion NMR-type gaussmeter, and frequency was measured with a Hewlett-Packard Model 5245L counter. The klystron frequency was measured with the same counter equipped with a 5255A frequency converter. All measurements were performed either at room temperature or near liquid N_2 temperature (196 K). Tetra-*n*-butylammonium perchlorate was added to all solutions to enhance resolution of the hyperfine structure.

Results and Discussion

Syntheses. The subject complexes M(XAcetDPT) and M(XBenzDPT), M = Ni(II) or Cu(II), were synthesized according to a standard procedure involving preformation of the potentially pentadentate Schiff base ligand in alcohol solution, followed by addition of an alcoholic solution of the appropriate metal acetate and an excess of sodium methoxide in methanol, in that order. In most cases, product could not be readily obtained unless base was used to deprotonate the pentadentate ligand.

Interestingly, syntheses of several similar complexes can be readily accomplished without addition of strong base.[4,14,15,21,39] On the other hand, deprotonation by base has apparently been found necessary in order to synthesize the complexes Co(XSalDAES),[16] Cu(XSalDAPE), and Cu(XSalDAPS)[39] for which triethylamine (Et_3N) was used, Co(XSalDAPE), Co(XSalDAPS), and Co(XSalPhDPT), for which alcoholic KOH was employed,[18] and the 5-MeBenzDPT and 5-ClBenzDPT complexes of Ni(II), Cu(II), and Zn(II), for which piperidine was utilized. In these cases, as with the hydroxyacetophenone and hydroxybenzophenone derivatives described here, the combination of low ligand acidity and weak donor–acceptor interactions between the metal and ligand (arising from extensive intraligand steric strain) apparently makes complex formation unfavorable in the absence of strong base.

Although we have used primarily ethoxide and methoxide as deprotonating agents in these syntheses, we have also prepared several of the complexes using Et_3N in this capacity. We felt it essential to establish that the strongly nucleophilic methoxide did not attack the carbon atoms of the imine functional groups of the ligand. The fact that the same product is obtained regardless of whether Et_3N or methoxide is used eliminates this possibility. It should be mentioned that the use of hydroxide as a deprotonating agent in our systems often led to formation of the metal hydroxide, which precipitated as a finely divided sludge. In fact, we find that even water has a deleterious effect in our systems, causing both the formation of the metal hydroxide and the hydrolysis of the ligands in many cases.

Physical Method Studies. The metal complexes which are the subject of this report have been characterized by infrared spectroscopy, visible–near-infrared spectrophotometry, solution magnetic susceptibility determinations, molecular weight measurements, and, in the case of the copper complexes, electron spin resonance spectroscopy. The results of these measurements, which will now be considered in turn, are consistent with the assignment of five-coordinate, monomeric structures to the M(XAcetDPT) and M(XBenzDPT) complexes, M = Ni(II) and Cu(II).

Solid-state IR spectra exhibit in general two pronounced features: an intense, relatively broad band in the region between 1586 and 1627 cm^{-1}, which presumably manifests absorption by both the imine linkages and the C=C bonds of the aromatic rings, and a medium intensity, sharp to medium–sharp band in the region between 3139 and 3252 cm^{-1} for the nickel complexes and between 3215 and 3287 cm^{-1} for the copper complexes. The latter band may be assigned to the N–H stretching mode associated with the secondary amine function of the ligand.

In contrast to the salicylaldehyde-derived ligands previously reported,[6,13,16,18,20,39] the AcetDPT and BenzDPT ligands do not show bands which can be specifically assigned to the imine stretching vibrations. The imine modes are expected to absorb at lower frequency in the latter ligands due to the increased mass of the groups appended to the imine carbon, and, in the case of the BenzDPT ligands, to an increased degree of conjugation of the imine π bond with the π systems of the aromatic rings. The frequency lowering is apparently large enough that the imine absorptions overlap those of the aromatic rings, with which they should be strongly coupled. This holds true also for the uncomplexed (protonated) ligand, H_2AcetDPT, which shows a single broad absorption in the 1600-cm^{-1} region.

