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Synthesis and Characterization of Cobalt(II) and Some Nickel(II) Complexes with *N,N'*-Ethylenebis(*p*-X-benzoylacetone iminato) and *N,N'*-Ethylenebis(*p*-X-benzoylmonothioacetone iminato) Ligands

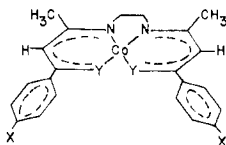
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A series of tetradentate thio imine ligands, *N,N'*-ethylenebis(*p*-X-benzoylmonothioacetone imine), where X = H, CH₃, CH₃O, Br, and Cl, have been prepared from the corresponding tetradentate keto amines via nucleophilic substitution with bisulfide ion. Cobalt(II) complexes with all ligands have been prepared and characterized and are of particular interest because of their ability to combine reversibly with molecular oxygen in nonaqueous solutions at low temperatures. The new ligands and complexes have been characterized by elemental analyses and IR, NMR, and visible spectral data. A few of the corresponding Ni(II) complexes have also been prepared to aid in characterization via NMR techniques when the free ligands proved too insoluble for study.

Introduction

During the course of our studies on the thermodynamic stability of oxygen adducts of tetradentate (thio iminato)-cobalt(II) complexes,²⁻⁴ it became necessary to synthesize a series of the para-substituted benzoylmonothioacetone iminato complexes. In most cases, the corresponding keto iminato precursors had likewise never been prepared or studied. In this paper we report the synthesis and characterization of nine such cobalt(II) complexes. The general structure of the compounds is illustrated in I along with the abbreviations used



- Ia, Co(benacen), X = H, Y = O
 b, Co(Cl(benacen)), X = Cl, Y = O
 c, Co(Br(benacen)), X = Br, Y = O
 d, Co(CH₃Obenacen), X = CH₃O, Y = O
 e, Co(CH₃benacen), X = CH₃, Y = O
 f, Co(bensacen), X = H, Y = S
 g, Co(Cl(bensacen)), X = Cl, Y = S
 h, Co(Br(bensacen)), X = Br, Y = S
 i, Co(CH₃Obensacen), X = CH₃O, Y = S
 j, Co(CH₃bensacen), X = CH₃, Y = S

in each case.⁵ Only Co(benacen)^{6,7} and Co(bensacen)⁸ have been prepared previously. Nickel(II) complexes with the *p*-XbensacenH₂ ligands have also been prepared to allow more complete NMR data correlation. We feel that the procedures reported here are adaptable to the synthesis of a wide variety of keto iminato- and thio iminato-metal chelate systems by selecting different unsymmetrical β-diketones and reacting them with the diamine and metal salt of choice.

Experimental Section

Materials. Unless otherwise noted, all materials were of reagent grade and were used as supplied. Acetophenone, *p*-chloroacetophenone, *p*-bromoacetophenone, *p*-methylacetophenone, and *p*-methoxyacetophenone were purchased from Aldrich Chemical Co., Inc. Ethylenediamine, 1-chloro-2,3-epoxypropane and boron trifluoride etherate were purchased from Matheson Coleman and Bell and freshly vacuum distilled prior to use. Acetic anhydride, purchased from Fisher Scientific, was fractionally distilled, and the fraction with bp 139–141 °C was used. Triethyloxonium tetrafluoroborate, [Et₃O]⁺[BF₄]⁻, was prepared following the method of Meerwein⁹ and stored under dry N₂. It was washed with anhydrous ether (3 × 100 mL) under a N₂ atmosphere prior to each synthesis. Technical grade sodium bisulfide was purchased from Matheson Coleman and Bell in flake form and was ground to a powder and dried under vacuum for 48 h prior to use. All solvents employed were deaerated before preparation of the sulfur ligands and cobalt(II) complexes. Deaeration was achieved either by bubbling catalytically purified dry N₂ through the solvent

for 15 min or by degassing the solvent three times under vacuum by the freeze-pump-thaw technique.

Physical Measurements. Melting points were recorded on a Thomas-Hoover capillary melting point apparatus in open capillary tubes. The values reported are uncorrected.

Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer. Potassium bromide pellet and Nujol mull techniques were employed.

