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Square-Planar Transition Metal Complexes with Tetradentate Thioiminato Schiff Base Ligands

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Three new series of transition metal complexes have been prepared from tetradentate Schiff base ligands with two sulfur and two nitrogen donor atoms. Ni(II), Cu(II), Pd(II), and Co(II) chelates were prepared with *N,N'*-ethylenebis(monothioacetylacetonimine), $H_2[(sacac)_2en]$, *N,N'*-propylenebis(monothioacetylacetonimine), $H_2[(sacac)_2pn]$, and *cis-N,N'*-cyclohexylbis(monothioacetylacetonimine), $H_2[(sacac)_2chxn]$. Zn(II) and Cd(II) chelates were also prepared with $H_2[(sacac)_2en]$ while *trans*-$H_2[(sacac)_2chxn]$ formed an isolable complex only with Pd(II). Characterization of the complexes by elemental analyses, molecular weight, magnetic susceptibility, and conductivity measurements and pmr, infrared, and electronic spectra has shown these chelates to be square-planar monomeric species with more charge delocalization in the sulfur-containing chelate rings than in the six-membered chelate rings in the oxygen analogs.

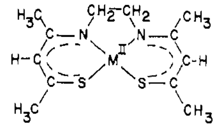
Introduction

The complexity of naturally occurring oxygen-carrying systems has made the study of factors affecting oxygenation extremely difficult. Therefore the study of synthetic model oxygen carriers has been of great interest in recent years. Iron(II) and copper(I), which function so well as reversible oxygen carriers in respiratory proteins, rarely display this property in simpler metal complexes which could be studied more easily. Of necessity, then, the most studied transition metal with an ability to act as a synthetic oxygen carrier has been cobalt(II).

Some of the most recent work in the area of 1:1 cobalt(II)–oxygen adducts involves a series of studies in which tetradentate potential oxygen-carrying chelates are dissolved in the presence of a Lewis base and then exposed to oxygen. The Lewis base coordinates in an axial position and molecular oxygen coordinates in the remaining position. Floriani and Calderazzo[1,2] have investigated the oxygen adducts which form when *N,N'*-ethylenebis(salicylideneiminato)cobalt(II), Co(salen), or its phenyl-substituted derivatives are dissolved in the presence of DMF, DMSO, or some other Lewis base and then slowly exposed to dry air. Crumbliss and Basolo have reported similar studies with *N,N'*-ethylenebis(acetylacetoniminato)cobalt(II).[3] Their work suggests that the role of the Lewis base is to stabilize the adduct by allowing octahedral coordination of the metal to be achieved upon oxygenation in solution.

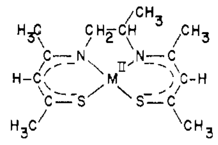
Although the majority of synthetic oxygen carriers contain tetradentate ligands with oxygen and/or nitrogen donor atoms, the work done by Vaska, *et al.*, on reversible oxygen carriers containing Ir, Rh, and Co metal ions with phosphine ligands,[4] suggests that a wider range of complexes should be investigated for oxygen-carrying properties. Although, to date, few studies have been made on oxygen-carrying metal chelates with nitrogen and sulfur donor atoms, several potential oxygen-carrying chelates of this type have recently been synthesized. Bertini, Sacconi, and Speroni have prepared a series of nickel(II) and cobalt(II) chelates with Schiff base ligands formed from *o*-mercaptobenzaldehyde and mono- or polyamines having donor sets of SN, S_2N_2, and S_2N_3.[5] Obviously these cobalt(II) chelates, which are planar and tetradentate, and even those which are pentadentate are prime candidates as oxygen carriers.

An interest in the novel properties of sulfur-containing chelates and a search for new oxygen-carrying metal complexes have led us to synthesize a series of new metal chelates (as shown in I–III) containing tetradentate Schiff base ligands with two nitrogen and two sulfur donor atoms. As these new chelates are quite similar to *N,N'*-ethylenebis(acetylacetoniminato)cobalt(II), which has been shown to coordinate reversibly with molecular oxygen in the presence of a Lewis base, it was expected that the cobalt(II) chelates of this study would form adducts with molecular oxygen. Indeed studies in our laboratory on the oxygen-carrying properties of *N,N'*-ethylenebis(monothioacetylacetoniminato)cobalt(II) have confirmed that in the presence of Lewis bases at low temperatures this compound does bind reversibly with molecular oxygen.[6] A full account of the oxygen reactivity will be published subsequently. In this paper, we wish to report the synthesis and characterization of three new series of tetradentate thioiminatometal chelates[7] *via* a method which should prove generally applicable to a wide variety of such complexes.[7a]



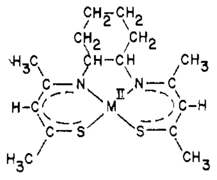
M(II) = Ni, Cu, Co, Pd, Zn, Cd

I



M(II) = Ni, Cu, Co, Pd

II



M(II) = Ni, Cu, Co, Pd

III

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(1) F. Calderazzo, C. Floriani, and J. J. Salzman, *Inorg. Nucl. Chem. Lett.*, 2, 379 (1966).

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(3) A. L. Crumbliss and F. Basolo, *Science*, 164, 1168 (1969); *J. Amer. Chem. Soc.*, 92, 55 (1970).

(4) L. Vaska, *Science*, 140, 809 (1963); *Accounts Chem. Res.*, 1, 335 (1968).

(5) I. Bertini, L. Sacconi, and G. P. Speroni, *Inorg. Chem.*, 11, 1323 (1972).

(6) M. E. Koehler and S. C. Cummings, Abstracts, 165th National Meeting of the American Chemical Society, Dallas, Tex., April 1973.

(7) A preliminary account of some of this work has already appeared: see R. M. C. Wei and S. C. Cummings, *Inorg. Nucl. Chem. Lett.*, 9, 43 (1973).