Table II. Molecular Weight and Magnetic Data

complex	μ_{eff}, μ_B Me_4Si	μ_{eff}, μ_B $CHCl_3$	mol wt found/mol wt calcd
Ni(AcetDPT	3.0	3.25	1.05
Ni(PropDPT)	3.0	3.3	1.04
Ni(4-MeOAcetDPT)		3.2	1.09
Ni(4-Me-5ClBenzDPT)		3.5	1.04
Cu(AcetDPT)	1.8	1.9	1.04
Cu(PropDPT)	1.9	2.0	1.08
Cu(5-MeAcetDPT)	1.8	1.9	0.99
Cu(4-MeOacetDPT)	2.0		1.09
Cu(4-MeOBenzDPT)	1.7		1.05
Cu(4-Me-5-ClBenzDPT)	2.0	2.1	0.95
Cu(5-MeBenzDPT)	1.7		1.05

The assignment of the band in the 3139–3287-cm^{-1} range to the N–H stretching mode is supported by the absence of a similar band in the complex Cu(5-MeAcetMeDPT) (MeDPT signifies bis(3-aminopropyl)methylamine), also synthesized in our laboratories. Ordinarily, N–H stretching vibrations in aliphatic secondary amines occur as low-intensity bands in the region between 3350 and 3310 cm^{-1}.[40] Consistent with this, we observe the N–H mode as a very sharp band occurring at 3297 cm^{-1} in the free ligand H_2AcetDPT. The reduced frequencies and relative sharpness of the bands in the M(XAcetDPT) and M(XBenzDPT) complexes are indicative of coordination of the secondary amine nitrogen by the metal ion. Moreover, in all cases except one, the N–H stretch occurs at higher frequency in the copper complex than in the corresponding Ni complex, the difference ranging from 22 cm^{-1} for 4-MeOAcetDPT to 50 cm^{-1} for PropDPT (an exception to the observed order occurs with the ligand 4-Me-5-ClBenzDPT). The higher frequency in the case of the copper complexes implies substantially weaker bonding interaction between copper and the central nitrogen donor than between this donor and nickel, which is consistent with the elongated Cu–central donor bond lengths observed by X-ray crystallography in the complexes Cu(mbpN)[25] and Cu(cbpS)[28,29] (in our abbreviation scheme, Cu(5-MeBenzDPT) and Cu(5-ClBenzDAPS), respectively).

Finally, we find that identical spectra are obtained regardless of whether samples are prepared as Nujol mulls or as KBr pellets, indicating that coordination of bromide to Ni(II) or Cu(II) does not occur to a noticeable extent in the KBr fusion mixture.

Molecular weight studies in chloroform (see Table II) indicate that the complexes are monomeric in solution. The deviation of the experimental from the calculated value is in most cases less than 5% and is in no case greater than 10%. Due to the extreme sensitivity of the vapor pressure osmometric method to small amounts of impurities which may be present in the solvent or the standard used to construct the resistance–concentration reference curve, accuracy in the 5% range is considered quite acceptable.

The results of magnetic susceptibility measurements performed on chloroform solutions of the new complexes are also presented in Table II. It can be seen that the nickel complexes are all high spin, in agreement with findings for the similar XSalDPT, TIBDPT, BenzDPT, and BenzDAPS complexes. Magnetic moments are somewhat lower in the case of the present complexes, however, than values previously reported. Typically, high-spin five-coordinate nickel complexes exhibit values of μ_{eff} in the range 3.23–3.46 μ_B,[4,21,28,41] both in the solid state and in relatively nonpolar solvents such as chloroform and benzene. As can be seen in Table II, the new Ni(AcetDPT) and Ni(BenzDPT) complexes give somewhat lower values, usually falling in the range 2.9–3.2 μ_B. Significantly, our moments were determined by using the NMR method of Evans,[38] whereas data on the similar complexes were measured

