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Synthesis, Characterization and Magnetic Studies of Some Metal Complexes of a Novel Binucleating Ligand (III): Sodium 1,2,4,5 tetra(5-sulfosalicylidene)-aminobenzene

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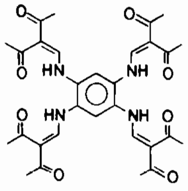
The Cu(II) and Ni(II) complexes of the binucleating ligand 1,2,4,5-tetra(5-sulfosalicylidene)aminobenzene have been prepared and characterized by the use of elemental analyses, melting points, infrared spectroscopy, electronic spectroscopy, and molar conductivities. Magnetic studies have been performed on Cu_2(TSAB), Cu_2(iPr-TSAB) and $Cu_2(SO_3$-TSAB)·$4H_2O$. The 2J interaction coupling parameter shows a small amount of antiferromagnetic coupling of the complexes which varies according to the substituent group on the phenyl rings.

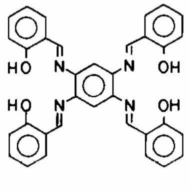
Introduction

The study of bimetallic complexes has been an area of great interest in recent years because of the unique magnetic and electrochemical properties of these compounds. Several studies of transition metal dimer complexes have indicated that electron spin interactions exist between the two metal atoms via a superexchange mechanism involving simple anionic bridging groups (*e.g.* Cl^-, Br^-, OAc^-) [1–3].

In 1973 Hendrickson and Coworkers reported the synthesis and characterization of a copper complex of the binucleating ligand(I) shown below, in which the interaction between the unpaired copper electrons must occur through an extensively conjugated system [4]. The ligand molecules, II, III, IV, represent a continuation of the study of metal–metal interactions across a conjugated system [5, 6]. Synthesis and characterization of metal complexes of the ligand 1,2,4,5-tetrasalicylideneaminobenzene (TSAB, II) was difficult because of the insolubility of both the ligand and the metal complexes [5]. The ligand 1,2,4,5-tetra(3-isopropylsalicylidene)aminobenzene (iPr-TSAB, III) and its metal complexes were synthesized and found to be soluble in many organic solvents (*e.g.* $CHCl_3$, THF, DMSO and many others) [6]. We would now like to report the synthesis and characterization of Cu(II) and Ni(II) complexes of the sodium sulfonate substituted ligand, sodium 1,2,4,5-tetra(5-sulfosalicylidene)aminobenzene (IV). The $NaSO_3$-groups are both ionic and electron withdrawing (with respect to the π-system of the ligand). Magnetic studies of $Cu_2(SO_3$-TSAB)·$4H_2O$, Cu_2(iPr-TSAB) and Cu_2(TSAB) have given evidence that the coupling interaction between the unpaired copper atoms varies with different substituents on the salicylidene rings.

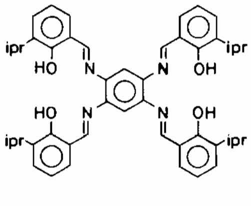


I



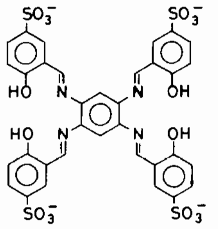
TSAB

II



iPr-TSAB

III



SO_3^--TSAB

IV

Experimental

All materials used were reagent grade unless otherwise noted. The DMSO and methanol used in the synthesis of both metal complexes were dried by CaH_2 and Mg turnings [7].

All infrared spectra were recorded on a Perkin–Elmer model 621 infrared grating spectrometer as KBr pellets. Electronic spectra were obtained on a Beckman model 24 recording ultraviolet–visible spectrophotometer. Melting points were determined at 760 torr on a model 6427-FLO Thomas–Hoover melting point apparatus and conductivity measurements were performed at 25 °C (specific conductance of 0.01N KCl is 0.00141 Ohm^{-1} cm^{-1}) [8]. All chemical analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Esr measurements were performed by the Dept. of Physics, Bowdoin College, Brunswick, Maine, through the courtesy of Dr. Frank Chambers. Magnetic susceptibility *vs.* temperature measurements were performed by the Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina, through the courtesy of Dr. William E. Hatfield and fit to the Van Vlick equation by Cliff Mason by use of a general least squares fitting program.