(7a) Note Added in Proof. We have recently extended these reactions to systems with different substituents on the thioimine

Table I. Analytical Data for $H_2[(sacac)_2B]$ and $M[(sacac)_2B]$

	Mol wt			% calcd					% found				
Compd	Calcd	Found[a]	Color	C	H	N	S	M	C	H	N	S	M
$H_2[(sacac)_2en]$	256.5	256	Yellow	56.20	7.86	10.92	25.00		56.27	7.40	10.99	25.24	
$H_2[(sacac)_2pn]$	270.4	268	Yellow	57.73	8.20	10.36	23.71		57.67	8.11	10.20	23.87	
$H_2[(sacac)_2chxn]$[b]	310.5	304	Yellow	61.88	8.44	9.02	20.65		61.98	8.11	8.93	20.86	
$Ni[(sacac)_2en]$	313.2	306	Green	46.02	5.75	8.94	20.48	18.75	46.24	5.36	8.96	20.48	18.81
$Ni[(sacac)_2pn]$	327.2	330	Green	47.69	6.16	8.56	19.60	17.95	47.67	6.15	8.41	19.43	18.16
$Ni[(sacac)_2chxn]$[c]	367.2	363	Green	52.33	6.59	7.63	17.46	15.99	52.45	6.20	7.83	17.71	16.32
$Cu[(sacac)_2en]$	318.0	324	Maroon	45.33	5.71	8.81	20.17	19.99	45.36	5.49	8.89	20.07	19.81
$Cu[(sacac)_2pn]$	332.1	325	Bronze	47.02	6.07	8.73	19.31	19.13	47.13	5.57	8.39	19.14	19.51
$Cu[(sacac)_2chxn]$[c]	372.1	382	Bronze	51.65	6.50	7.53	17.23	17.08	51.51	6.51	7.44	16.94	17.09
$Pd[(sacac)_2en]$	360.8	358	Gold	39.95	5.03	7.76	17.77	29.49	39.92	4.86	7.98	17.62	29.35
$Pd[(sacac)_2pn]$	374.8	370	Gold	41.66	5.38	7.47	17.11	28.39	41.75	5.40	7.54	17.05	28.18
$Pd[(sacac)_2chxn]$[b]	414.9	408	Gold	46.32	5.83	6.75	15.46	25.64	46.26	5.79	6.88	15.56	25.33
$Pd[(sacac)_2chxn]$[d]	414.9	404	Gold	46.32	5.83	6.75	15.46	25.64	46.39	5.48	6.63	15.48	25.51
$Co[(sacac)_2en]$	313.3	321	Red	46.00	5.79	8.94	20.47	18.81	46.11	5.25	9.13	20.48	19.04
$Co[(sacac)_2pn]$	327.4	323	Red	47.69	6.16	8.56	19.59	18.01	47.59	6.19	8.38	19.44	18.25
$Cd[(sacac)_2en]$	366.9	624[e]	Yellow	39.29	4.95	7.63	17.49	30.64	39.34	4.94	7.50	17.66	30.42
$Zn[(sacac)_2en]$	319.8	316	Yellow	45.07	5.67	8.76	20.05	20.44	45.08	5.28	8.88	20.12	20.62

[a] Chloroform solvent. [b] Cis and trans isomer mixture. [c] Cis isomer. [d] Trans isomer. [e] Probably due to interaction of this complex with $CHCl_3$ molecules.

Experimental Section

Materials. Acetylacetone, ethylenediamine, 1-chloro-2,3-epoxypropane, and boron trifluoride etherate were purchased from Matheson Coleman and Bell. The latter two were freshly vacuum distilled prior to use. Propylenediamine and 1,2-cyclohexanediamine (gc analyzed as a mixture of 33% cis and 67% trans isomers) were purchased from Aldrich Chemical Co. Pure *trans*-cyclohexanediamine was prepared by the method of Smith.[8] All of the metal salts were reagent grade and were used without further purification. Technical grade sodium hydrosulfide was purchased from Matheson Coleman and Bell in flake form and was ground to a powder and dried under vacuum for 24 hr prior to use.

N,N'-Ethylenebis(acetylacetonimine), $H_2[(acac)_2en]$, *N,N'*-propylenebis(acetylacetonimine), $H_2[(acac)_2pn]$, and *N,N'*-cyclohexylbis(acetylacetonimine), $H_2[(acac)_2chxn]$, were prepared by condensation of the appropriate β-diketones and diamines in absolute ethanol as reported by Martell, Belford, and Calvin.[9]

Triethyloxonium tetrafluoroborate, $[Et_3O]^+[BF_4]^-$, was prepared following the method of Meerwein[10] and stored at 5° in an airtight container.

Physical Measurements. Infrared Spectra. Infrared spectra were taken on a Perkin-Elmer Model 457 grating infrared spectrophotometer. Potassium bromide pellet and Nujol mull techniques were employed.

Magnetic Measurements. Magnetic measurements were made using the Faraday technique. Measurements were made at two field strengths of approximately 8 and 10 kG. The susceptibilities of the ligands were calculated using Pascal's constants.[11]

Conductivity Measurements. Conductivities were obtained using a YSI (Yellow Springs Instrument Co., Inc.) Model 31 conductivity bridge. Measurements were made at room temperature on approximately 5×10^{-4} *M* solutions using spectroquality solvents at a frequency of 1 kHz.

Electronic Spectra. Electronic spectra were obtained using a Cary 14 recording spectrophotometer with 0.1-, 1-, and 5-cm matched quartz cells. Weighed samples were dissolved in spectroquality methanol and/or dichloroethane to give approximately 5×10^{-4} *M* solutions. Solid-state spectra were obtained by the diffuse transmittance technique.[12]

Elemental Analyses and Molecular Weight Data. Elemental analyses and molecular weight measurements in chloroform were performed by Alfred Bernhardt Microanalytisches Laboratorium, Elbach, West Germany. All elemental analyses and molecular weight data are listed in Table I.

Nuclear Magnetic Resonance Spectra. Proton nuclear magnetic resonance spectra were obtained using a Varian HA-60-IL or A-60 nuclear magnetic resonance spectrometer. Weighed samples were dissolved in chloroform and diluted to give concentrations of approximately 10-20% when solubility of the compound permitted. The proton resonance of the solvent was used as the internal standard.