Table III. Electronic and Electron Spin Resonance Spectral Data

Nickel Complexes

complex	medium	ν_{max}, μm^{-1} (ϵ, M^{-1} cm^{-1})	ref
NiSalDPT	$CHCl_3$	<0.500, 0.885 (26.2), 0.98 (sh), 1.181 (6.7), 1.70 (26)	1
Ni(SalMeDPT)	$CHCl_3$	<0.500, 0.84 (39), 1.00 (sh), 1.18 (13), 1.67 (69.5)	1
Ni(5-ClBenzDPT)	CH_2Cl_2	0.851 (12.5), 1.053 (6.5), 1.65 (30.2)	28
Ni(5-MeBenzDPT)	CH_2Cl_2	0.847 (26.6), 1.053 (sh), 1.667 (75)	28
Ni(5-ClBenzDAPS)	CH_2Cl_2	0.870 (130), 1.667 (sh)	28
Ni(AcetDPT)	$CHCl_3$	0.543 (br), 0.805 (19.41), 1.040 (8.2), 1.652 (52.3)	this work
Ni(PropDPT)	$CHCl_3$	0.543 (br), 0.803 (19.0), 1.042 (5.2), 1.65 (52.4)	this work
Ni(4-MeOAcetDPT)	$CHCl_3$	0.543 (br), 0.803 (19.2), 1.02 (8.3), 1.65 (48.0)	this work
Ni(4-Me-5-ClBenzDPT)	$CHCl_3$	0.531 (12.8), 0.833 (24.3), 1.058 (10.9), 1.65 (68.4)	this work
Ni(TIBMeDPT)	solid	0.836, 1.000, 1.358 (sh), 1.579	21

Copper Complexes

complex	medium	ν_{max}, μm^{-1} (ϵ, M^{-1} cm^{-1})	g_{iso}	$10^4 A_{iso}$, cm^{-1}	$g_{\parallel}$[a]	$g_{\perp}$[b]	$10^4 A_{\parallel}$,[c] cm^{-1}	ref
Cu(SalDPT)	$CHCl_3$	1.24 (213)						4
Cu(SalMeDPT)	solid	1.10, 1.23						4
Cu(5-ClBenzDPT)	CH_2Cl_2	1.34 (172)						28
Cu(5-MeBenzDPT)	CH_2Cl_2	1.35 (192)						28
Cu(5-ClBenzDAPS)	CH_2Cl_2	1.47 (153)						28
Cu(AcetDPT)	$CHCl_3$	1.46 (189)	2.12	63	2.32		162	this work
Cu(PropDPT)	$CHCl_3$	1.47 (174)	2.13	65	2.32	2.06	170	this work
Cu(5-MeAcetDPT)	$CHCl_3$	1.44 (214)	2.13	65	2.31	2.06	170	this work
Cu(4-MeOAcetDPT)	$CHCl_3$	1.41 (181)	2.13	61	2.31	2.06	166	this work
Cu(5-MeBenzDPT)	$CHCl_3$	1.41 (183)	2.13					this work
Cu(4-MeOBenzDPT)	$CHCl_3$	1.36 (172)						this work
Cu(4-Me-5-ClBenzDPT)	$CHCl_3$		2.13	65	2.28	2.08	129	this work

[a] Estimated relative standard deviation in $g_{\parallel}$ and g_{iso}, 0.7%. [b] Estimated standard deviation in $g_{\perp}$, 1%. [c] Estimated relative standard deviation in $A_{\parallel}$, 0.7%.

by the Gouy technique. It is important to realize that results obtained by using the NMR method will in many cases depend upon the particular resonance which is used to obtain the bulk susceptibility shift. The accuracy of the shift depends upon there being a uniform distribution of the molecule whose resonance is being observed with respect to the paramagnetic centers. If this is not attained, the observed shift will be either somewhat too small or somewhat too large, depending upon whether the observed molecule is excluded from or preferentially retained near the immediate environment of the paramagnetic solute. In the present case, the shifts were measured from the Me_4Si resonance, in chloroform solution. Although chloroform is normally considered a nonpolar solvent, nonetheless it is substantially more polar than Me_4Si. It is thus likely that the nickel complexes will be preferentially solvated by chloroform, the Me_4Si thereby being excluded from the immediate environment of the complex. The bulk susceptibility shift observed for the Me_4Si resonance will therefore be somewhat small and will lead to low calculated magnetic moments. We felt that this may be an explanation for the fact that our moments are consistently lower than expected. To confirm this, we have calculated the magnetic moments for several of the complexes from the observed susceptibility shift of the chloroform resonance. These values are also presented in Table II. In these cases, higher values for μ_{eff} are invariably obtained. Moreover, these values fall within the range expected from previous work. This lends support to the explanation given above and calls attention to a potential pitfall associated with the NMR method for determining magnetic susceptibilities.