Preparation of 5-Sulfosalicylaldehyde [9]

Preparation of salicylideneaniline

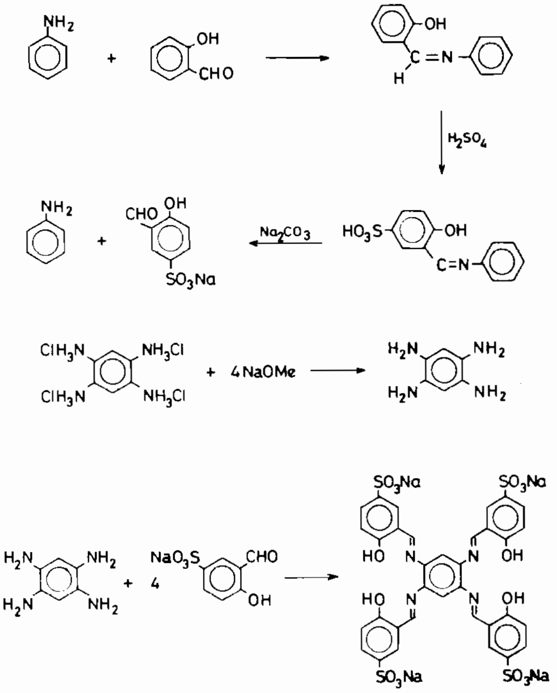
A 21.7 ml (.239 m) sample of aniline was added dropwise to 25 ml (.239 m) of salicylaldehyde (Aldrich) in 50 ml benzene. The solution was refluxed overnight and H_2O was removed as a benzene/H_2O azeotrope with the use of an azeotrope trap column. The volume of water collected was 4.3 ml (theory = 4.3 ml). The volume of the solution was reduced to an orange oil which was solidified at −78 °C (CO_2) to a yellow solid. The solid was recrystallized from MeOH: Crop 1 = 34.6 g, Crop 2 = 2.5 g. Theory = 47.3 g.

Sulfonation of salicylideneaniline

34.6 g (.175 m) of salicylideneaniline and 48.8 ml (5-fold excess) of 96% H_2SO_4 were mixed and heated on a steam bath for one hour. After this time oil formation is still observed when a small aliquot is put in cold H_2O. The heating was continued for an additional 45 min. About 50 ml of H_2O was added dropwise during continued heating. The solution was allowed to cool slowly and a flocculent yellow precipitate slowly appeared (this solution was allowed to stand over a weekend before filtering off the yellow precipitate). It was recrystallized with difficulty from water and dried *in vacuo* at 78 °C. Yield 23.8 g. M.p. > 260 °C.

Hydrolysis of sulfosalicylideneaniline to sulfosalicylaldehyde

17 g (.061 m) of sulfosalicylideneaniline was mixed with 500 ml H_2O and 5 g of Na_2CO_3 were added. The solution was heated for 1.5 hr and the aniline was removed by steam distillation. The volume of the solution is made strongly acidic with HCl. The addition of solid NaCl precipitates the sodium salt of sulfosalicylaldehyde as feathery matter yellow crystals. A second crop of crystals is obtained by reducing the volume of the filtrate. Recrystallization from hot H_2O yields a flocculent precipitate which is dried *in vacuo* at 130 °C. Yield 10.2 g. M.p. > 260 °C.



SO_3-TSAB

Figure 1. Synthetic route to metal SO_3-TSAB Complexes.