Syntheses. Ligand Syntheses. The three thioimine ligands, $H_2[(sacac)_2en]$, $H_2[(sacac)_2pn]$, and $H_2[(sacac)_2chxn]$, were prepared by the same general method. To a solution of 0.05 mol of $H_2[(acac)_2en]$, $H_2[(acac)_2pn]$, *cis-* and *trans*-$H_2[(acac)_2chxn]$, or pure *trans*-$H_2[(acac)_2chxn]$ in 100 ml of dichloromethane was added, over a period of 15 min with stirring under dry nitrogen, 0.10 mol of $[Et_3O]^+[BF_4]^-$ which had been dissolved in 50 ml of dichloromethane. After the addition was complete, the mixture was stirred at room temperature for an additional 30 min. At the end of this time a fine suspension of 8-10 g (an excess) of NaHS in approximately 100 ml of absolute ethanol was added to the mixture. This mixture was stirred for 60 min and the solution turned deep yellow. The mixture was filtered to remove the insoluble sodium tetrafluoroborate and the filtrate was evaporated to dryness under vacuum at room temperature. The crude ligand was recrystallized twice from acetone and water. Yield of the purified ligand ranged from 50 to 60% for $H_2[(sacac)_2en]$ and $H_2[(sacac)_2pn]$. For the mixture of *cis-* and *trans-* and the pure *trans*-$H_2[(sacac)_2chxn]$ the yield was 70%. Analytical data are presented in Table I.

Metal Chelate Syntheses. $Ni[(sacac)_2en]$, $Ni[(sacac)_2pn]$, *cis*-$Ni[(sacac)_2chxn]$, $Zn[(sacac)_2en]$, and $Cd[(sacac)_2en]$ were all prepared similarly. A 0.01-mol sample of the required metal acetate was dissolved in 100 ml of methanol. To this was added 0.01 mol of the appropriate ligand. Each mixture was heated for 30 min on a steam bath and then cooled overnight in the refrigerator. Each of the crude complexes was isolated by filtration and purified by recrystallization from acetone or acetone and water.

$Co[(sacac)_2en]$, $Co[(sacac)_2pn]$, and *cis*-$Co[(sacac)_2chxn]$ were prepared by the same method as reported above except that deaerated solvents were used and all operations were carried out under an atmosphere of dry nitrogen.

$Pd[(sacac)_2en]$, $Pd[(sacac)_2pn]$, *cis-* and *trans*-$Pd[(sacac)_2chxn]$, and *trans*-$Pd[(sacac)_2chxn]$ were prepared by a slightly different method. $PdCl_2$ (0.006 mol) was dissolved in approximately 250 ml of hot H_2O. The required ligand (0.006 mol) was dissolved in a minimum amount of acetone and added dropwise to the metal salt solution. Each of the mixtures was refrigerated overnight. The crude Pd(II) chelates were isolated by filtration and purified by recrystallization from acetone. Analytical data and yields of the metal chelates are reported in Table I.

Results and Discussion

Synthesis and Characterization of the Ligands. The general reaction scheme for the synthesis of these new ligands involves a nucleophilic substitution and is an extension of the method first reported by Holm.[13] In each case the starting material, $H_2[(acac)_2en]$, $H_2[(acac)_2pn]$, *cis-* and *trans*-H_2-

rings simply by using different β-diketones, *e.g.*, benzoylacetone (D. R. Treter, M.S. Thesis, Wright State University, Aug 1973). Details will be published in *Inorg. Syn.*, Vol. XVI.

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(9) A. E. Martell, R. L. Belford, and M. Calvin, *J. Inorg. Nucl. Chem.*, **5**, 170 (1958).

(10) H. Meerwein, *Org. Syn.*, **46**, 113 (1966).

(11) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience, New York, N. Y., 1960.

(12) R. H. Lee, E. Griswold, and J. Kleinberg, *Inorg. Chem.*, **3**, 1279 (1964).

Table II. Proton Magnetic Resonance Spectral Data[a]

Compd	$-CH_3$ adj to N	$-CH_3$ adj to S	$=CH-$	$-SH$	Bridging group resonances		
					$-CH_2CH_2-$		
$H_2[(sacac)_2en]$	2.06	2.47	6.07	14.16	3.67, 3.70, 3.73		
$D_2[(sacac)_2en]$	2.06	2.48	6.07		3.70		
$Ni[(sacac)_2en]$	2.01	2.14	6.00		3.40		
$Pd[(sacac)_2en]$	2.10	2.31	6.03		3.67		
$Zn[(sacac)_2en]$	2.05	2.22	6.04		3.60		
$Cd[(sacac)_2en]$	2.03	2.19	6.00		3.66		
Integration	6	6	2	2	4		
					$-CH_3$	$-CH_2-$	$-\overset{\vert}{C}H-$
$H_2[(sacac)_2pn]$	2.03, 2.07	2.47	6.03, 6.07	14.15	1.37, 1.47	3.03, 3.53,[b] 3.63	4.03[c]
$D_2[(sacac)_2pn]$	2.02, 2.06	2.47	6.04, 6.07		1.38, 1.48	3.52, 3.63[b]	3.91, 4.01, 4.11, 4.21
$Ni[(sacac)_2pn]$	1.96, 2.02	2.12	5.96, 6.00		1.31, 1.41	3.18,[b] 3.27, 3.36	3.56, 3.66, 3.76, 3.86
$Pd[(sacac)_2pn]$	2.02, 2.08	2.25	5.95, 5.99		1.15, 1.25	3.52,[b] 3.57, 3.65	3.85, 3.95, 4.05, 4.14
Integration	6	6	2	2	3	2	1
					$-CH_2-$	$-\overset{\vert}{C}H-$ and $-CH_2-$	
cis- and *trans-*$H_2[(sacac)_2chxn]$	1.94	2.40	5.94, 6.04	14.35	1.77,[d] 1.44[e]	3.10–4.20[f]	
trans-$H_2[(sacac)_2chxn]$	1.94	2.37	5.94	14.35	1.77,[d] 1.44[e]	3.10–3.80[f]	
cis-$Ni[(sacac)_2chxn]$	2.01	2.10	5.86		1.54[g]	3.52–4.19[f]	
cis- and *trans-*$Pd[(sacac)_2chxn]$	2.05, 2.09	2.22	5.80, 5.87		1.51[g]	3.54–4.31[f]	
trans-$Pd[(sacac)_2chxn]$	2.08	2.21	5.78		1.48[g]	3.93[g]	
Integration	6	6	2	2	6	4	

