

## Synthesis and Characterization of Some Metal Complexes of a Novel Binucleating Ligand (II): 1,2,4,5-Tetra(3-isopropylsalicylidene)aminobenzene

PHILIP H. MERRELL\* and LEO J. MAHEU

Department of Chemistry, Bowdoin College, Brunswick, Maine 04011, U.S.A.

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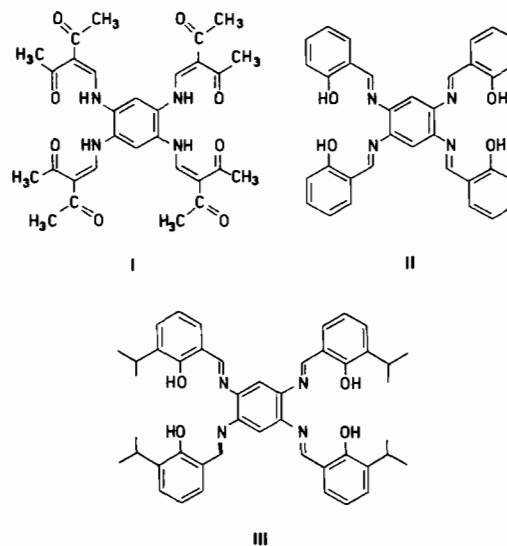
The Co(II), Cu(II), Ni(II), and Zn(II) complexes of the binucleating ligand, 1,2,4,5-tetra(3-isopropylsalicylidene)aminobenzene, have been prepared and characterized by the use of elemental analyses, melting points, infrared spectroscopy, electronic spectroscopy, nmr spectroscopy, and molar conductivity. These compounds show a marked increase in solubility compared to the complexes of the parent ligand, 1,2,4,5-tetrasalicylideneaminobenzene.

### Introduction

In recent years, the study of bimetallic complexes has been of considerable interest to the inorganic chemist because of the unique magnetic and electrochemical properties of these complexes. Early magnetic susceptibility measurements made on the transition metal salt, copper(II) acetate monohydrate, showed an abnormally low room temperature magnetic moment [1]. Attempts to explain this phenomenon led to many of the current ideas of the superexchange mechanism where the two metals are interacting directly.

Many studies on transition metal dimer complexes have since been reported [2–5] in which indirect electron spin interactions exist between the two metal atoms *via* a superexchange mechanism involving relatively simple bridging moieties (e.g., Cl<sup>-</sup>, Br<sup>-</sup>, OAc<sup>-</sup> and the like). In these complexes the typical metal–metal interatomic distances are slightly longer than that of the copper acetate dimer (which is 2.56 Å) and are in the range of 3.0–4.0 Å. Study on these complexes has led to new theories and much better understanding of superexchange interactions.

Recently, Hendrickson and coworkers have reported the synthesis and study of a copper complex of the binucleating ligand shown below (I) in which the interaction between the odd copper electrons must occur through a large  $\pi$  system [6]. We have reported earlier the synthesis and study of some metal



complexes of 1,2,4,5-tetrasalicylideneaminobenzene (TSAB, II) [7]. This ligand is designed to bind two metal ions about 8 Å apart and contains an extensively conjugated system through which the electrons on the metal atoms may interact. Synthesis and characterization of the TSAB complexes was difficult because of the insolubility of both the ligand and the metal complexes. Because of this inherent insolubility, we have now synthesized and would like to report the synthesis and characterization of the isopropyl-substituted ligand 1,2,4,5-tetra(3-isopropylsalicylidene)aminobenzene (iPr-TSAB, III) and several of its first row transition metal complexes. The ligand itself is very soluble in many organic solvents (e.g., CHCl<sub>3</sub>, THF, DMSO, and many others), and the metal complexes are fairly soluble also. Because of this solubility, we are able to prepare pure compounds and characterize them much more readily.

### Experimental

#### Materials and Physical Measurements

All materials employed were reagent grade unless otherwise noted. In addition, the reagents were

\*To whom correspondence should be addressed.

used as supplied from the manufacturers, with no further purification.

All infrared spectra were recorded on a Perkin-Elmer Model 621 infrared grating spectrometer either as potassium bromide pellets or as Nujol mulls while ultraviolet-visible spectra were obtained on a Beckman Model 24 recording ultraviolet-visible spectrophotometer. Nmr spectra (60 MHz) were obtained at room temperature on a Hitachi Perkin-Elmer Model R-24B high resolution spectrometer. Melting points were determined at 760 Torr on a Model 6427-F10 Thomas-Hoover melting point apparatus, and conductivity measurements were performed at 25 °C. (Specific conductance of 0.01N KCl is 0.00141 ohm<sup>-1</sup> cm<sup>-1</sup>) [8]. All chemical analyses were performed by the Department of Chemistry, University of New Hampshire, Durham, New Hampshire, through the courtesy of Dr. N. Dennis Chasteen.