Preparation of Sodium 1,2,4,5-Tetra(5-Sulfosalicylidene)aminobenzenedicopper(II)·4H_2O, $Cu_2(SO_3$-TSAB$)\cdot 4H_2O$

Under dry N_2, .48 g (1.67 mmol) of 1,2,4,5-tetraaminobenzene tetrahydrochloride (Pfaltz and Bauer), TAB·4HCl, is dissolved in 50 ml anhydrous DMSO + 50 ml anhydrous MeOH in a 500 ml round bottom flask. Slowly, 1–2 g of $NaOCH_3$ (Ventron 97%) is added until the dehydrohalogenation reaction is complete (Note: during the dehydrohalogenation of TAB·4HCl the reaction mixture undergoes various color changes in the following order: light blue–purple–pink–flamingo–yellow. No further color change results upon continuous addition of $NaOCH_3$ after the reaction mixture turns yellow. Therefore, this is taken to be the point at which the dehydrohalogenation reaction is complete) [6]. Dropwise, a solution of 3.00 g (13.2 mmol) of 5-sulfosalicylaldehyde dissolved in 100 ml anhydrous DMSO is added to the reaction mixture as refluxing is begun. The reaction mixture turns a dark red orange and this mixture is refluxed for approx. 1 hour. At this point, .7 g (3.5 mmol) of $Cu(CH_3COO)_2\cdot H_2O$ (Fisher) dissolved in 50 ml anhydrous DMSO is added dropwise to the reaction mixture. The product is obtained as a red precipitate that is washed with EtOH and ethyl ether and dried *in vacuo* at 100 °C. M.p. > 260 °C.

Anal. calcd. for $C_{34}H_{26}N_4O_{20}Na_4S_4Cu_2$: C, 35.29; H, 2.25; N, 4.84; Cu, 10.98. Found: C, 35.52; H, 2.36; N, 5.10; Cu, 10.01.

Preparation of Sodium 1,2,4,5-Tetra(5-sulfosalicylidene)aminobenzenedinickel(II)·4H₂O, Ni₂(SO₃-TSAB)·4H₂O

The nickel complex is prepared in the same manner as the copper complex. The only change is that .85 g (3.4 mmol) of $Ni(CH_3COO)_2 \cdot H_2O$ (Fisher) in 100 ml anhydrous DMSO is added dropwise to the reaction mixture. The product is obtained as a red precipitate that is washed with EtOH and ethyl ether and dried *in vacuo* at 100 °C. M.p. >260 °C. *Anal.* calcd. for $C_{34}H_{26}N_4O_{20}Na_4Ni_2$: C, 35.57; H, 2.26; N, 4.88. Found: C, 35.38; H, 2.70; N, 4.86.

Results and Discussion

The bimetallic complexes $Cu_2(SO_3\text{-TSAB}) \cdot 4H_2O$ and $Ni_2(SO_3\text{-TSAB}) \cdot 4H_2O$ have been prepared and characterized by the use of elemental analysis, melting points, molar conductivities, infrared spectroscopy and electronic spectroscopy. Magnetic studies (determination of g through esr spectroscopy and the determination of J values using magnetic susceptibility *vs.* temperature data) have been performed on $Cu_2(\text{TSAB})$, $Cu_2(\text{iPr-TSAB})$, $Cu_2(SO_3\text{-TSAB}) \cdot 4H_2O$. Attempts have been made to synthesize $Zn_2(SO_3\text{-TSAB})$ but a pure product has not been isolated nor has the free ligand, SO_3-TSAB, been isolated as a pure product.

Synthesis

The preparation of 5-sulfosalicylaldehyde is a three step process (see Fig. 1). Salicylaldehyde is reacted with aniline to form salicylideneaniline. The imine thus formed is more activated toward electrophilic attack than is the original aldehyde. The salicylideneaniline is sulfonated using concentrated sulfuric acid. Lastly, the Schiff base compound, sulfosalicylideneaniline is hydrolyzed back to the aldehyde, 5-sulfosalicylaldehyde.