[a] Chemical shifts are in ppm (δ) relative to TMS at 60 MHz with the solvent, $CHCl_3$, the internal reference. [b] Most intense peak caused by overlapping multiplets. [c] Major peak of complex multiplet. [d] Sharp peak at low-field end of complex multiplet over the 1.91–1.15-ppm range. [e] Central broad band in same complex multiplet as above. [f] Broad complex multiplet. [g] Major peak near center of a complex multiplet which extends over *ca.* 0.8 ppm.

$[(acac)_2chxn]$, or *trans*-$H_2[(acac)_2chxn]$, was alkylated with $[Et_3O]^+[BF_4]^-$ to form the tetrafluoroborate salt. The purpose of this alkylation was to increase the positive charge on the carbon atoms adjacent to the alkylated oxygen atoms. Subsequent treatment of the tetrafluoroborate salt with sodium hydrosulfide resulted in the replacement of the two oxygen atoms with two sulfur atoms.

Infrared spectra of these new ligands exhibit several absorptions in common. The very intense bands at approximately 1590 and 1525 cm^{-1} have been assigned to the C=C and C=N stretching vibrations respectively. The bands between ~1100 and 1125 cm^{-1} (depending upon the ligand) are probably due to the coupling of $\nu(C-CH_3) + \nu(C-S)$ and the series of bands from ~840 to 780 cm^{-1} are assigned to a mixture of $\nu(C-S) + \nu(C-CH_3)$. The bands at ~720 and 600 cm^{-1} are probably due to the C–S stretching vibration.[14] In addition to these bands a broad band of medium intensity at 2660 cm^{-1} appears in the spectra of $H_2[(sacac)_2pn]$, *cis*- and *trans*-$H_2[(sacac)_2chxn]$, and *trans*-$H_2[(sacac)_2chxn]$ (but not in the spectrum of $H_2[(sacac)_2en]$). This band is assigned to the –SH stretching vibration. The band disappears upon coordination of the ligand to a metal ion, thus confirming that it is due to relatively easily ionized hydrogens. There is no explanation for the absence of this band in the spectrum of $H_2[(sacac)_2en]$.

The pmr spectra of these new ligands are reported in Table II. The spectra of all the new ligands are very similar except for those resonances which are due to protons located on the individual bridging groups. An examination of the spectrum of $H_2[(sacac)_2pn]$ allows an unambiguous assignment of the methyl peaks in the spectra of all of the ligands. Resonances at 2.03 and 2.07 ppm (area equal to 6) with 1:1 peak intensity are attributed to protons of the $-CH_3$ groups adjacent to the nitrogens. The peak at 2.47 ppm (relative area of 6), which exhibits a shoulder when the spectrum is expanded, is assigned to protons of the CH_3 groups adjacent to sulfur. These assignments are based on the fact that those methyls adjacent to the nitrogens would feel most strongly the asymmetry of the bridging group which accounts for the larger difference in chemical shifts of the upfield signals.

In the spectrum of $H_2[(sacac)_2pn]$ a doublet with peaks at 1.37 and 1.47 ppm is assigned to the bridge CH_3 protons. A set of overlapping multiplets, resulting in a three-line pattern with the center of gravity at 3.53 ppm has been attributed to the bridge methylene protons. These protons are diastereotopic by virtue of the chiral carbon and this nonequivalence cannot be removed by rotation in solution. Upon deuteration, the pattern collapses to two lines of unequal intensity which indicates that the complex pattern is due to coupling of the methylene signals with both the methine proton and the ionizable protons of the ligand. A possible explanation for this might involve very strong hydrogen bonding of the –SH protons to the nitrogen atoms, thus enabling these to couple with the methylene resonances. Evidence for strong hydrogen bonding of these protons is obtained from their extremely low-field resonance at 14.15 ppm. The –SH proton resonances for various thio-β-diketones which exhibit hydrogen bonding have also been observed in this region. The remainder of the pmr resonances are reported in Table II. All of the resonances of the sulfur-containing ligands, when compared to those of the analogous oxygen-containing compounds, occur at lower field strength. The largest downfield shifts involve those protons closest to the sulfur atoms, *i.e.*, the vinylic protons and the ionizable protons. This seems to indicate that the sulfurs are more deshielding than the oxygens, which means that inductive effects are not of great importance in this system. Perhaps the empty d orbitals of the more polarizable sulfur atoms are accepting electron density from adjacent atoms leading to a more delocalized electron system.

Synthesis and Characterization of the Metal Chelates. Nickel(II), copper(II), cobalt(II), and palladium(II) chelates were prepared with $H_2[(sacac)_2en]$, $H_2[(sacac)_2pn]$, and

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(13) D. H. Gerlach and R. H. Holm, *J. Amer. Chem. Soc.*, 91, 3457 (1969).