#### Preparation of 3-Isopropylsalicylaldehyde [9, 10]

In a 1-liter, 3-neck flask, a mixture of 250 ml (2.714 mol) of glycerine (Purpac, U.S.P.) and 70.5 ml (1.140 mol) of boric acid, H<sub>3</sub>BO<sub>3</sub>, (Mallinckrodt), was heated for 1–2 hours, after which time the temperature of the mixture was maintained at 170 °C for 0.5 hour. The mixture was then cooled to 160 °C, and a total of 50 g (0.357 mol) of hexamethylenetetramine (Aldrich, 98%) and 50 g (0.367 mol) of 2-isopropylphenol (Aldrich, 97%) were added rapidly and alternately in small portions. The reaction mixture was maintained at 150 °C for approximately 7 minutes and then rapidly cooled to ~110 °C by passing a stream of water over the outside of the reaction flask. A mixture of 45 ml of conc. H<sub>2</sub>SO<sub>4</sub> and 150 ml of H<sub>2</sub>O was added, and the product was steam distilled from the reaction mixture. Approximately 2–3 liters of steam distillate were collected and extracted with ~500 ml of anhydrous ethyl ether. The ether layer was then dried over anhydrous CaCl<sub>2</sub>, and the ether was subsequently evaporated. The resulting residue was distilled at ~2 mm of Hg, and the product, a yellow oil, was collected as the fraction boiling at 60–66 °C. Yield: 20–25 g, 30–40%.

#### Preparation of 1,2,4,5-tetra(3-isopropylsalicylidene)-aminobenzene, iPr-TSAB

The ligand, iPr-TSAB, was prepared by a method similar to that reported earlier for the compound, TSAB [7]. Under dry N<sub>2</sub>, a 5 g (17.6 mmol) sample of 1,2,4,5-tetraaminobenzenetetrahydrochloride (Pfaltz & Bauer) was dissolved in methanol in a 1-liter, 3-neck flask fitted with a reflux condenser, dropping funnel, and mechanical stirrer. Slowly, 5–10 g of NaOCH<sub>3</sub> (Ventron, 97+%) was added, until the dehydrohalogenation reaction was complete (Note: During the dehydrohalogenation of 1,2,4,5-tetraaminobenzenetetrahydrochloride, the reaction

mixture undergoes various color changes in the following order: gray–purple–pink–flamingo–yellow. Since no further color change has resulted upon continuous addition of NaOCH<sub>3</sub>, after the reaction mixture has turned yellow, this is taken to be the point at which total dehydrohalogenation has occurred). Dropwise, 15 g (91.5 mmol) of 3-isopropylsalicylaldehyde was added to the reaction mixture as refluxing with stirring was begun. The mixture was allowed to reflux overnight, and the resulting orange precipitate was recrystallized from CHCl<sub>3</sub>, washed with cold methanol, and allowed to dry in a vacuum desiccator. Yield: 9.30 g, 73.2%. M.p. = 252 °C. *Anal.* Calcd. for C<sub>46</sub>H<sub>50</sub>N<sub>4</sub>O<sub>4</sub>: C, 76.45; H, 6.93; N, 7.76. Found: C, 76.01; H, 7.15; N, 7.64%.

#### Preparation of 1,2,4,5-tetra(3-isopropylsalicylidene)-aminobenzene Dicopper(II), Cu<sub>2</sub>(iPr-TSAB)

A 0.559 g (2.80 mmol) sample of Cu(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O (Fisher) in 150 ml of absolute ethanol was added dropwise to 1.00 g (1.39 mmol) of iPr-TSAB in 250 ml CHCl<sub>3</sub>. This mixture was refluxed with stirring for 5 hours, after which time it was allowed to stand at room temperature in the stoppered reaction flask overnight. The mixture was then filtered, and the reddish-brown precipitate was recrystallized from diphenyl ether. The resulting dark reddish-brown, needle-like crystals of Cu<sub>2</sub>(iPr-TSAB) were washed with absolute ethanol and dried *in vacuo* at 80 °C. M.p. > 260 °C. *Anal.* Calcd. for C<sub>46</sub>H<sub>46</sub>N<sub>4</sub>O<sub>4</sub>·Cu<sub>2</sub>: C, 65.32; H, 5.44; N, 6.63. Found: C, 64.86; H, 5.30; N, 6.83%.

#### Preparation of 1,2,4,5-tetra(3-isopropylsalicylidene)-aminobenzene Dinickel(II), Ni<sub>2</sub>(iPr-TSAB)

A 0.723 g (2.97 mmol) sample of Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (Baker) in 150 ml of absolute ethanol was added dropwise to 1.01 g (1.40 mmol) of iPr-TSAB in 250 ml of CHCl<sub>3</sub>. The mixture was allowed to reflux with stirring overnight, and subsequently allowed to stand at room temperature in the stoppered reaction flask for 24 hours. The brown precipitate was filtered from solution and recrystallized from diphenyl ether. The resulting dark brown, needle-like crystals of Ni<sub>2</sub>(iPr-TSAB) were washed with absolute ethanol and dried *in vacuo* at 80 °C. M.p. > 260 °C. *Anal.* Calcd. for C<sub>46</sub>H<sub>46</sub>N<sub>4</sub>O<sub>4</sub>Ni<sub>2</sub>: C, 66.08; H, 5.51; N, 6.70. Found: C, 65.47; H, 5.76; N, 6.83%.