The synthesis of the ligand, SO_3-TSAB, involves a Schiff base condensation of 5-sulfosalicylaldehyde with the tetraamine, 1,2,4,5-tetraaminobenzenetetrahydrochloride, TAB·4HCl, (see Fig. 1). Sodium methoxide was added to a solution of TAB·4HCl in MeOH/DMSO to dehydrohalogenate the salt. The reaction must be carried out under dry O_2-free N_2 because 1,2,4,5-tetramminobenzene decomposes to brown by-products if exposed to air for a relatively short time. Once the Schiff base condensation is complete, protection by N_2 is no longer necessary. Anhydrous solvents were used to drive the reaction equilibrium toward the Schiff base product and the metal complexes were prepared without isolation of the free ligand in 30–40% yields. A solution of metal acetate is slowly added to the ligand reaction mixture which allowed incorporation of the metal ions into the ligand upon removal of the hydroxyl protons by the acetate ions.

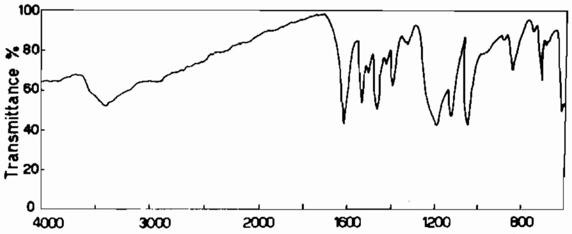


Figure 2. IR spectrum of $Cu_2(SO_3\text{-TSAB}) \cdot 4H_2O$.

The ligand has an $N_2O_2^{2-}$ donor set forming 6-, 5-, and 6-membered rings with each metal ion. The entire ligand is believed to be planar in order to maintain the extended conjugation throughout the ligand [10, 11].

The ligand and both metal complexes are insoluble in most organic solvents. All three of the compounds are moderately soluble in DMSO and slightly soluble in DMF and MeOH. All of the compounds dissolve in water but they readily decompose as the Schiff base is hydrolyzed. Because of their limited solubility, no recrystallization process could be found for the ligand or the Cu(II) and Ni(II) complexes. The metal complexes precipitate out in fairly pure form but the ligand itself does not precipitate out readily and thus could not be isolated as a pure compound (the reaction is run in 4:1 excess aldehyde, and as the volume of reaction mixture is lowered to precipitate the ligand, the aldehyde precipitates also, thus yielding an impure product). This was not a problem in the synthesis of TSAB or iPr-TSAB because the aldehydes used to make these compounds (salicylaldehyde, and 3-iso-propylsalicylaldehyde respectively) were liquids which were readily soluble in the solvent systems used to run the reactions [6].

Although the ligand could not be isolated as a pure solid, an electronic spectrum of it was obtained by removing an aliquot of the reaction mixture. This aliquot contained excess aldehyde so that when the spectrum was run, a reference cell with approximately the same amount of aldehyde was to be used to cancel out the aldehyde components of the spectrum.

Both complexes contain four waters of hydration. These waters could not be removed even with repeated drying *in vacuo* at 100 °C. These water molecules could be associated with the $NaSO_3$ groups of the molecule or directly complexed with the metal ions in the axial positions.

IR Spectra

The IR spectra of the two metal complexes are essentially identical and Fig. 2 shows the IR spectrum

TABLE I. Electronic Spectra of SO_3-TSAB and Metal Complexes of SO_3-TSAB.

Compound	Solvent	Concentration ($\times 10^{-5}$ *M*)	λ_{max} (log ϵ) (cm^{-1})
SO_3-TSAB	DMOS/MeOH	0.865	26,700 (4.79), 28,200 (4.76) 29,600 (4.58)
$Cu_2(SO_3$-TSAB)•$4H_2O$	DMSO	1.38	19,800 (4.59), 21,200 (4.64) 22,200 (4.62) sh, 28,600 (4.47) 30,300 (4.48)
$Ni_2(SO_3$-TSAB)•$4H_2O$	DMSO	1.63	18,600 (4.13) sh, 21,300 (4.37) 23,800 (4.35) 26,800 (4.50), 28,000 (4.43), 31,000 (4.40)