(14) O. Siiman and J. Fresco, *Inorg. Chem.*, 8, 1846 (1969).

cis- and *trans*-$H_2[(sacac)_2chxn]$. Cadmium(II) and zinc(II) chelates were also prepared with $H_2[(sacac)_2en]$. With *trans*-$H_2[(sacac)_2chxn]$ only the palladium(II) chelate could be prepared. Syntheses of all the metal complexes were essentially the same and involved heating and stirring stoichiometric amounts of the appropriate ligand and metal salt in a suitable solvent, such as methanol or acetone and water mixtures. The desired complexes crystallized upon cooling or upon the addition of water. When cobalt(II) was the metal ion being used, all solvents were deaerated with nitrogen and the entire procedure was carried out under an inert atmosphere. Only *cis*-$H_2[(sacac)_2chxn]$ reacts with nickel(II), cobalt(II), and copper(II) to form chelates; whereas both isomers coordinate with palladium(II). Differences in bite size of the two isomers or differences in steric strain due to unfavorable overlap between the cyclohexyl bridge and the methyl groups adjacent to the nitrogens in the two isomers may account for the stereospecificity of these reactions. Similar results have been noted for $H_2[(acac)_2chxn]$ complexes.[15]

The three series of thioiminatometal chelates have been characterized on the basis of elemental analyses, molecular weight determinations, conductivity and magnetic susceptibility measurements, and infrared, nuclear magnetic resonance, and electronic spectra.

Molecular weight data and elemental analyses, listed in Table I, indicate that all of the complexes are monomeric species formed by coordination of 1 mol of the metal ion and 1 mol of the appropriate ligand. All of the metal chelates of this study are insoluble in water but soluble in most organic solvents, the $M[(sacac)_2pn]$ complexes being the most soluble series. Electrical conductivity measurements on dichloroethane or methanol solutions of the metal chelates give Λ_M values of ~0.5 mho cm^2/mol and confirm that they are nonelectrolytes.

Infrared spectra of the metal complexes are also helpful in the characterization of the metal chelates. The spectrum of $Ni[(sacac)_2en]$ is representative of the new series of compounds and exhibits bands at 1575 and 1505 cm^{-1} which are assigned to the $C\overset{\cdots}{-}C$ and $C\overset{\cdots}{-}N$ stretching vibrations. Bands at 1145 and 1134 cm^{-1} are attributed to the coupling of $\nu(C{-}CH_3) + \nu(C\overset{\cdots}{-}S)$. Bands at 822 and 800 cm^{-1} are probably due to a mixture of $\nu(C\overset{\cdots}{-}S) + \nu(C{-}CH_3)$. A band at 726 cm^{-1} is attributed to the $C\overset{\cdots}{-}S$ stretching frequency, while a band at 394 cm^{-1} is assigned to the Ni–S stretching vibration. All of the bands except that assigned to the Ni–S stretch are observed in the ligand spectrum. The absorptions which are attributed to C=C and C=N in the free ligand occur at lower energies in the complex, whereas those due to the C–S vibration shift to higher energies upon coordination, which substantiates the ir assignments made for the ligand (*vide infra*).

Nuclear magnetic resonance spectra obtained for those metal complexes which are diamagnetic also aid in the characterization. The pmr data on these new metal chelates are listed in Table II and the spectrum of $Ni[(sacac)_2pn]$ is illustrated in Figure 1. As the spectrum of $Ni[(sacac)_2pn]$ is most informative, it will be discussed in preference to the other compounds. The high-field doublet at 1.31 and 1.41 ppm in the spectrum of $Ni[(sacac)_2pn]$ is assigned to protons of the bridge methyl group. Two singlets assigned to the protons of methyl groups adjacent to nitrogen occur at 1.96 and 2.02 ppm. The difference in shielding results from the asymmetry of the propylene backbone and the singlet at 1.96 ppm most probably represents the CH_3 protons nearest the bridge CH_3 group. The resonance due to the protons of methyl groups adjacent to sulfur occurs as two overlapping singlets at 2.12 ppm. The bridge methylene protons produce a three-line pattern at 3.18, 3.27, and 3.36 ppm. The resonance attributed to the bridge methine proton occurs as a multiplet with four major peaks at 3.56, 3.66, 3.76, and 3.86 ppm. Singlets at 5.96 and 6.00 ppm are assigned to the vinylic protons. As can be seen from the pmr spectrum of free ligand, the resonance assigned to the CH_3 protons adjacent to the sulfur atoms displays a large upfield shift upon coordination, whereas the resonances due to the CH_3 protons located adjacent to nitrogen atoms remain essentially unchanged after coordination. This suggests that protons of the methyl groups adjacent to sulfur experience more shielding in the coordinated ligand than in the free ligand. This is consistent with increased σ-electron density on the sulfur atoms which can be explained by removal of the thiol proton on coordination and subsequent electron delocalization into the ring. Some electron delocalization is confirmed by the infrared spectral data (*vide infra*). Those resonances due to the bridge methylene and methine protons also show an upfield shift upon chelation. This appears to be a measure of the strain in the backbone that results upon coordination. This upfield shift of the bridge resonances depends upon the size of the metal ion; the upfield shift in the nickel(II) chelate is ~0.30 ppm greater than the shift in the palladium(II) chelate. The strain that results from coordination to the small nickel(II) ion is quite significant, whereas very little strain in the bridging group results from coordination to the much larger palladium(II) ion. These same upfield shifts are observed in the pmr spectra of the other metal chelates. The spectra of $M[(sacac)_2chxn]$ chelates are similar to those of $M[(sacac)_2en]$ and $M[(sacac)_2pn]$ chelates except for the resonances due to the more complicated bridging cyclohexyl group which occur as broad multiplets in the regions of 1.5 and 3.5–4.2 ppm.

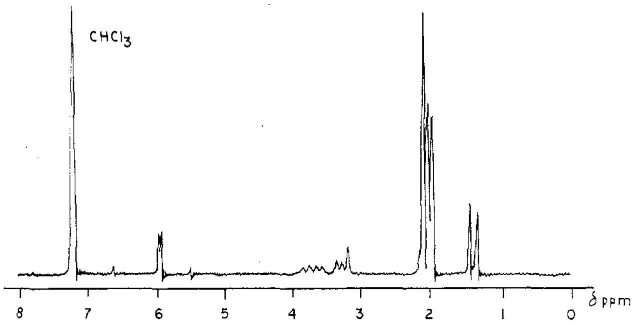

Figure 1. The 60-MHz pmr spectrum of $Ni[(sacac)_2pn]$ in $CHCl_3$.