Also shown in Table II are the effective magnetic moments, μ_{eff}, for the new Cu(AcetDPT) and Cu(BenzDPT) complexes. It is seen that the values lie in the range between 1.7 and 2.0 μ_B, the majority being in the lower half of this range, which is consistent with the presence of one unpaired electron. In addition, the values are of such a magnitude as to preclude extensive metal–metal interactions in solution. As for the nickel complexes, the values we observe are somewhat lower than values which have been reported for similar XSalDPT and XBenzDPT complexes of copper(II), which lie in the range 1.82–2.17 μ_B.[4,28] As detailed above, these results are considered to be an artifact of the method of measurement rather than an indication of major structural differences between the complexes studied here and those previously reported. The results of other physical method studies rule out the latter possibility.

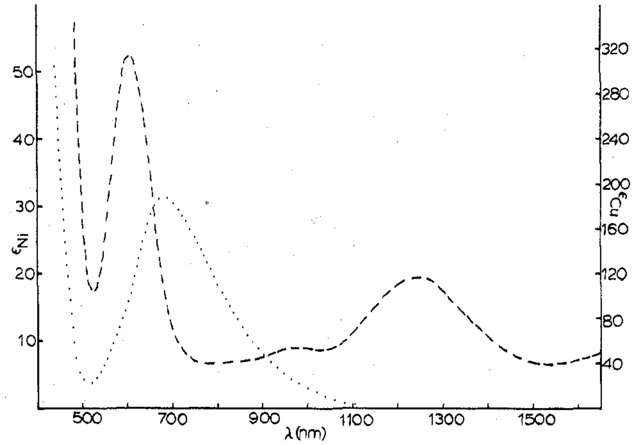


Figure 1. Electronic absorption spectra of Cu(AcetDPT) (···) and Ni(AcetDPT) (- - -). The right-hand ordinate represents the extinction coefficient for copper and the left-hand ordinate that for nickel.

The electronic spectra of the complexes have been measured in chloroform solution between 340 and 2400 nm. The data are presented in Table III, along with data for similar complexes, and typical spectra are shown in Figure 1. For the nickel complexes, major bands are observed at ca. 600, 970, and 1245 nm, with a very broad absorption centered about 1840 nm. The latter absorption is a low-energy ligand field band which was observed for the XSalDPT complexes of nickel[4] but was not mentioned in connection with those of BenzDPT and BenzDAPS described in ref 28. This small discrepancy notwithstanding, the observed spectra are very similar to those of known five-coordinate nickel complexes[4,28,42,43] and serve to substantiate five-coordination in Ni(XAcetDPT) and Ni(XBenzDPT).