Nuclear magnetic resonance spectra were obtained using a Varian EM-360 NMR spectrometer. Me₄Si was used as an internal reference in CDCl₃ solutions which contained approximately 15% or greater sample concentrations.

Magnetic susceptibilities were measured by the Faraday method. Measurements were taken in 50 mm of He at room temperature and at two field strengths, approximately 8 and 10 kG. Ni(en)₃S₂O₃ was used to calibrate the system while susceptibilities of the ligands were calculated using Pascal's constants.¹⁰

Electronic spectra were obtained on a Cary 14 recording spectrophotometer using an 8-cm low-temperature quartz cell. Weighed samples were dissolved in deaerated, spectroquality toluene to give ~5 × 10⁻⁴ M solutions. Spectral data for the cobalt(II) complexes were recorded under vacuum.

All elemental chemical analyses were performed by the Alfred Bernhard Microanalytisches Laboratorium, Elbach, West Germany.

Syntheses. (1) Preparation of *p*-X-benzoylacetone (X = Cl, Br, CH₃O, CH₃). The procedures reported here for the acetylation of methyl alkyl ketones to yield the required β-diketones involve modifications of a standard method.¹¹

(a) *p*-Bromobenzoylacetone. A mixture of 49.8 g (0.25 mol) of *p*-bromoacetophenone and 51.0 g (0.50 mol) of acetic anhydride was stirred at 25 °C for 30 min. Boron trifluoride etherate (71.0 g, 0.50 mol) was then slowly added to the solution. After a few minutes, a yellow-orange mixture was obtained which was stirred at room temperature for 18 h. A solution of 136 g (1.00 mol) of Na(OAc)·3H₂O in 250 mL of water was added, followed by 2 h of heating at reflux temperature. At the end of this time, the mixture was cooled and the product was extracted with benzene (3 × 100 mL). The combined benzene extracts were washed with aqueous 5% sodium bicarbonate (2 × 100 mL) and with saturated aqueous sodium chloride (2 × 100 mL) and then were extracted with cold aqueous 2% sodium hydroxide. The combined alkaline solution was acidified with glacial acetic acid at 0 °C. The mixture was filtered and the solid product washed with water (10 × 50 mL). The crude product was dried in air for several days; mp 90–93 °C. The yield was 14.5 g (24%).

(b) *p*-Methylbenzoylacetone. This compound was prepared in a manner similar to that given in (a) except that the combined benzene solutions were dried over anhydrous magnesium sulfate prior to completely removing the solvent at 30 °C with a rotary evaporator. The oily residue was vacuum distilled and the product, a pale yellow liquid, was collected; bp 104–108 °C (4 mm). The yield was 24.1 g (54%).

(c) *p*-Methoxybenzoylacetone. The pure product, mp 51–53 °C, was prepared using the procedure given in part (a); yield ~32%.

(d) *p*-Chlorobenzoylacetone. This compound was also prepared by the procedure reported in part (a). The pure product, mp 68–71 °C, was obtained in 46% yield.

Table I. Physical Properties and Proton Magnetic Resonance Spectral Data for XbenacenH₂, XbensacenH₂, and Ni(Xbensacen) Complexes