#### Preparation of 1,2,4,5-tetra(3-isopropylsalicylidene)-aminobenzene Dicobalt(II), Co<sub>2</sub>(iPr-TSAB)

Under dry N<sub>2</sub>, 0.694 g (2.79 mmol) of Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (Mallinckrodt) in 150 ml of absolute ethanol was added dropwise to a solution of 1.00 g (1.39 mmol) of iPr-TSAB in CHCl<sub>3</sub>. After having refluxed with stirring for 6 hours, the mixture was allowed to stand at room temperature overnight

under  $N_2$ . The brownish-black precipitate was then filtered from solution and recrystallized from diphenyl ether. The dark brownish-black, needle-like crystals of  $Co_2$  (iPr-TSAB) were washed with absolute ethanol, dried *in vacuo* at 25 °C, and stored under  $N_2$ . M.p. > 260 °C. *Anal.* Calcd. for  $C_{46}H_{46}N_4O_4Co_2$ : C, 66.04; H, 5.50; N, 6.70. Found: C, 65.35; H, 5.60; N, 6.71%.

*Preparation of diaquodimidazole-1,2,4,5-tetra(3-isopropylsalicylidene)aminobenzene Dicobalt(II),  $Co_2$ -(iPr-TSAB)(imid) $_2$ (H $_2$ O) $_2$*

Under dry,  $O_2$ -free  $N_2$  0.08 g (1.2 mmol) imidazole was added to a solution of 0.5 g (0.59 mmol)  $Co_2$ -(iPr-TSAB) and THF. The solution remains deep brown and was warmed and stirred for about 20 minutes. Air was then bubbled through the brown solution and the solution slowly (5 minutes) turned a deep maroon. The solution was taken to dryness and a deep maroon powder resulted. Yield .5 g (~90%). *Anal.* Calcd. for  $C_{52}H_{58}N_8O_6Co_2$ : C, 61.9; H, 5.75; N, 11.11. Found: C, 63.09; H, 5.84; N, 11.48%.

*Preparation of 1,2,4,5-tetra(3-isopropylsalicylidene)aminobenzene Dizinc(II),  $Zn_2$ (iPr-TSAB)*

A 0.614 g (2.80 mmol) sample of  $Zn(CH_3COO)_2 \cdot 2H_2O$  (Baker) in 150 ml of absolute ethanol was added dropwise to 1.00 g (1.39 mmol) of iPr-TSAB in 250 ml of  $CHCl_3$ . The mixture was refluxed overnight with stirring, and the bright orange precipitate was, subsequently, filtered from solution. The product was recrystallized from a 50:50 mixture of EtOH:THF, washed with cold EtOH, and dried *in vacuo* at 80 °C for 24 hours. M.p. > 260 °C. *Anal.* Calcd. for  $C_{46}H_{46}N_4O_4Zn_2$ : C, 65.04; H, 5.42; N, 6.60. Found: C, 63.32; H, 5.57; N, 6.74%.

## Results and Discussion

Metal complexes of the ligand, 1,2,4,5-tetra(3-isopropylsalicylidene)aminobenzene (iPr-TSAB) have been prepared and characterized by the use of elemental analysis, melting points, molar conductances, infrared spectroscopy, and electronic spectroscopy. The bimetallic complexes prepared were those of divalent metal ions of the first row transition series, namely, Co(II), Ni(II), Cu(II), and Zn(II). Attempts have been made to synthesize the Fe(II) and the Mn(II) complexes of this ligand, but the pure products have not been isolated.

One of the starting materials, 3-isopropylsalicylaldehyde, used in the synthesis of the ligand, has been characterized by infrared and by nmr spectroscopy. In addition, nmr data has been obtained for the ligand and the Zn(II) complex; however nmr data for the other metal complexes of the ligand were not

obtained due to their limited solubility in most nmr solvents.

## Syntheses

The synthesis of 3-isopropylsalicylaldehyde was accomplished by a Duff reaction using 2-isopropylphenol as the starting material [9–11]. The temperature of the glycerine-boric acid mixture used at the onset of the synthesis was maintained at 170 °C for 0.5 hour in order to expel all water from the reaction mixture. Should water be present during the addition of the 2-isopropylphenol and hexamethylenetetramine to the reaction mixture, a significant decrease in yield of the desired aldehyde would occur due to competing side reactions. The yield in this reaction is 30–40%.

The synthesis of the ligand, iPr-TSAB, involves a Schiff base condensation of the previously prepared mono-substituted aldehyde, 3-isopropylsalicylaldehyde, with the tetraamine, 1,2,4,5-tetraaminobenzene (TAB). Sodium methoxide was added to a slurry of the TAB tetrahydrochloride salt in  $CHCl_3$  in order to effect a dehydrohalogenation of the salt. Because the 1,2,4,5-tetraaminobenzene will decompose if exposed to air for a relatively brief period of time, it was used immediately upon completion of the dehydrohalogenation reaction, and the entire reaction was carried out under dry,  $O_2$ -free  $N_2$ . After the total addition of the 3-isopropylsalicylaldehyde and the Schiff base condensation is complete, protection from the atmosphere is no longer necessary. The Schiff base reaction proceeds with generally high yields (75–100%) and the product, iPr-TSAB, is soluble in many nonpolar organic solvents.