Assignment of the electronic spectra of high-spin five-coordinate nickel complexes containing pentadentate ligands has proven to be a difficult task, primarily because of their inherently low electronic symmetry (at most D_{3h}, and more realistically C_{2v}). Crystal field calculations have been performed for D_{3h},[44] C_{4v}, and C_{2v}[45] symmetries, and assignment of the ligand field bands of Ni(SalMeDPT) in C_{2v} symmetry has been made.[41,45,46] According to this assignment (see Table 8, ref 41), the band occurring near 1.68 μm^{-1} is assigned to the transition $^3A_1 \rightarrow {}^3B_2(F), {}^3B_1(F)$, that near 1.00 μm^{-1} to $^3A_1 \rightarrow {}^3A_2(F)$, and that near 0.84 μm^{-1} to $^3A_1 \rightarrow {}^3B_2(F)$ (see Figure 10 of ref 41). As can be seen in Table III, there is very little variation in band positions as the ligand is varied from XSalDPT through XAcetDPT to XBenzDPT. The greatest variation is in the positions of the 1.0–1.05 μm^{-1} and the 0.8–0.89-μm^{-1} bands. According to Figure 10 of ref 41, the ratio of the energy of the $^3A_1 \rightarrow {}^3A_2(F)$ to that of the $^3A_1 \rightarrow {}^3B_2(F)$ transition should decrease as the ligand field strength increases for $Dq > 0.08$ μm^{-1}. According to this criterion, the SalDPT ligands are the strongest and the AcetDPT and BenzDPT ligands are weaker and are of comparable strength. The relative strength of the SalDPT ligands is understandable on steric grounds; the AcetDPT and particularly the BenzDPT ligands would be expected to suffer more extensive crowding when coordinated to a metal ion. On the other hand, the apparent relative strengths of the AcetDPT and BenzDPT ligands is somewhat surprising, since BenzDPT should be weaker on both steric *and* electronic grounds. The additional phenyl ring attached to the imine function should withdraw electron density from the imine nitrogen, thereby reducing its donor strength. It may also be noted that phenyl substituents seem to have little effect on band positions. This has also been previously observed[4] but is somewhat puzzling, particularly in view of the startling substituent effects observed by Taylor et al. for cobalt(II) complexes of some pentadentate ligands derived from salicylaldehyde.[18]

The electronic spectra of the copper complexes are also included in Table III. The spectra exhibit only one asymmetric band in the region 1.4–1.48 μm^{-1} which presumably represents at least two closely spaced transitions. Although the electronic spectra of copper(II) complexes are not in general good indications of geometry, a criterion for distinguishing trigonal-bipyramidal (TBP) and square-pyramidal (SPY) geometries has been proposed.[47,48] An absorption band in the region 550–670 nm (1.49–1.82 μm^{-1}) is suggested to be indicative of SPY geometry, whereas an absorption in the 800–850 nm (1.18–1.25 μm^{-1}) region is supposedly characteristic of TBP stereochemistry. While this generalization must be viewed cautiously, since it implicitly assumes a nearly constant ligand field independent of ligand, it would imply that the Cu(XAcetDPT) and Cu(XBenzDPT) complexes have geometries intermediate between the two extremes, but much more nearly SPY than TBP. This is consistent with previous studies of Cu(5-ClBenzDAPS), which was found by X-ray crystallography[29] to have a distorted SPY structure and which exhibits an absorption band at 680 cm^{-1}, just outside the range given above for SPY stereochemistry. On the other hand the complex Cu(SalDPT), which is almost certainly five-coordinate,[39] absorbs at 813 nm, which indicates TBP geometry. There is no obvious reason for a change from TBP to SPY stereochemistry when the azomethine hydrogens of SalDPT are replaced by CH_3 groups. In fact, similar stereochemistries are expected in both cases, so that the electronic spectral criterion is shown to be somewhat unreliable.

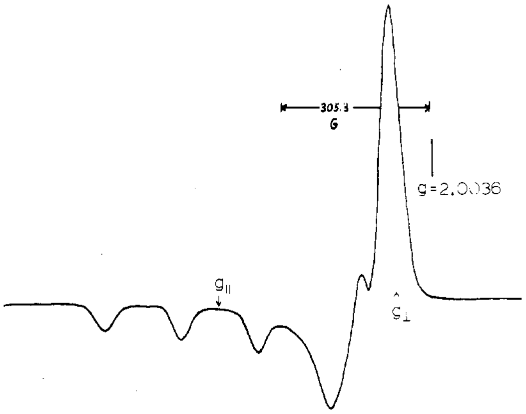


Figure 2. Frozen-solution X-band EPR spectrum of Cu(5-MeAcetDPT).