sh = shoulder

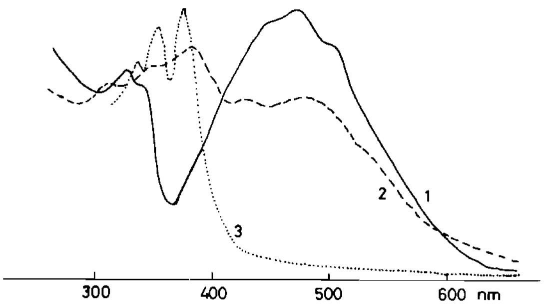


Figure 3. Electronic spectra of 1) $Cu_2(SO_3$-TSAB)•$4H_2O$, 2) $Ni_2(SO_3$-TSAB)•$4H_2O$, 3) SO_3-TSAB.

of $Cu_2(SO_3$-TSAB)•$4H_2O$. The broad band at approx. 3400 cm^{-1} is due to the O–H stretching vibration of the waters of hydration. The imine C=N vibration gives a strong band at 1610 cm^{-1} which is about the usual position for C=N stretching bands [12]. The medium bands at 1530 cm^{-1} and 1450 cm^{-1} are assigned to aromatic ring breathing modes [13] and the strong bands at 1190 cm^{-1} and 1050 cm^{-1} are characteristic of the RSO_3Na group [13].

Electronic Spectra

The λ_{max} values and the extinction coefficients (ϵ) in the electronic spectra of SO_3-TSAB, $Cu_2(SO_3$-TSAB)•$4H_2O$, and $Ni_2(SO_3$-TSAB)•$4H_2O$ are given in Table I. Spectra of all three compounds are shown in Fig. 3. In general, concentrations of approx. 10^{-5} molar were used and the extinction coefficients were of the order of 10^4.

The electronic spectrum of SO_3-TSAB is very similar to the spectra reported for both TSAB and iPr-TSAB [6]. It exhibits three strong ligand to ligand charge transfer bands which occur at 26,700 cm^{-1}, 28,200 cm^{-1} and 29,600 cm^{-1} with extinction coefficients ranging from 38,000 to 62,000. The spectrum of $Ni_2(SO_3$-TSAB)•$4H_2O$ exhibits 3 bands in the region between 26,800 cm^{-1} and 31,000 cm^{-1} and $Cu_2(SO_3$-TSAB)•$4H_2O$ exhibits 2 bands in the region between 28,500 cm^{-1} and 30,300 cm^{-1}. These may correspond to the charge transfer bands of the free ligand (mentioned above). The extinction coefficients of these metal complex ligand to ligand bands are smaller than for the corresponding bands in the free ligand, which indicates that the binding of the metals to the ligand results in a decrease in the efficiency of the $\pi \rightarrow \pi^*$ transitions in the aromatic system of the ligand. Because of the presence of the strong $\pi \rightarrow \pi^*$ charge transfer bands in the metal complexes, absorptions due to the weaker d → d transitions were not observed. Both of the metal complexes exhibit three bands in the region between 18,000 cm^{-1} and 24,000 cm^{-1} (in both cases, one of these bands is a shoulder). These bands are probably due to metal to ligand charge transfer.

TABLE II. Molar Conductances of $Cu_2(SO_3$-TSAB)•$4H_2O$ and $Ni_2(SO_3$-TSAB)•$4H_2O$.

Compound (H_2O is solvent for both compounds)	Concentration ($\times 10^{-4}$ *M*)	λ_m (mhos)
$Cu_2(SO_3$-TSAB)•$4H_2O$	4.25	351
$Ni_2(SO_3$-TSAB)•$4H_2O$	5.31	373

Molar Conductivities

Values for the molar conductivities of $Cu_2(SO_3$-TSAB)•$4H_2O$ and $Ni_2(SO_3$-TSAB)•$4H_2O$ were obtained in distilled water (see Table II). Concentrations of approx. 5 × 10^{-4} *M* were used. All conductivities were determined after the solutions had equilibrated to 25 °C for five minutes. This short amount of time at room temperature is not thought to be sufficient to decompose the complexes.