compd	% yield	color	mp (dec), °C	proton magnetic resonance, ^a δ						
				CH ₃	CH ₂	=CH	C ₆ H ₄	NH	SH	other protons
Cl(benacenH ₂)	44	pale yellow	212-215	2.06 s	3.57 t	5.63 s	7.56 q	11.60 br		
Br(benacenH ₂)	44	pale yellow	237-240	2.06 s	3.57 t	5.61 s	7.56 q	11.52 br		
CH ₃ benacenH ₂	55	pale yellow	180-183	2.03 s	3.52 t	5.73 s	7.54 q	11.65 br		2.34 s (CH ₃) ^b
CH ₃ ObenacenH ₂	84	pale yellow	170-173	2.00 s	3.46 t	5.61 s	7.30 q	11.41 br		3.75 s (OCH ₃) ^b
CH ₃ ObenacenH ₂ -d	85	pale yellow	171-174	2.00 s	3.50 s, br	5.63 s ^c	7.33 q	11.50 br ^c		3.77 s (OCH ₃) ^b
benacenH ₂ -d		pale yellow	185	2.04 s	3.52 t	5.66 s		11.5 br		7.3-7.8 (C ₆ H ₄)
benacenH ₂ -d	86	pale yellow	183-186	2.04 s	3.58 s, br	5.76 s ^c		11.6 br ^c		7.5-7.9 (C ₆ H ₄)
Cl(bensacenH ₂)	12	yellow-orange	188-191	2.23 s	3.80 t	6.50 s	7.43 q		14.57 br	
Cl(bensacenH ₂)-d	84	yellow-orange	189-192	2.23 s	3.83 s, br	6.54 s ^c	7.47 q		14.60 br ^c	
Br(bensacenH ₂)	36	yellow-orange	180-183	2.21 s	3.77 t	6.44 s	7.43 q		14.53 br	
CH ₃ bensacenH ₂	20	yellow	224-227							
CH ₃ ObensacenH ₂	37	yellow	198-201							
Ni(Cl(bensacen))	85	brown	270-274	2.16 s	3.47 s	6.34 s	7.36 q			
Ni(Br(bensacen))	84	brown	282-285	2.12 s	3.42 s	6.31 s	7.37 q			
Ni(CH ₃ bensacen)	80	brown	236-239	2.21 s	3.60 s	6.56 s	7.49 q			2.40 s (CH ₃) ^b
Ni(CH ₃ Obensacen)	70	brown	171-174	2.09 s	3.44 s	6.31 s	7.17 q			3.77 s (OCH ₃) ^b
Ni(bensacen) ^f	40	brown	210-213	2.14 s	3.49 s	6.40 s				7.3-7.6 (C ₆ H ₄)

^a Measured in CDCl₃ solution. Abbreviations: s, singlet; t, triplet; q, quartet A₂B₂ system; br, broad; s, br, apparent broad singlet.

^b Phenyl ring substituent. ^c The relative area of the deuterated compounds, compared with that of methylene group "CH₂, 4".

CH₃ObenacenH₂-d, "=CH, 0.9", "NH, 1.1"; benacenH₂-d, "=CH, 1.1", "NH, 0.9"; Cl(bensacenH₂)-d, "=CH, 1.3", "SH, 0.7". ^d From ref 14. ^e Not recorded due to the very limited solubility in every solvent tried. ^f From ref 8.

Table II. Analytical Data and Some Physical Properties of Co(Xbenacen) and Co(Xbensacen) Complexes

compd	% yield	color	dec pt, °C	% Co		% C		% H		% N		% S	
				calcd	found	calcd	found	calcd	found	calcd	found	calcd	found
Co(CH ₃ Obenacen)	83	orange	226-230	12.66	12.27	61.94	61.92	5.63	5.75	6.02	5.85		
Co(CH ₃ benacen)	93	red-orange	288-290	13.60	13.76	66.51	66.52	6.05	6.02	6.46	6.50		
Co(Br(benacen))	86	red	258-270	10.46	10.42	46.92	46.63	3.58	3.56	4.97	4.87		
Co(Cl(benacen))	84	red	258-270	12.43	12.79	55.72	55.54	4.25	4.24	5.91	6.02		
Co(bensacen) ^a	40	maroon	280-283	13.47	13.12	60.39	60.34	5.08	5.17	6.40	6.22	14.65	14.44
Co(CH ₃ Obensacen)	60	maroon	180-183	11.84	11.44	57.94	57.78	5.27	5.34	5.63	5.61	12.89	12.58
Co(CH ₃ bensacen)	70	maroon	210-213	12.66	12.74	61.92	61.87	5.63	5.70	6.02	6.10	13.77	13.79
Co(Br(bensacen))	85	maroon	270-273	9.90	9.82	44.39	44.27	3.39	3.33	4.71	4.62	10.77	10.86
Co(Cl(bensacen))	87	maroon	269-272	11.64	11.78	52.18	52.16	3.98	4.03	5.53	5.46	12.66	12.53

^a From ref 8.