At the present time, there are varying opinions in the literature regarding the question of coordination of the central donor in 3d metal complexes of Schiff base pentadentate ligands. The uncertainty centers on those ligands in which the central donor is a sulfur or oxygen atom and the metal is cobalt or copper. On the one hand, Taylor and co-workers have shown that the complexes Co(SalDAPS) and Co(SalDAPE) exhibit electronic spectra which are characteristic of tetrahedral stereochemistry about cobalt.[17,18] When electron-withdrawing substituents are placed on the salicylaldehyde rings, however, the complexes exhibit altered spectra which are consistent with pentacoordination. These workers have concluded that the sulfur and oxygen atoms are too weakly basic to coordinate in the unsubstituted complexes but can be induced to coordinate when substituents are present which deplete the electron density on the metal ion. On the other hand, Mockler and co-workers have performed X-ray structural determinations on a variety of metal complexes containing the ligands 5-ClBenzDPT and 5-ClBenzDAPS and the corresponding ligands derived from 5-methyl-2-hydroxybenzophenone. In all cases, they have found metal–nitrogen and metal–sulfur distances which are consistent with bonding between the metal ion and the central donor, and they conclude that metal–central donor bonding is to be considered normal in complexes of this type, including those cobalt(II) complexes which Taylor claims to be four-coordinate on the basis of electronic and infrared spectra. We feel it important to point out that most of the complexes for which structural determinations have been done are expected to be five-coordinate by Taylor's criterion: the presence of an electron-withdrawing substituent on the phenyl ring (Cl) should deplete the donor strength of phenol oxygen, thereby enhancing the tendency for central donor coordination in the 5-ClBenzDPT and 5-ClBenzDAPS complexes. Moreover, these species exhibit electronic spectra consistent with pentacoordination in all cases. Similarly, the 5-MeBenzDPT and 5-MeBenzDAPS complexes exhibit spectra consistent with 5-coordination. The X-ray structural studies which have been performed on complexes containing ligands derived from substituted 2-hydroxybenzophenones therefore do not convincingly eliminate the possibility of four-coordination in unsubstituted Co(SalDAPS) and Co(SalDAPE). There are quite substantial structural differences between the salicylaldehyde- and *o*-hydroxybenzophenone-derived ligands, and behavior characteristic of one type need not necessarily be characteristic of the other.

Finally, we have obtained solution and frozen-solution electron spin resonance spectra of the Cu(XAcetDPT) and Cu(XBenzDPT) complexes. The data are displayed in Table III, and a typical spectrum is pictured in Figure 2. In general, the Cu(XAcetDPT) complexes and Cu(PropDPT) exhibit spectra consistent with near-axial symmetry and have very similar g values. In all cases, we observe $g_{\parallel} > g_{\perp}$ in the frozen-solution spectra. This is quite typical of tetragonal Cu(II) in which the tetragonal distortion arises from elongation of axial bonds and serves to eliminate a TBP structure, which would be expected to have $g_{\perp} > g_{\parallel}$.[49] The values of $A_{\parallel}$ which we observe ($\sim 160 \times 10^{-4}$ cm^{-1}) are very similar for the Cu(XAcetDPT) and Cu(PropDPT) complexes and are also quite typical of N- or O-bonded Cu in tetragonal stereochemistry.

The Cu(XBenzDPT) species show less well-resolved spectra with smaller values of $g_{\parallel}$ and $A_{\parallel}$ and larger values of $A_{\perp}$ than the Cu(XAcetDPT) derivatives. Their solution spectra show greater broadening of the low field hyperfine components, consistent with the longer rotational correlation time expected for these larger species. The values of $g_{\parallel}$, $g_{\perp}$, and $A_{\parallel}$ are reasonably similar to those reported by Mockler et al. for Cu(5-MeBenzDPT).[25] Although we do not observe superhyperfine coupling with ligand nitrogen atoms, in contrast to the results reported in ref 25, tetragonal geometry is again indicated for these complexes by the relative magnitudes of $g_{\parallel}$ and $g_{\perp}$. The EPR results are thus consistent with the results of electronic spectral and infrared spectral studies, all of which support near-square-pyramidal stereochemistry in the copper complexes.