Thus far, the data examined indicate that the complexes are monomeric metal chelates containing a tetradentate thioiminato ligand with some electron delocalization in the thioimine rings. As the chelates are monomeric with tetradentate ligands the only possible geometries of these chelates are square planar or tetrahedral, although some weak solid-state interactions between adjacent molecules of metal complex which could result in tetragonal distortion might be anticipated. The coordination geometry around the metal ion has been deduced from magnetic susceptibiltiy measurements and electronic spectral data.

Magnetic moments of the metal complexes have been calculated from measured magnetic susceptibilities and are reported in Table III. The nickel(II), palladium(II), cadmium-

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Table III. Magnetic Data for $\mathrm{M[(sacac)_2B]}$ Complexes[a]

Compd	$10^{-6}\chi_M$ (uncor), cgsu	T, °K	μ_{eff}, BM
$\mathrm{Ni[(sacac)_2en]}$	−119.3	297	0.28 ± 0.05
$\mathrm{Ni[(sacac)_2pn]}$	−130.8	296	0.30 ± 0.05
cis-$\mathrm{Ni[(sacac)_2chxn]}$	−71.6	298	0.55 ± 0.03
$\mathrm{Cu[(sacac)_2en]}$	1230.0	297	2.09 ± 0.05
$\mathrm{Cu[(sacac)_2pn]}$	1245.4	296	1.83 ± 0.02
cis-$\mathrm{Cu[(sacac)_2chxn]}$	1305.0	298	1.92 ± 0.03
$\mathrm{Pd[(sacac)_2en]}$	−83.8	297	0.40 ± 0.03
$\mathrm{Pd[(sacac)_2pn]}$	−145.5	298	0.14 ± 0.07
cis- and *trans*-$\mathrm{Pd[(sacac)_2chxn]}$	−161.4	298	0.28 ± 0.04
trans-$\mathrm{Pd[(sacac)_2chxn]}$	−150.4	298	0.20 ± 0.04
$\mathrm{Co[(sacac)_2en]}$	1856.0	297	2.19 ± 0.07
$\mathrm{Co[(sacac)_2pn]}$	1929.3	296	2.20 ± 0.02
$\mathrm{Cd[(sacac)_2en]}$	−97.2	298	0.37 ± 0.07
$\mathrm{Zn[(sacac)_2en]}$	−83.8	297	0.52 ± 0.03

[a] Corrections for the ligand susceptibilities were calculated from Pascal's constants to be -138.5×10^{-6} cgsu for $\mathrm{(sacac)_2en^{2-}}$, -149.4×10^{-6} cgsu for $\mathrm{(sacac)_2pn^{2-}}$, and -180.5×10^{-6} cgsu for $\mathrm{(sacac)_2chxn^{2-}}$.

(II), and zinc(II) chelates are essentially diamagnetic and exhibit room-temperature magnetic moments of ~0.5 BM or less. A small amount of residual paramagnetism of this type can be expected due to temperature-independent contributions.[11] A low-spin d^8 electron configuration is consistent with either a square-planar or strong tetragonal field distortion.[16] The calculated moments for the copper(II) and cobalt(II) chelates are approximately 2.0 BM, which indicates that these d^9 and d^7 ions have one unpaired electron each. The magnetic moments found for the copper(II) complexes are consistent with either tetrahedral or square-planar geometries and cannot be used to distinguish between the two.[16] The magnetic moments found for the cobalt(II) chelates, however, strongly suggest a square-planar geometry, as square-planar cobalt(II) complexes are always low spin whereas tetrahedral cobalt(II) complexes are invariably high spin, with magnetic moments of 3.8-4.6 BM.[16,17] The square-planar geometries of these complexes have been confirmed by the nature of the absorptions which appear in the visible spectra of the various metal chelates.

Electronic spectral data for the $\mathrm{M[(sacac)_2B]}$ chelates are listed in Table IV. The spectra of $\mathrm{M[(sacac)_2pn]}$ chelates have been measured in methanol, dichloroethane, and the solid state; the spectra of $\mathrm{M[(sacac)_2en]}$ chelates have been measured in methanol and the solid state; the spectra of $\mathrm{M[(sacac)_2chxn]}$ were measured in dichloroethane and in the solid state. In general there is agreement between the solution- and solid-state spectra and therefore the geometry is thought to be the same in both states. Hence the possibility of solid-state interactions resulting in tetragonal distortion of the metal ion is unlikely.

The spectra are characterized by the presence of a large number of bands in the visible and ultraviolet regions. In addition, some of the complexes exhibit bands in the near-infrared region. Spectra of all of the complexes are similar to each other in the ultraviolet region where absorptions involving the ligands predominate. Bands at energies of approximately 20,000-35,000 $\mathrm{cm^{-1}}$ are assigned as either M → L, L → M, or ligand transitions. Spectra of all of the free ligands exhibit one or more bands in the 26,000-$\mathrm{cm^{-1}}$ region due to intraligand transitions of the $\pi \rightarrow \pi^*$ type. The dissimilarity between the spectra of the free ligands and the metal chelates may be taken as evidence for the highly covalent character of the metal-donor bonds of the metal chelates.[18]

The square-planar geometry of the $\mathrm{M[(sacac)_2en]}$, $\mathrm{M[(sacac)_2pn]}$, and $\mathrm{M[(sacac)_2chxn]}$ chelates is strongly indicated by similarities in the visible spectra of these chelates with those of known square-planar complexes containing oxygen-nitrogen, oxygen-sulfur, nitrogen-sulfur, and sulfur-sulfur donor atoms. Few molecular orbital calculations have been made for such systems; therefore the absorption bands for the most part cannot be assigned to specific transitions.[18a]

The electronic spectra of the nickel(II) complexes all exhibit one band at ~16,600 $\mathrm{cm^{-1}}$ which can be assigned as a d-d transition of the metal ion. The average energy of this absorption is comparable to d-d transitions of other square-planar Schiff base nickel(II) chelates with sulfur donor atoms,[19,20] which have reported values in the range of 15,000-17,850 $\mathrm{cm^{-1}}$.