(2) Preparation of Tetradentate Schiff Base Ligands. (a) Keto Amines. The four new ligands, Cl(benacenH₂), Br(benacenH₂), CH₃benacenH₂, and CH₃ObenacenH₂, were prepared by modification of the method reported for *N,N'*-ethylenebis(acetylacetonimine).¹² Ethylenediamine (0.05 mol) was slowly added to a suspension of 0.08 mol of the β-diketone, resulting from (1), in 50-80 mL of absolute methanol under N₂. The yellow solution which resulted was heated to reflux and acidified with glacial acetic acid to pH 6. After 1-2 h, the mixture was cooled in an ice bath. The solid was isolated by filtration and the product washed with water (10 × 50 mL) and dried with hexane (3 × 50 mL). The crude product was recrystallized from toluene. Yields, physical properties, and ¹H NMR spectral data on the individual ligands are listed in Table I.

(b) Thio Imines. The four new ligands, Cl(bensacenH₂), Br(bensacenH₂), CH₃bensacenH₂, and CH₃ObensacenH₂, were prepared in a manner similar to that reported previously.^{8,13} A dichloromethane solution of [Et₃O]⁺[BF₄]⁻ (0.05 mol in 10 mL) was added to a dichloromethane suspension of the appropriate XbenacenH₂ compound (0.02 mol in 50-70 mL). After 1-3 h, a fine suspension of NaHS (0.08 mol) in 50 mL of absolute ethanol was added to this yellow solution. The mixture was stirred for 10-18 h and the dichloromethane was evaporated with a stream of dry N₂ for ~2 h at 25 °C. The solid residue, consisting of product, NaBF₄, and excess NaHS, was filtered off and washed with anhydrous ether (3 × 50 mL). The thio Schiff base was separated from the inorganic salts by extraction into dichloromethane (three to eight 100-mL portions). The solvent was evaporated to 50-100 mL with a stream of dry air. Hexane (200 mL) was then added to precipitate the product. The crude product was isolated by filtration and then recrystallized from benzene at 25 °C. The yields, physical properties, and ¹H NMR spectra of the new thio ligands are reported in Table I.

(c) Preparation of Deuterated Ligand Samples. Deuteration was achieved by adding 0.5 mL of CD₃OD to a dichloromethane solution of the keto amine or thio amine ligand (~0.3-0.4 mmol in 50 mL)

under dry N₂. After the solution was stirred for 2 h, the solvent was almost completely removed at 25 °C by the rotary evaporator (or until crystals began to appear), and then 50 mL of hexane was added. The product which precipitated was separated by filtration and washed with hexane (3 × 10 mL). The yields, physical properties, and ¹H NMR spectra are given in Table I.

(3) Preparation of Schiff Base-Metal Complexes. (a) Co(Cl(benacen)), Co(Br(benacen)), Co(CH₃benacen), and Co(CH₃Obenacen) were prepared by identical methods using a modification of literature procedures.¹² In a typical preparation, 0.60 mmol of Co(OAc)₂·4H₂O in 25 mL of deaerated absolute methanol was added dropwise under N₂ to 150 mL of a dichloromethane solution containing 0.50 mmol of the keto amine. The mixture was heated under reflux and a weak stream of dry N₂ for 18 h. The dichloromethane was slowly evaporated and red crystals appeared. The hot methanol mixture which remained was filtered, and the red crystals were washed with absolute methanol (3 × 40 mL) under dry N₂ and then dried under vacuum for 2 days. The yields, physical properties, and elemental analyses for these new compounds are reported in Table II.

(b) Co(Cl(bensacen)), Co(Br(bensacen)), Co(CH₃bensacen), Co(CH₃Obensacen), Ni(Cl(bensacen)), Ni(Br(bensacen)), Ni(CH₃bensacen), and Ni(CH₃Obensacen) were prepared by procedures similar to that reported in (a) except that larger volumes of dichloromethane were required to dissolve the less soluble thio imine ligands. Analytical data and some physical properties for the new Co(II) complexes are listed in Table II while ¹H NMR spectral data for the Ni(II) complexes have been included in Table I.

Results and Discussion

Synthesis and Characterization of the Ligands. The series of XbenacenH₂ ligands are formed readily via Schiff base condensation of ethylenediamine with the required unsymmetrical β-diketones as long as the reaction solutions are kept

slightly acidic, pH \sim 6. The pure products are soluble in chloroform, acetone, and benzene, moderately soluble in methanol and ethanol, and sparingly soluble in saturated hydrocarbons. They exhibit good thermal stability. In contrast to this, the sulfur-containing XbensacenH₂ ligands, prepared from the above tetradentate keto amines via nucleophilic substitution with HS⁻, are much less soluble. In general, these ligands precipitated from the reaction solutions along with the NaBF₄ side product and excess NaHS. The ligands were recovered by washing the solid mixture with anhydrous ether followed by extraction with large amounts of dichloromethane at room temperature. All of the sulfur ligands exhibit moderate solubility in chloroform, acetone, and benzene, the last being most suitable for recrystallizations. They are also sparingly soluble in methanol and ethanol and insoluble in hexane and other hydrocarbon solvents. All of the thio imine ligands are thermally unstable and decompose slowly in air even at room temperatures after a few weeks.