The molar conductivities observed for both compounds are in the range of 350–375 mhos. This is in the range of what would be expected for a 4:1 electrolyte in H_2O [14].

Magnetic Studies

With the preparation of $Cu_2(SO_3$-TSAB)•$4H_2O$ the effects of different substituents on the TSAB

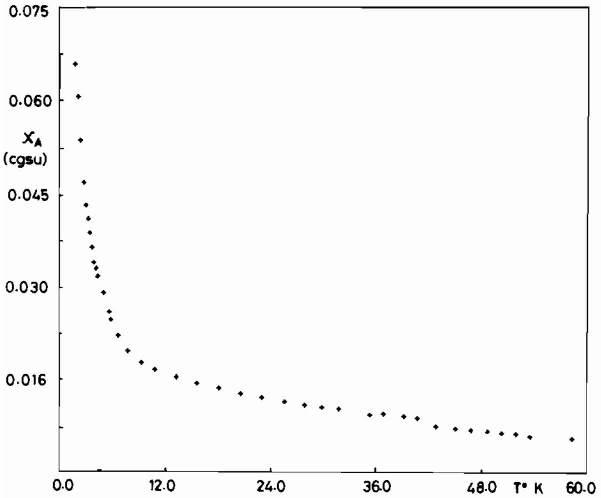


Figure 4. Magnetic susceptibility *vs.* temperature for $Cu_2(SO_3\text{-}TSAB)\cdot 4H_2O$.

backbone to the 2J coupling constants for the unpaired electrons in Cu_2(TSAB), Cu_2(iPr-TSAB), and $Cu_2(SO_3\text{-}TSAB)\cdot 4H_2O$ can be correlated. In complexes where two Cu(II) ions are interacting antiferromagnetically, the spin triplet state is $-2J$ above the spin singlet state [15]. The value of 2J for each of the complexes was determined by fitting magnetic susceptibility *vs.* temperature data to the Van Vleck equation [3]:

$$\chi_m = g^2NB^2/3KT\{1 + 1/3 \exp(-2J/KT)\}^{-1} + N\alpha$$

where χ_m = Susceptibility per mol copper ion
N = Avogadro's
B = Bohr Magneton
K = Boltzmann's constant
J = Antiferromagnetic coupling constant
g = Gyromagnetic ratio for an electron
T = Temperature
$N\alpha$ = Temperature independent magnetic susceptibility

g was determined independently through esr spectroscopy. The data was fit to the Van Vleck equation using a general least squares program where J and $N\alpha$ are the undetermined parameters. In each case, between 10–18 points at the low temperature end of the data had to be disregarded in order to fit the equation reasonably well (for all three compounds the standard deviation of the best fit curve from the data points was 10^{-3} or less). This is due to small amounts of paramagnetic monomer impurity found in the samples. The Cu(II) ions in the monomer maintain their paramagnetism while those in the dimer complexes are interacting antiferromagnetically across the π-system of the ligand causing the monomeric impurity to become increasingly dominant in the equation as 0 °K is approached. Figure 4 shows the magnetic susceptibility *vs.* temperature data for $Cu_2(SO_3\text{-}TSAB)\cdot 4H_2O$. The data does not exhibit the Neel point expected for complexes where antiferromagnetic interactions are taking place. This is due to the paramagnetism of the monomer impurity. The antiferromagnetic nature of the complex is more apparent in the effective magnetic moment (per copper ion) *vs.* temperature data (Fig. 5). The effective magnetic moment increases linearly with temperature between approx. 10° and 30 °K. At higher temperatures the effective magnetic moment levels off to a constant value of approx. 1.7 B.M./Cu atom.