The ligand has a planar  $N_2O_2^{2-}$  donor set forming 6-, 5-, and 6-membered rings with each metal ion, and the entire ligand is believed to be planar in order to maintain the extended conjugation throughout the ligand [7, 12, 13].

The metal complexes of iPr-TSAB were prepared by gradual addition of the metal acetate into a  $CHCl_3$  solution of the ligand (see Figure 1). Incorporation of the metal ions into the ligand occurs upon the removal of the hydroxyl protons from the ligand by the basic acetate anion. The water of hydration of the metal acetates used does not enter into the reaction as elemental analysis shows no evidence for coordination of water to the metal ions in any of the bimetallic complexes of iPr-TSAB.

The syntheses of the Cu(II) and the Ni(II) complexes of the ligand were carried out in air, since these complexes are stable to air oxidation. A striking feature of these complexes is their highly limited solubility in  $CHCl_3$ , in which the free ligand is quite soluble. Diphenyl ether is employed as the recrystallization solvent and is most effective when used in accordance with the following procedure. Approximately 500 ml of the diphenyl ether (b.p. =

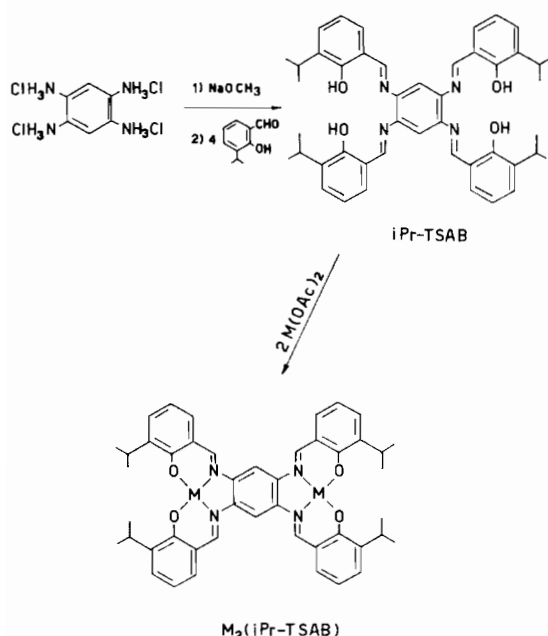


Figure 1. Reaction scheme for the synthesis of iPr-TSAB and metal complexes of iPr-TSAB, designated  $M_2(iPr-TSAB)$ .

259 °C) are heated and maintained near boiling. Small amounts of the crude metal complex to be recrystallized are added to the hot solution until a saturated solution is obtained. Once the saturation point has been reached, the solution is slowly cooled to room temperature over a period of approximately 2–3 hours to allow for proper crystal formation. The product, upon filtration from solution, is obtained as fine, deeply brown-colored, needle-like crystals. Because diphenyl ether is quite miscible with ethanol, the crystals were washed with several aliquots of absolute ethanol to remove all traces of the diphenyl ether. Unlike the free ligand, the Cu(II) and the Ni(II) complexes are not soluble to any great extent in most organic solvents. However, the solubility of these complexes, in general, is greater than that of the previously reported metal complexes of the ligand, TSAB [7], and has greatly facilitated the study of their solution chemistry.

The synthesis, isolation, and purification of  $Co_2(iPr-TSAB)$  were done under dry,  $O_2$ -free  $N_2$ . The solubility of this complex in organic solvents is very similar to that of the Cu(II) and Ni(II) complexes, and the crude reaction product was recrystallized from diphenyl ether in the same manner as were the Cu(II) and Ni(II) complexes.

The Zn(II) complex of the ligand, iPr-TSAB, was prepared under the same conditions as the Cu(II) and Ni(II) complexes; however, this complex exhibits physical properties different from those of all the other metal complexes prepared. The complex is generally more soluble in most organic solvents than

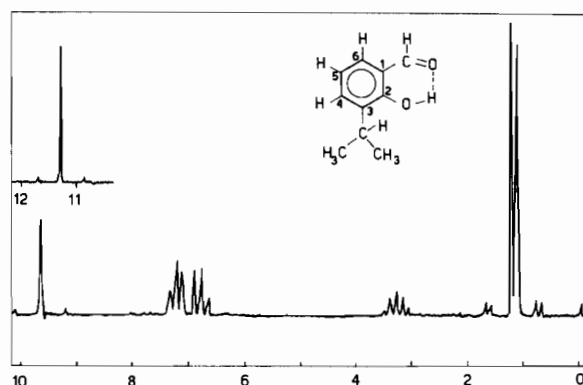


Figure 2. Nmr spectrum of 3-isopropylsalicylaldehyde in  $CCl_4$ .