Both infrared and NMR spectral techniques have been used to characterize the ligands. The IR spectra exhibit numerous bands, particularly between 1600 and 400 cm⁻¹, and only a few have been assigned. Spectra of the new N₂S₂ ligands are characterized by (1) a weak, broad absorption at 2750–2650 cm⁻¹, which shifts to 2140–2060 cm⁻¹ upon deuteration and which is assigned as the SH stretching vibration, (2) a very strong, major absorption with intense shoulders at 1602–1585 cm⁻¹ which is attributed to C=C stretching vibrations, and (3) a very strong band with intense shoulders in the region 1558–1527 cm⁻¹ which is probably due to the C=N stretching mode. The C-S vibrational modes give rise to other strong bands in the 1300–1100-cm⁻¹ region. The data suggest that the ligands are correctly formulated as thio imines, with the ionizable proton bonded to the sulfur, at least in the solid state. In contrast to this, spectral evidence obtained on the N₂O₂ ligands points to their existence in the keto amine form. IR spectral data which support this conclusion include the existence of (1) very weak absorptions at 3080–3052 cm⁻¹, which shift to 2320 cm⁻¹ on deuteration and are assigned as the NH stretching vibrations, and (2) a very strong but broad envelope covering the region 1600–1500 cm⁻¹ which is thought to include vibrational modes due to C=C and C=O functional groups. Exact assignments are complicated by the presence of other bands in this region due to the para-disubstituted benzene moiety.

NMR spectra of the ligands have been listed in Table I. It will be seen that the resonances observed for each thio imine ligand are shifted downfield from those of the corresponding keto amine. The shift is largest in the resonances of those protons which are part of the six-membered, H-bonded ring (N-H...O, N...H-S) or directly attached to the ring (=CH). For example, the =CH resonance shifts by 0.8–0.9 ppm and the NH (SH) resonance by \sim 3.0 ppm. Shifts observed for the CH₃ and bridging -(CH₂)₂- proton signals are smaller, being $<$ 0.2 ppm in both cases. Of particular interest is the fact that the center of the A₂B₂ pattern due to the para-substituted phenyl protons shifts upfield by \sim 0.13 ppm in the N₂S₂ compared to the N₂O₂ ligands. The deshielding effect of the phenyl groups in benacpnH₂ compared to that in acacenH₂ and tfacenH₂ has been noted previously¹⁵ and explained by a resonance interaction between the phenyl groups and the pseudoaromatic chelate ring. This type of interaction is illustrated in Figure 1.

While the chelate ring protons are deshielded, it is obvious that the phenyl ring protons should experience increased shielding. This is entirely consistent with the observed upfield shift of the phenyl proton pattern. The presence of sulfur atoms in the chelate ring further enhances the deshielding effect. Even in N₂S₂ ligands without phenyl substituents, the

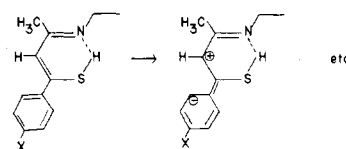


Figure 1. Resonance interaction leading to deshielding of chelate ring protons by phenyl group.

downfield shift is substantial: e.g., =CH (δ 4.99), NH (δ 10.84) for acacenH₂,¹⁶ =CH (δ 6.07), SH (δ 14.16) for sacsacenH₂.¹⁷ This may be related to the ease of polarizability of the sulfur atoms compared to the keto oxygens and their ability to delocalize charge into empty d orbitals.

Synthesis and Characterization of Metal Complexes. Nine new cobalt(II) and five new nickel(II) complexes have been prepared by reaction of the tetradentate Schiff base ligands with the metal acetates. Analytical data and some physical properties of the cobalt(II) complexes are reported in Table II while NMR data on the nickel(II) derivatives are listed in Table I.