Conclusion

Ni(II) and Cu(II) complexes of an extensive series of potentially pentadentate ligands derived from bis(3-aminopropyl)amine and substituted *o*-hydroxyacetophenones and *o*-hydroxybenzophenones have been synthesized. The complexes are monomeric and five-coordinate, as shown by the results of infrared spectral, electronic spectral, magnetic, and molecular weight measurements, which give results consistent with those obtained for other known five-coordinate complexes of these two metal ions. In addition, EPR spectra have been obtained for the copper complexes, and the relative magnitudes of $g_{\parallel}$ and $g_{\perp}$ support a tetragonal stereochemistry about Cu(II). Finally, the question of the generality of M–X bonding in complexes of this type, where X represents the central donor atom, has been discussed in terms of the available structural and spectral data. It has been concluded that the reported spectroscopic criteria for coordination have not been convincingly invalidated by available X-ray data.

Acknowledgment. We wish to express our thanks to Professor H. C. Allen, Jr., of the Department of Chemistry at Clark University, Worcester, MA, for allowing us unrestricted use of his EPR spectrometer.

Registry No. Ni(AcetDPT), 70197-14-7; Ni(PropDPT), 70197-15-8; Ni(4-MeOAcetDPT), 70197-16-9; Ni(4-Me-5-Cl-BenzDPT), 70197-17-0; Cu(AcetDPT), 70197-18-1; Cu(5-MeAcetDPT), 70197-19-2; Cu(PropDPT), 70197-20-5; Cu(4-MeOAcetDPT), 70197-21-6; Cu(5-MeBenzDPT), 56811-15-5; Cu(4-MeOBenzDPT), 70197-22-7; Cu(4-Me-5-ClBenzDPT), 70197-23-8.