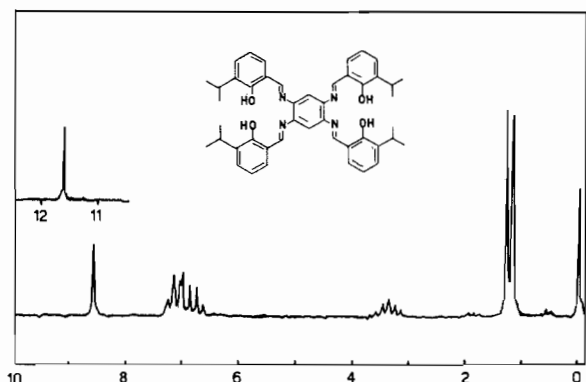


Figure 3. Nmr spectrum of iPr-TSAB in  $CDCl_3$ .

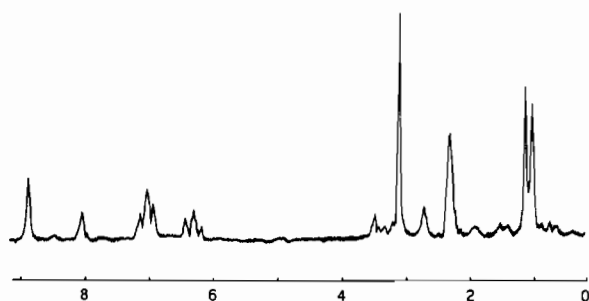


Figure 4. Nmr spectrum of  $Zn_2(iPr-TSAB)$  in  $d_6$ -DMSO.

all of the other metal complexes and is not nearly as deeply colored as the other metal complexes prepared (see Experimental).

#### Nmr Spectra

The nmr spectra of 3-isopropylsalicylaldehyde, iPr-TSAB and  $Zn_2(iPr-TSAB)$  are reproduced in Figures 2, 3, and 4, respectively. Nmr spectra of the other metal complexes of iPr-TSAB were not obtained due to their limited solubility in most common nmr solvents and their paramagnetism.

The isopropyl group in 3-isopropylsalicylaldehyde is reflected in the signals occurring at 1.15 $\delta$  and at 3.28 $\delta$ . The methyl doublet at 1.15 $\delta$  integrates for six protons and the other alkyl proton integrates for one proton and is the expected septet. The aromatic region may be viewed as two closely placed triplets. The triplet occurring at 6.77 $\delta$  integrates for one proton and is attributed to the aromatic proton at the 5-position on the benzene ring; the splitting of this signal occurs as a result of coupling with the two adjacent aromatic protons at the 4- and 6-positions of the ring. The triplet at 7.22 $\delta$ , which integrates for two protons, is attributed to the aromatic protons at the 4- and 6-positions of the ring. The peak at 9.67 $\delta$  integrating for one proton is assigned to the aldehyde proton, and the peak at 11.30 $\delta$  also integrating for one proton is due to the hydroxyl proton. The hydroxyl proton position is similar to closely related compounds such as 2-hydroxy-3-methoxybenzaldehyde, 4-isopropylsalicylaldehyde, and 5-nitrosalicylaldehyde [14].

As is expected, the nmr spectrum of iPr-TSAB exhibits many similarities to that of 3-isopropylsalicylaldehyde. The methyl protons of the isopropyl groups are reflected in the doublet at 1.24 $\delta$ , integrating for 24 protons, and the other alkyl protons are reflected in the septet at 3.37 $\delta$ , integrating for four protons. The complex multiplet occurring in the region from 6.6–7.3 $\delta$  and integrating for fourteen protons is due to the fourteen aromatic protons. The peak at 8.59 $\delta$  integrates for four protons and can be assigned to the four azomethine protons. This assignment is not unreasonable since, in going from 3-isopropylsalicylaldehyde to the ligand, the environment of these protons is not drastically altered (note that the signal assigned to the aldehyde proton of 3-isopropylsalicylaldehyde occurs at 9.67 $\delta$ ). Finally, the signal at 11.63 $\delta$ , which also integrates for four protons, is assigned to the four hydroxyl protons of the free ligand. The appearance of this peak occurring well into the deshielded region of the spectrum suggests the presence of strong intramolecular hydrogen bonding between the hydroxyl protons and the nitrogen atoms of the four C=N groups.

The Nmr spectrum of the zinc complex is very similar to that of the free ligand without the hydroxy-protons. The spectrum shows the imine proton at 9.0 $\delta$  which is slightly downfield from the imine of the free ligand (8.59 $\delta$ ) showing that the bonding to the metal has lowered the electron density of this proton somewhat. The aromatic protons which now appear as two separated triplets positioned at 6.4 and 7.1 $\delta$  correspond closely to those in the free ligand. The septet from the isopropyl hydrogen is covered by a solvent ( $d_6$ DMSO) peak but the methyl doublet is clear and positioned at 1.26 $\delta$ .