The spectra of the copper(II) chelates each exhibit two bands at ~13,600 and ~21,000 $\mathrm{cm^{-1}}$ which are attributed to d-d transitions. The large molar absorptivity of the second band is attributed to intensity stealing from the adjacent charge-transfer band. The spectra of these copper(II) chelates are similar to those reported for $\mathrm{Cu(acac)_2pn}$[18] and other square-planar Schiff base copper(II) complexes.[21]

The palladium(II) chelates exhibit spectra with intense charge-transfer bands at 21,000-24,000 $\mathrm{cm^{-1}}$ which obscure the expected d-d transition. The spectra are similar to those of the nickel(II) chelates (both are d^8 ions) except for this shift of the d-d transition to higher energies in the palladium(II) chelates which reflects the larger crystal field splitting for the series II ion. These data are consistent with those reported for palladium(II) complexes with maleonitriledithiolate[22] and monothio-β-diketonate[23] ligands.

The electronic spectra of $\mathrm{Co[(sacac)_2en]}$ and $\mathrm{Co[(sacac)_2pn]}$ were measured in deaerated methanol and in the solid state. The spectrum of *cis*-$\mathrm{Co[(sacac)_2chxn]}$, which was slightly contaminated with some unreacted *trans*-$\mathrm{H_2[(sacac)_2chxn]}$, was measured only in the solid state. The spectra of these three chelates are very similar to one another and to that reported for $\mathrm{Co(sacsac)_2}$.[24] The spectra of the three cobalt(II) complexes exhibit two bands at ~10,000 and 15,000-18,000 $\mathrm{cm^{-1}}$ both in the solid state and in solution which are assigned as d-d transitions. In addition, a lower energy absorption at ~5350 $\mathrm{cm^{-1}}$ ($\epsilon \simeq 20$) has been observed in tetrachloroethylene solutions of the cobalt(II) complexes. This band is too broad and of too low an intensity to be seen in the solid-state spectra. Such low-energy bands have re-

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Table IV. Electronic Spectra of Metal Complexes

Compd	Methanol		Solid st	Compd	Methanol		Solid st	Dichloroethane		Compd	Dichloroethane		Solid st
	λ, cm^{-1}	ε	λ, cm^{-1}		λ, cm^{-1}	ε	λ, cm^{-1}	λ, cm^{-1}	ε		λ, cm^{-1}	ε	λ, cm^{-1}
Ni[(sacac)$_2$en]	16,530	70	16,530	Ni[(sacac)$_2$pn]	16,597	123	16,666	16,764	170	*cis*-Ni[(sacac)$_2$chxn]	16,611	262	16,597
	21,500 sh		21,270		21,276	1,029	21,390	21,276	1,156		21,739	740	21,739
	23,365	2,500	22,940		23,391	3,116	22,727	23,121	2,738				
	24,690 sh		24,500				24,092	26,143	3,930		25,445	5,354	24,390
	28,900	4,600	28,900		28,985	5,515	27,972	28,169	5,240		26,178	5,163	26,178
	34,000	10,800	33,900		34,129	13,235	33,613	33,898	10,590		33,613	8,222	34,782
	39,200	26,600	38,760		39,062	34,099	38,167	38,759	24,017		38,910	26,769	38,834
	44,250	31,000	43,290		44,444	25,735	43,478	43,956	21,397		43,196	25,335	
Cu[(sacac)$_2$en]	14,490	80	13,600	Cu[(sacac)$_2$pn]	13,880	111	13,793	13,605	88	*cis*-Cu[(sacac)$_2$chxn]	13,404	85	13,245
			20,830		20,833	708	20,833	20,833	902		22,222	1,453	22,222
	27,780	7,800	26,320				25,974	26,845	7,377		26,666	8,430	26,490
					28,169	5,973	27,027	27,777	7,480				
	32,260	12,400	31,850		32,258	9,248	31,746	32,051	14,139		31,746	16,570	30,674
	42,740	19,400	42,370		43,688	15,819	42,553	42,918	21,516		38,022	9,981	
					45,871	14,491					46,511	20,543	42,553
Co[(sacac)$_2$en]	10,300	38	10,200	Co[(sacac)$_2$pn]	10,416	68	10,256			A mixture of *cis*-Co[(sacac)$_2$chxn] and *trans*-H$_2$[(sacac)$_2$-chxn]			9,478
			16,700		14,925	87							
	18,870	1,600	18,200		18,867	1,243	18,348						18,181
			19,700										
	20,830	2,300	20,900		20,661	2,236	20,408						20,202
	24,400	4,380	23,640		23,952	4,913	23,391						23,391
	26,900	5,200	26,450		26,881	3,930	26,490						25,641
	30,000	7,400	28,200		29,585	6,550	29,850						
	33,300	9,400			33,613	8,734	33,057						33,613
	38,460	12,800	37,730		37,735	15,721	37,383						
	43,860	23,000	43,500		39,840	15,502	39,215						40,000
			46,700		46,511	27,074	46,296						46,296
Pd[(sacac)$_2$en]	24,100 sh		21,370	Pd[(sacac)$_2$pn]			23,255			*trans*-Pd[(sacac)$_2$chxn]	21,321	1,653	21,413
	25,510	17,800	25,320		25,641	5,388	25,000	25,316	5,378		27,932	9,061	27,397
	32,790	21,800	31,250		33,613	7,328	32,786	33,112	7,570		29,673	5,568	29,411
	42,470	29,100	47,620		43,103	50,000	42,918	42,918	40,438		42,105	39,410	44,052
					46,511	32,651					46,511	36,463	
Cd[(sacac)$_2$en]			21,500	Zn[(sacac)$_2$en]			21,050			*cis*- and *trans*-Pd[(sacac)$_2$chxn]	21,367	1,255	21,505
	25,640 sh		26,100		28,170 sh		28,570				27,027	4,943	25,974
	27,500 sh				30,580	7,000					33,333	5,228	32,000
	31,050	17,800	38,900		47,850	10,700					42,194	35,932	42,105
	46,080	22,300	44,640								46,511	32,129	
			47,850										

cently been shown to be characteristic of square-planar cobalt(II) chelates.[24,25]