References and Notes

(1) Calvin, M.; Barkelew, C. H. *J. Am. Chem. Soc.* **1946**, *68*, 2267.
(2) Harle, O. L.; Calvin, M. *J. Am. Chem. Soc.* **1946**, *68*, 2612.
(3) Bailes, R. H.; Calvin, M. *J. Am. Chem. Soc.* **1947**, *69*, 1886.
(4) Sacconi, L.; Bertini, I. *J. Am. Chem. Soc.* **1966**, *88*, 5180.
(5) Gray, H. B. *Adv. Chem. Ser.* **1971**, *No. 100*, 365, 1971.
(6) Coleman, W. M.; Taylor, L. T. *J. Am. Chem. Soc.* **1971**, *93*, 5446.
(7) Taylor, L. T.; Dillard, J. G. *Inorg. Chem.* **1974**, *13*, 2620.
(8) Burness, J. H.; Dillard, J. G.; Taylor, L. T. *J. Am. Chem. Soc.* **1975**, *97*, 6080.
(9) Tovrog, B. S.; Drago, R. S. *J. Am. Chem. Soc.* **1977**, *99*, 2203.
(10) Niswander, R. H.; Taylor, L. T. *J. Am. Chem. Soc.* **1977**, *99*, 5935.
(11) Edmondson, S. R.; Niswander, R. H.; Taylor, L. T. *J. Coord. Chem.* **1977**, *7*, 113.
(12) Kildahl, N. K.; Drago, R. S. *J. Am. Chem. Soc.* **1973**, *95*, 6245.
(13) Coleman, W. M.; Taylor, L. T. *Inorg. Chem.* **1971**, *10*, 2195.
(14) Coleman, W. M.; Taylor, L. T. *J. Inorg. Nucl. Chem.* **1971**, *33*, 3049.
(15) Coleman, W. M.; Taylor, L. T. *J. Am. Chem. Soc.* **1970**, *92*, 1449.
(16) Edmondson, S. R.; Coleman, W. M.; Taylor, L. T. *Inorg. Chem.* **1973**, *12*, 1191.
(17) Niswander, R. H.; St. Clair, A. K.; Edmondson, S. R.; Taylor, L. T. *Inorg. Chem.* **1975**, *14*, 478.
(18) Niswander, R. H.; Taylor, L. T. *Inorg. Chem.* **1976**, *15*, 2360.
(19) Spencer, C. T.; Taylor, L. T. *Inorg. Chem.* **1971**, *10*, 2407.
(20) Spencer, C. T.; Taylor, L. T. *Inorg. Chem.* **1973**, *12*, 644.
(21) Bertini, I.; Sacconi, L.; Speroni, G. P. *Inorg. Chem.* **1972**, *11*, 1323.
(22) Wallis, W. N.; Cummings, S. C. *Inorg. Chem.* **1974**, *13*, 988.
(23) DiVaira, M.; Orioli, P. L.; Sacconi, L. *Inorg. Chem.* **1971**, *10*, 553.
(24) Seleborg, M.; Holt, S. L.; Post, B. *Inorg. Chem.* **1971**, *10*, 1501.
(25) Healy, P. C.; Mockler, G. M.; Freyberg, D. P.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1975**, 691.
(26) Freyberg, D. P.; Mockler, G. M.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1976**, 447.
(27) Boge, E. M.; Mockler, G. M.; Sinn, E. *Inorg. Chem.* **1977**, *16*, 467.
(28) Boge, E. M.; Freyberg, D. P.; Kobot, E.; Mockler, G. M.; Sinn, E. *Inorg. Chem.* **1977**, *16*, 1655.
(29) Freyberg, D. P.; Mockler, G. M.; Sinn, E. *Inorg. Chem.* **1977**, *16*, 1660.
(30) Kannan, T. S.; Chakravorty, A. *Inorg. Chem.* **1970**, *9*, 1153.
(31) Balundgi, R. H.; Chakravorty, A. *Inorg. Chem.* **1973**, *12*, 981 and references therein.
(32) Mockler, G. M.; Chaffey, G. W.; Sinn, E.; Wong, H. *Inorg. Chem.* **1972**, *11*, 1308 and references therein.
(33) Butcher, R. J.; Jasinski, J.; Mockler, G. M.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1976**, 1099.
(34) Chia, P. C.; Freyberg, D. P.; Mockler, G. M.; Sinn, E. *Inorg. Chem.* **1977**, *16*, 254.
(35) Scullane, M. I.; Allen, H. C., Jr., *J. Coord. Chem.* **1975**, *4*, 255.
(36) Maslen, H. S.; Waters, T. N. *Coord. Chem. Rev.* **1975**, *17*, 137.
(37) Schwarzenbach, G. "Die Komplexometrische Titration", 3rd ed.; F. Enke: Stuttgart, West Germany, 1956.
(38) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.
(39) Lane, L. W.; Taylor, L. T. *J. Coord. Chem.* **1973**, *2*, 295.
(40) Rao, C. N. R. "Chemical Applications of Infrared Spectroscopy"; Academic Press: New York, 1963; p 247.
(41) Morassi, R.; Bertini, I.; Sacconi, L. *Coord. Chem. Rev.* **1973**, *11*, 343.
(42) Sacconi, L.; Nanneli, P.; Nardi, N.; Campigly, U. *Inorg. Chem.* **1965**, *4*, 943.
(43) Sacconi, L.; Ciampolini, M.; Speroni, G. P. *J. Am. Chem. Soc.* **1965**, *87*, 3102.
(44) Bertini, I.; Ciampolini, M.; Dapporto, P.; Gatteschi, D. *Inorg. Chem.* **1972**, *11*, 2254.
(45) Bertini, I.; Gatteschi, D. *J. Coord. Chem.* **1971**, *1*, 285.
(46) Nemiroff, M.; Holt, S. L. *Inorg. Chem.* **1973**, *12*, 2032.
(47) Hathaway, B. J.; Dudley, R. J.; Nicholls, P. *J. Chem. Soc. A* **1969**, 1845.
(48) Hathaway, B. J.; Proctor, I. N.; Slade, R. C.; Tomlinson, A. A. *J. Chem. Soc. A* **1969**, 2219.
(49) McGarvey, B. R. *Transition Met. Chem.* **1966**, *3*, 89.