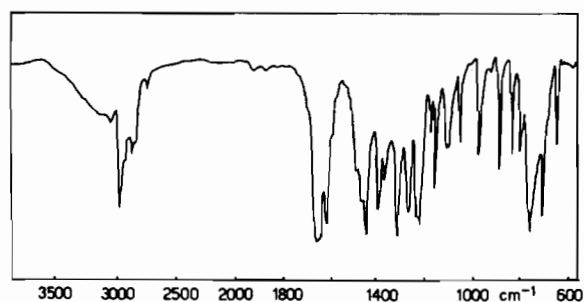


Figure 5. Ir spectrum of 3-isopropylsalicylaldehyde.

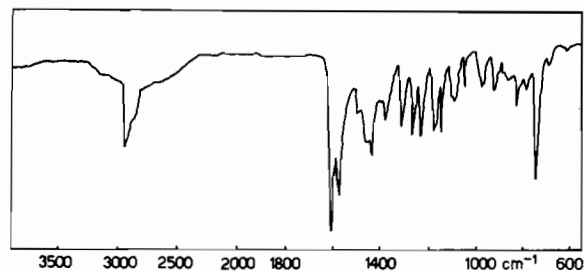


Figure 6. Ir spectrum of iPr-TSAB KBr pellet.

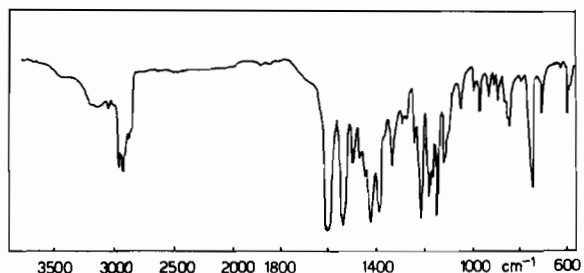


Figure 7. Ir spectrum of Zn<sub>2</sub>(iPr-TSAB) KBr pellet.

### Infrared Spectra

The infrared spectra of 3-isopropylsalicylaldehyde, iPr-TSAB and a typical metal complex are shown in Figures 5, 6, and 7, respectively. As is characteristic of most aromatic compounds, the infrared spectrum of 3-isopropylsalicylaldehyde exhibits many strong, well-defined bands. The weak bands at 3040 and 2740  $\text{cm}^{-1}$  are attributed to aromatic C–H and to the aldehyde C–H stretching modes, respectively. The isopropyl group gives rise to a series of bands between 2840  $\text{cm}^{-1}$  and 2980  $\text{cm}^{-1}$  that are due to saturated C–H stretching vibrations, and to a characteristic doublet at 1375  $\text{cm}^{-1}$  that is due to the resonance splitting of the symmetric C–H bending mode of the gem-dimethyl group. Strong intramolecular hydrogen bonding between the carbonyl and the hydroxyl proton is indicated by the unusually low carbonyl stretching vibration at 1650–1660  $\text{cm}^{-1}$ . In addition, this phenomenon is indicated by an extremely broad O–H stretching absorption from 2500 to 3600  $\text{cm}^{-1}$ , which is superimposed over

TABLE I. Electronic Spectra of iPr-TSAB and Metal Complexes of iPr-TSAB.

Compound	Solvent	Concentration ( $\times 10^{-5} M$ )	$\lambda_{\max}(\log \epsilon)$ ( $\text{cm}^{-1}$ )
iPr-TSAB	<i>p</i> -Dioxane	1.16	25,800(4.59) <sup>a</sup> ; 27,800(4.62); 35,800(4.50);
Cu <sub>2</sub> (iPr-TSAB)	Tetrahydrofuran	1.64	19,900(4.49); 20,700(4.51); 27,900(4.27); 29,700(4.26)
Ni <sub>2</sub> (iPr-TSAB)	Tetrahydrofuran	1.10	18,200(4.46); 19,700(4.53) <sup>a</sup> ; 21,600(4.62); 25,800(4.59); 27,200(4.51) <sup>a</sup> ; 31,500(4.55)
Co <sub>2</sub> (iPr-TSAB)	Tetrahydrofuran	2.36	19,200(4.09) <sup>a</sup> ; 21,600(4.32); 27,400(4.14) <sup>a</sup> ; 30,300(4.30) <sup>b</sup>
Zn <sub>2</sub> (iPr-TSAB)	<i>p</i> -Dioxane	0.99	20,000(4.74) <sup>a</sup> ; 20,700(4.76); 22,000(4.67) <sup>a</sup> ; 28,200(4.44) <sup>a</sup> ; 30,700(4.57)

<sup>a</sup>Shoulder. <sup>b</sup>Suspect – very near solvent cutoff frequency.

the C–H stretching region of the spectrum. The strong band at  $1615 \text{ cm}^{-1}$  is attributed to an aromatic ring breathing mode, and evidence for 1,2,3-trisubstitution is given by a strong band at  $750 \text{ cm}^{-1}$ , which also appears rather invariantly in iPr-TSAB and in the metal complexes of iPr-TSAB. Bellamy [15] has assigned absorptions in the region between  $960$  and  $1175 \text{ cm}^{-1}$  to 1,2,3-trisubstituted systems, and a series of bands appears somewhat invariantly in this region in the spectra of 3-isopropylsalicylaldehyde, iPr-TSAB, and the metal complexes of iPr-TSAB, though the intensities of these bands differ slightly from compound to compound.