Conclusion

Nickel(II), copper(II), palladium(II), and cobalt(II) chelates have been prepared with $H_2[(sacac)_2en]$, $H_2[(sacac)_2pn]$, and *cis*-$H_2[(sacac)_2chxn]$, which are new tetradentate thioimine ligands. Zinc(II) and cadmium(II) chelates were prepared with $H_2[(sacac)_2en]$ while *trans*-$H_2[(sacac)_2chxn]$ formed only the palladium(II) chelate. All of the complexes are square-planar monomeric species. Infrared and pmr spectral data indicate that there is more charge delocalization in the sulfur-containing chelates than in their well-studied oxygen analogs. This has been attributed to some d-orbital participation on the part of the sulfur atoms which serves to drain some of the electron density from the metal ion. An alternate explanation might attribute this effect to the greater polarizability of the sulfur atom. Since the electron density around the metal ion is known to play an important role in determining the stability of $M-O_2$ bonds in oxygen adducts,[4,26] some of these new complexes are proving to be ideal species for the evaluation of inductive, π-bonding, and polarizability effects in synthetic oxygen-carrying systems. Results of thermodynamic studies on these systems will be reported in a forthcoming paper.

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Registry No. NaSH, 16721-80-5; $H_2[(acac)_2en]$, 6310-76-5; $H_2[(acac)_2pn]$, 16087-26-6; *cis*-$H_2[(acac)_2chxn]$, 41013-19-8; *trans*-$H_2[(acac)_2chxn]$, 42996-22-5; $H_2[(sacac)_2en]$, 40006-83-5; $H_2[(sacac)_2pn]$, 42996-17-8; *cis*-$H_2[(sacac)_2chxn]$, 42996-18-9; *trans*-$H_2[(sacac)_2chxn]$, 42946-00-9; $Ni[(sacac)_2en]$, 41258-78-0; $Ni[(sacac)_2pn]$, 42996-32-7; *cis*-$Ni[(sacac)_2chxn]$, 42996-33-8; $Cu[(sacac)_2en]$, 41192-46-5; $Cu[(sacac)_2pn]$, 42996-35-0; *cis*-$Cu[(sacac)_2chxn]$, 42996-36-1; $Pd[(sacac)_2en]$, 41391-03-1; $Pd[(sacac)_2pn]$, 42996-38-3; *cis*-$Pd[(sacac)_2chxn]$, 42996-39-4; *trans*-$Pd[(sacac)_2chxn]$, 42996-40-7; $Co[(sacac)_2en]$, 41254-15-3; $Co[(sacac)_2pn]$, 42996-42-9; $Co[(sacac)_2chxn]$, 42996-44-1; $Cd[(sacac)_2en]$, 41254-14-2; $Zn[(sacac)_2en]$, 41192-47-6.

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Transition Metal Complexes Containing Phosphorus Ligands. XII.[1] Cationic Dialkyl Phenylphosphonite and Alkyl Diphenylphosphinite Derivatives of Copper, Silver, Gold and the Platinum Metals

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Ligand displacement reactions performed in polar solvents afford a convenient general route to an extensive series of cationic complexes containing dialkyl phenylphosphonite, $P(OR)_2Ph$, and alkyl diphenylphosphinite, $P(OR)Ph_2$, ligands (R = Me, Et) which may be isolated as their tetraphenylborate salts. These products were characterized by elemental analysis, proton nmr spectroscopy, and conductivity measurements. Complex cations isolated and characterized in this manner include the hydrides $[RuHL'_5]^+$ and $[IrHL'_5]^{2+}$, the dinuclear species $[L_3RuX_3RuL_3]^+$, and the mononuclear cations $[RuL'_6]^{2+}$, $[IrL'_5]^+$, $[IrL_4]^+$, $[PdL_4]^{2+}$, $[PtL_4]^{2+}$, $[CuL_4]^+$, $[AgL_4]^+$, and $[AuL_4]^+$ [$L' = P(OMe)_2Ph$; $L = P(OR)_2Ph$, $P(OR)Ph_2$; R = Me, Et; X = Cl, Br]. Qualitative descriptions of the coupling patterns observed in the nmr spectra of the complex cations are given and are interpreted in terms of ligand dissociation and rearrangement processes.

Introduction

Transition metal complexes containing tertiary phosphine[2] and, more recently, tertiary phosphite[3] ligands have been extensively studied. However, the ligand properties of the related phosphonites, $P(OR)_2R'$, and phosphinites, $P(OR)R'_2$, have attracted relatively little attention, and no systematic investigation of their coordinating abilities toward the platinum metals has been reported. As part of a study of phosphorus donor ligands we have described the synthesis of cationic trialkyl phosphite complexes of gold, silver, and the platinum metals;[1] we now report a similar study on the synthesis of related complex cations containing dialkyl phenylphosphonite, $P(OR)_2Ph$, and alkyl diphenylphosphinite, $P(OR)Ph_2$, ligands (R = Me, Et).

Until recently very little was known concerning the coordinating properties of these phosphorus donor ligands, and few transition metal derivatives had been described. However a small selection of important compounds of this type have now been reported and some spectroscopic investigations have been undertaken. Complexes isolated include the salts $\{Cu[P(OR)_2Ph]_4\}Cl$,[4] the zero oxidation state nickel and palladium species, $M[P(OR)_2Ph]_4$,[4,5] and the four- and five-coordinate nickel(II) derivatives, $Ni(CN)_2[P(OR)Ph_2]_2$ and $Ni(CN)_2[P(OR)_2Ph]_3$.[6] During the course of the present study other workers have reported the complex hydrides, $FeH_2[P(OR)_2Ph]_4$,[7] $RuH_2[P(OR)_2Ph]_4$,[7] $\{RuH[P(OMe)_2Ph]_5\}\{BPh_4\}$,[8] and $CoH[P(OR)_2Ph]_4$[9] together with an ex-

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