All of the metal complexes are readily soluble in chloroform, acetone, and benzene, slightly soluble in methanol and ethanol, and insoluble in saturated hydrocarbons. The Ni(Xbensacen) and Co(Xbensacen) compounds are stable in air in the solid state; however, the Co(Xbenacen) complexes decompose within a few hours in air at room temperature.

Infrared spectra of the M(Xbensacen) and M(Xbenacen) complexes are somewhat different. While the IR spectra of XbensacenH₂ ligands generally show two very strong absorption bands in the 1600–1500-cm⁻¹ region, spectra of the Ni(II) and Co(II) complexes exhibit only one strong band at \sim 1550 cm⁻¹, which probably includes both C=C and C=N vibrational modes. The Co(Xbenacen) complexes invariably show two bands in this region, at 1550 and \sim 1580 cm⁻¹. The lower energy band is again assigned to the C=C and C=N modes while the higher energy absorption may reflect the C=O stretching vibration. The C=S stretching frequency expected for Xbensacen complexes should be out of this range and may correlate with a strong absorption at \sim 1380 cm⁻¹.

¹H NMR spectra of the diamagnetic Ni(Xbensacen) complexes have been used to confirm the structural integrity of these compounds. From the data presented in Table II, it can be seen that complexation causes an upfield shift of all proton resonances compared to that of the free ligands. The rather large shift in the bridging methylene resonance, \sim 0.35 ppm, has been noted in other keto amine and thio imine complexes^{8,15–17} and is thought to reflect steric changes which accompany complexation. The shifts of the =CH protons should be closely related to changes in the electron density in the chelate ring. The dinegative charge associated with the thio imine coordinated ligands should increase the ring proton shielding and result in shifts to higher field. This effect is well documented in both keto amine^{15,16} and thio imine systems.^{8,17} It is interesting to note that the shift is always greater in the thio iminato metal complexes. For example: Δ (=CH) = 0.02 ppm for benacenH₂ and Ni(benacen)¹⁶ but Δ (=CH) = 0.16 ppm for Cl(bensacenH₂) and Ni(Cl(bensacen)). The same trend, though to a lesser extent, is observed for the methyl resonances. The protons of the phenyl rings also shift upfield by \sim 0.07 ppm, an amount which is substantially less than that recorded for the CH₃ protons adjacent to the S atoms of Ni(sacsacen) where a shift of \sim 0.33 ppm has been observed.¹⁷ The presence of increased electron density in the phenyl ring as well as in the chelate ring suggests that the resonance contribution of the phenyl groups in the coordinated ligands may be through resonance structures of the type pictured in Figure 2. This interaction is just the opposite of that discussed earlier in which the phenyl groups acted as electron sinks;

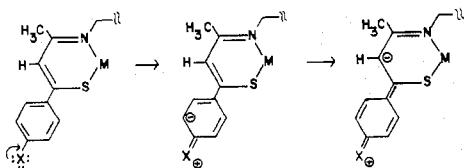


Figure 2. Possible resonance contributions of phenyl rings to coordinated ligands.

Table III. Electronic Absorption Spectral Data and Magnetic Moments for Co(Xbenacen) and Co(Xbensacen) Complexes

compd	major electronic absorption ^a bands			
	λ_{\max} , nm	E_{\max} , cm ⁻¹ × 10 ³	ϵ , M ⁻¹ cm ⁻¹	μ_{eff} , ^c μ _B
Co(Cl(benacen))	422	23.7	4438	2.28
	480	20.8	4031	
Co(Br(benacen))	423	23.7	4041	2.21
	480	20.8	3561	
Co(CH ₃ benacen)	418	23.9	4819	2.24
	475	21.1	4232	
Co(CH ₃ Obenacen)	416	24.0	4703	2.25
	472	21.2	4104	
Co(benacen)	417	24.0	4988	2.21
	475	21.1	4032	
Co(Cl(bensacen))	449	22.3	4418	2.25
	537	18.6	3953	
Co(Br(bensacen))	449	22.3	3918	2.23
	537	18.6	3474	
Co(CH ₃ bensacen)	445	22.5	4654	2.24
	534	18.7	2558	
Co(CH ₃ Obensacen)	448	22.3	4597	2.22
	534	18.7	3214	
Co(bensacen)	448	22.3	4983	2.19
	533	18.8	4023	