The infrared spectrum of the free ligand (iPr-TSAB) exhibits a broad band in the region between  $2400$  and  $3200 \text{ cm}^{-1}$  which again is attributed to the O–H stretching mode of the hydroxyl groups. This band indicates strong intramolecular hydrogen bonding between the hydroxyl protons of the salicylidene moieties and the nitrogen atoms of the tetraamino-benzene moiety. This strongly hydrogen bonded O–H absorption disappears in the infrared spectra of the metal complexes of iPr-TSAB. Both the spectrum of the free ligand and of the metal complexes of the ligand exhibit strong absorptions at  $1600$ – $1610$  and at  $1580 \text{ cm}^{-1}$ . The former can be attributed to the imine stretching frequency, which is lower than that normally observed due to conjugation, and the latter to an aromatic ring breathing mode [7].

The degree of splitting of the symmetric  $\text{CH}_3$ -deformation absorption at  $1375 \text{ cm}^{-1}$  from the isopropyl groups varies markedly from compound to compound. In the free ligand, the Cu(II) complex, and the Zn(II) complex, the splitting is poor. The upper band of the doublet appears at  $1380 \text{ cm}^{-1}$ , while the lower band appears very weakly (almost as a shoulder) at  $1360 \text{ cm}^{-1}$ . In the Ni(II) and Co(II)

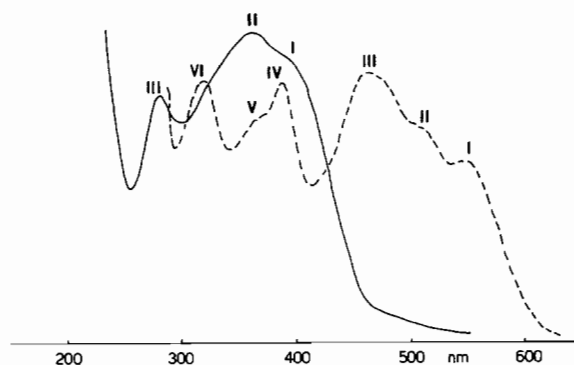


Figure 8. Electronic spectrum of: iPr-TSAB — (dioxane), Ni<sub>2</sub>(iPr-TSAB) --- (THF).

complexes, the splitting observed is more typical of that normally observed for the symmetric  $\text{CH}_3$ -deformation absorption of an isopropyl group.

#### Electronic Spectra

The band positions ( $\lambda_{\max}$ ) and the extinction coefficients ( $\epsilon$ ) in the electronic spectra of iPr-TSAB and the metal complexes of iPr-TSAB are given in Table I. Spectra of the ligand and a metal complex are shown in Figure 8. In general, concentrations of approximately  $10^{-5}$  molar were used, and the extinction coefficients were on the order of  $10^4$ . Due to the presence of numerous strong charge transfer bands (mainly  $\pi \rightarrow \pi^*$  transitions) in the spectra of all the metal complexes of iPr-TSAB, absorptions due to the weaker d–d transitions of the metal ions were not observed.

The spectrum of the free ligand exhibits three strong charge transfer bands whose extinction coefficients range from  $32,000$  to  $42,000$ . The bands occur at  $25,800$ ,  $27,800$  and  $35,800 \text{ cm}^{-1}$  which are very

TABLE II. Molar Conductances of *iPr*-TSAB and Metal Complexes of *iPr*-TSAB.

Compound	Solvent	Concentration ( $\times 10^{-4} M$ )	$\Lambda_M$ (mhos)
<i>iPr</i> -TSAB	Acetone	9.33	0.8
$Cu_2$ ( <i>iPr</i> -TSAB)	Nitrobenzene	1.56	2.3
$Ni_2$ ( <i>iPr</i> -TSAB)	Nitrobenzene	1.10	1.7
$Co_2$ ( <i>iPr</i> -TSAB)	Nitrobenzene	1.00	2.7
$Zn_2$ ( <i>iPr</i> -TSAB)	Dimethyl sulfoxide	2.12	26.8

similar to the three bands in the parent ligand TSAB which occur at 25,600, 28,300, and 36,700  $cm^{-1}$  [7].

The spectra of all of the metal complexes have two bands in the region between 25,800 and 30,700  $cm^{-1}$ , though one of which may be a shoulder, that may be thought to correspond to the two bands at 25,800 and 27,800  $cm^{-1}$  in the spectrum of the free ligand. These bands are ligand to ligand charge transfer bands, and their lower extinction coefficients suggest that binding of the metals to the ligand results in a decrease in the efficiency of the  $\pi \rightarrow \pi^*$  transitions in the aromatic backbone of the ligand.

Each of the metal complexes show a series of absorptions in the region below 25,000  $cm^{-1}$  which are most probably due to metal to ligand charge transfer. In addition, the spectrum of the  $Ni_2$ (*iPr*-TSAB) complex exhibits a band at 31,500  $cm^{-1}$  that does not appear in the spectra of the other metal complexes of *iPr*-TSAB.