TABLE III. g and 2J (cm^{-1}) Values for Cu_2(TSAB), Cu_2(iPr-TSAB), and $Cu_2(SO_3\text{-}TSAB)\cdot 4H_2O$.

Compound	g	2J (cm^{-1})
Cu_2(TSAB)	2.0042	−13.4
Cu_2(iPr-TSAB)	2.0038	−20.8
$Cu_2(SO_3\text{-}TSAB)\cdot 4H_2O$	2.0048	−8.0

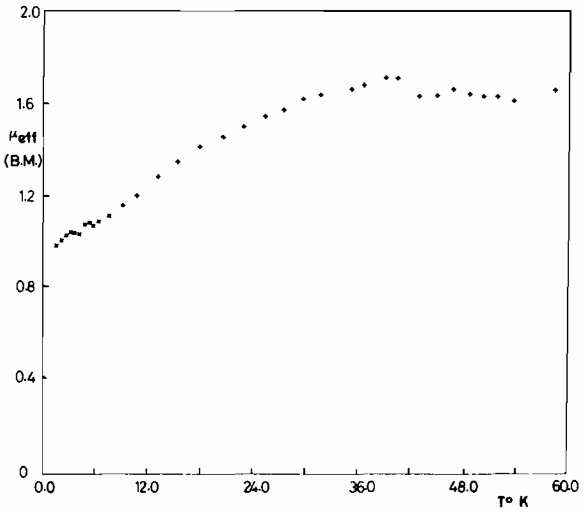


Figure 5. Effective magnetic moment *vs.* temperature for $Cu_2(SO_3\text{-}TSAB)\cdot 4H_2O$.

The antiferromagnetic interactions between the copper ions varies as a function of electron donating or withdrawing capability of the substituents on the salicylidene rings. In the case of the two substituted complexes Cu_2(iPr-TSAB) and $Cu_2(SO_3\text{-}TSAB)\cdot 4H_2O$, the substituents are either ortho (for iPr-substitution) or para (for SO_3-substitution) to the hydroxyl oxygen and in both cases the substituents are meta to the C=N group. The values for g and 2J for each of the molecules are given in Table III. The 2J value for the iPr-substituted compound is the greatest while the value for the SO_3-substituted compound was the lowest. The value for the unsubstituted compound is roughly in the middle. This indicates that electron withdrawing groups (SO_3) hinder antiferromagnetic coupling in the system while electron donating groups (iPr) favor it. This trend is the same as that reported by Hatfield for oxygen bridged pyridine N-oxide- copper halide bimetallic complexes [16]. In his work it was found that electron withdrawing substituents on the pyridine ring lowered the antiferromagnetic coupling between the copper ions, while electron donating substituents increased it. This trend can be explained in terms of the proposed superexchange mechanism taking place between the metal ions. As electron density is removed (or added) to the aromatic system of the complex, the ability of ligand orbitals to couple the spins of the unpaired copper electrons varies. If spin–spin coupling occurred directly through space or through a metal–metal bond mechanism, the substitution change would not have as great an effect on the 2J exchange energy.

Conclusions

Cu(II) and Ni(II) complexes of the binucleating ligand, sodium 1,2,4,5-tetra(5-sulfosalicylidene)-aminobenzene have been prepared and both contain four waters of hydration. The solubilities of these complexes is limited in organic solvents. Both complexes have been characterized by both physical and spectroscopic methods. The free ligand was not isolated as a pure compound but has been characterized in solution by means of electronic spectroscopy.

Magnetic studies on $Cu_2(TSAB)$, $Cu_2(iPr\text{-}TSAB)$ and $Cu_2(SO_3\text{-}TSAB)\cdot 4H_2O$ have indicated that electron withdrawing substituents reduce the antiferromagnetic interaction between the odd copper electrons, while electron donating substituents increase the interaction. Future studies using different substituents may afford a quantitative correlation between the Hammett sigma values of the substituents and the degree of antiferromagnetic coupling between the copper ions.

Acknowledgements

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