^a Measured in deaerated toluene under vacuum at 250 K for Co(Xbenacen) and 210 K for Co(Xbensacen). ^b Peaks, at ca. 440 nm for Co(Xbenacen) and ca. 515 nm for Co(Xbensacen), appear as shoulders on those listed. ^c Measured at 297 K under helium. Corrections for the ligand susceptibilities were calculated from Pascal's constants.¹⁰

however, it is well-known that the phenyl moiety can serve as either an electron donor or acceptor. It would appear that the critical factors involved here are (1) the ability of the para-phenyl substituent to π bond with the phenyl ring and stabilize the resonance forms shown in Figure 2 and (2) the nature of the metal-ligand interaction. The importance of item one is suggested by the increase in shielding of the =CH protons within the Ni(Xbensacen) series of complexes, i.e., CH₃ < H < Cl \approx Br \approx CH₃O, where the strong π -bonding Cl, Br, and CH₃O substituents produce the greatest enhancement. It is not unreasonable to assume that the metal ion could also affect the electron density in the ring. Strong σ bonding between the sulfur donors and the metal ion should shift electron density toward the metal ion, thus favoring an electron-donating resonance contribution by the phenyl rings as shown in Figure 2. Back-donation between π orbitals on the metal ion and empty d orbitals on the sulfur (or simple σ bonding to the hard-acid proton) should contribute more electron density to the chelate ring and induce via a symbiosis effect the opposite type of phenyl resonance contribution, Figure 1. Some support for these concepts derive from earlier dipole moment studies on M(acacpn) and M(tfacpn) compounds¹⁸ and our own thermodynamic studies.²

Characterization of the cobalt(II) species was completed by measuring magnetic susceptibilities of the complexes and recording their visible spectra. These data are listed in Table III. All of the magnetic moments fall in the range 2.19–2.25 μ_B indicative of one unpaired electron on the Co(II) ion and

an $S = 1/2$ ground state. Two absorption bands of high intensity occur in the 18 600–24 000-cm⁻¹ region of the solution electronic spectra of the Co(Xbenacen) and Co(Xbensacen) complexes. In both series of complexes, a third band is observed as a low-energy shoulder at either 440 nm (\sim 22 700 cm⁻¹), Co(Xbenacen), or 515 nm (\sim 19 400 cm⁻¹), Co(Xbensacen). In addition, a band in the 10 000-cm⁻¹ region, of very low intensity ($\epsilon < 50$), has been observed which is typical of square-planar cobalt(II) complexes.^{17,19,20}

Oxygenation of the Co(II) complexes in solutions containing Lewis bases causes the high-energy visible spectral bands to undergo distinct shifts reflecting the change to octahedral coordination. Results of thermodynamic studies on the oxygen adducts of Co(Xbenacen) and Co(Xbensacen) complexes as determined via variable-temperature visible spectral techniques will be reported elsewhere.²

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Registry No. Ia, 36802-28-5; Ib, 66984-42-7; Ic, 66984-43-8; Id, 66984-44-9; Ie, 66984-45-0; If, 66984-46-1; Ig, 66984-47-2; Ih, 66984-48-3; Ii, 66984-49-4; Ij, 66984-50-7; Ni(Cl(bensacen)), 66984-51-8; Ni(Br(bensacen)), 66984-52-9; Ni(CH₃bensacen), 66984-53-0; Ni(CH₃Obensacen), 66984-54-1; Ni(bensacen), 66984-55-2; *p*-bromobenzoylacetone, 4023-81-8; *p*-methylbenzoylacetone, 4023-79-4; *p*-methoxybenzoylacetone, 4023-80-7; *p*-chlorobenzoylacetone, 6302-55-2; Cl(benacenH₂), 67031-22-5; Br(benacenH₂), 67031-23-6; CH₃benacenH₂, 67031-24-7; CH₃ObensacenH₂, 16087-37-9; Cl(bensacenH₂), 67031-25-8; Br(bensacenH₂), 67031-26-9; CH₃bensacenH₂, 67031-27-0; CH₃ObensacenH₂, 67031-28-1.

References and Notes

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