#### Conductivities

Values obtained for the molar conductivities ( $\Lambda_M$ ) of *iPr*-TSAB and the metal complexes of *iPr*-TSAB in either acetone, nitrobenzene, or dimethyl sulfoxide are shown in Table II. Concentrations on the order of  $10^{-4}$ – $10^{-3}$  molar were employed, and the solvents (reagent grade) were purified by drying and distillation if they showed conductivities of their own. All conductivities were determined after the solutions had equilibrated to 25 °C for five minutes.

The low molar conductivities observed for the ligand, *iPr*-TSAB, in acetone and for the  $Cu$ (II),  $Ni$ (II), and  $Co$ (II) complexes of *iPr*-TSAB in nitrobenzene indicate that these compounds are non-electrolytes [16], as should be expected. The low conductivity value for  $Zn_2$ (*iPr*-TSAB) in DMSO also indicated that it is a non-electrolyte. This evidence, in addition to elemental analyses (see Experimental), provides support for the conclusion that the metal ions are in a four-coordinate, square planar environment.

#### Magnetic Susceptibility

Preliminary magnetic susceptibility measurements performed on  $Cu_2$ (*iPr*-TSAB) and on  $Ni_2$ (*iPr*-TSAB)

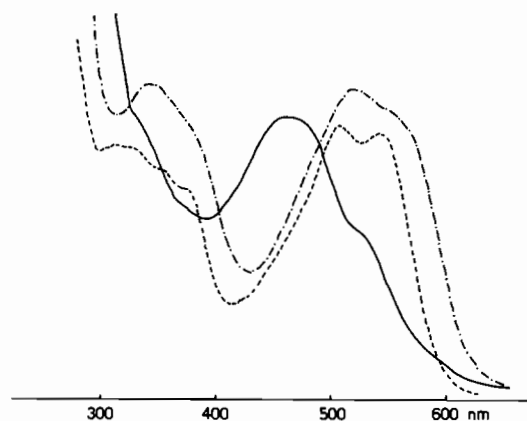


Figure 9. Electronic spectra of:  $Co_2$ (*iPr*-TSAB) —;  $Co_2$ (*iPr*-TSAB) + imid +  $O_2$  - -;  $Co_2$ (*iPr*-TSAB)(imid) $_2$ ( $H_2O$ ) $_2$  - · · ·. THF as solvent.

indicate the presence of an electronic exchange interaction similar to that previously reported for the complex, 1,2,4,5-tetraaminobenzene dicopper(II),  $Cu_2$ (TSAB) [7]. Though thorough magnetic susceptibility measurements have not yet been performed on any of the metal complexes of *iPr*-TSAB, these measurements are expected to be completed in the near future and will be fully reported later.

#### Chemistry of the $Co_2$ (*iPr*-TSAB) Complex

Several attempts have been made at isolating an  $O_2$ -carrying Co complex. When the parent  $Co_2$ (*iPr*-TSAB) complex is dissolved in THF under dry- $N_2$  and imidazole is added in a two to one (imid: complex) mole ratio and then  $O_2$  bubbled through the dark brown solution, the solution turns deep maroon. Isolation of the maroon species is very difficult because it is very soluble in many solvents. The original  $Co_2$ (*iPr*-TSAB) complex is not very soluble in organic solvents as discussed earlier but is fairly soluble in THF and diphenylether from which it is recrystallized. However, the new species formed seems to be very soluble in all organic solvents. It has been isolated as a solid only by taking the solvent to dryness. The isolated compound analyzes for  $Co_2$ (*iPr*-TSAB)(imid) $_2$ ( $H_2O$ ) $_2$  and is not extremely soluble in organic solvents. This solid is not the same



compound as the original compound in solution as is shown by the UV-Vis spectra in Figure 9. It is clearly shown that the compound formed when the imidazole and O<sub>2</sub> are added is not the same compound as either the starting material or the diaquo-species that is isolated. The intermediate species is most likely the oxygen adduct species.

### Summary and Conclusions

Bimetallic complexes of the binucleating ligand, 1, 2, 4,5-tetra(3-isopropylsalicylidene)aminobenzene, have been prepared utilizing the divalent transition metal ions, Co(II), Ni(II), Cu(II), and Zn(II). The water of hydration of the metal acetates employed does not enter into the reaction, as is shown by elemental analysis. The solubilities of these complexes in organic solvents, though limited, is significantly greater than that of the previously reported metal complexes of the "unsubstituted" ligand, 1,2,4,5-tetrasalicylideneaminobenzene [7], and has greatly facilitated the study of their solution chemistry.

The ligand, iPr-TSAB, has a planar N<sub>2</sub>O<sub>2</sub><sup>2-</sup> donor set forming 6-, 5-, and 6-membered rings with each metal ion, and each metal ion is in a four-coordinate, square planar environment.

All of the bimetallic complexes prepared in this investigation have been characterized by both physical and spectroscopic methods, and magnetic susceptibility measurements will be performed on these complexes in the near future and reported later. In addition, electrochemical studies on these complexes in solution will provide further insight as to the nature of the metal-metal interactions inherent in these complexes.

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