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The Synthesis and Characterization of Some Metal Complexes of a Novel Ligand that Binds Two Metals

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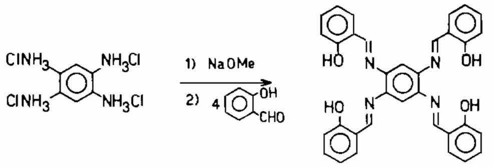
The study of novel ligands which can bind two metals in proximity to one another has recently created much interest among chemists because the magneto- and electrochemical properties of such complexes show promise in developing theories whereby electron transport phenomena can be further understood.[1,2] We would like to report the synthesis and characterization of some new bimetallic complexes in which the ligand is designed to incorporate two metals. The ligand 1,2,4,5-tetrasalicylalideneaminobenzene (TSAB) is prepared by a method similar to that reported earlier by Fleischer *et al.*[3] in which the tetrahydrochloride of 1,2,4,5-tetraaminobenzene is dehydrohalogenated by addition of sodium methoxide and then a Schiff Base condensation of salicylaldehyde with the four primary amine units forms the ligand TSAB (Calcd. for $C_{34}H_{26}O_4N_4$, C: 73.65; H: 4.69; N: 10.11. Found, C: 72.11; H: 4.53; N: 10.04).



TSAB

The metal complexes are then formed by Soxhlet extraction of the TSAB into a THF solution of the metal acetate. An alternative route which has led to some success is to form the metal–salicylaldehyde complexes first and slowly add them to the dehydrohalogenated 1,2,4,5-tetraaminobenzene solution.

These metal complexes have been prepared in order to study the interactions between the two metals both magnetically and electrochemically to observe the amount of interaction through the π-system of the phenyl ring (M–M distance approximately 8 Å).[3] The ligand has a planar $N_2O_2^{2-}$ donor set for each metal ion and the total ligand is presumed planar in order to maintain the extended conjugation throughout the ligand.[4,5] This ligand is insoluble in polar solvents as well as most non-polar solvents; however, it does have limited solubility in THF, 1,2-dimethoxyethane, and DMSO. These solvents are utilized throughout in the syntheses of the metal complexes. The complexes formed from TSAB are in general even more insoluble but do have some solubility (however even more limited) in THF, 1,2-dimethoxyethane, and DMSO.

The metal complexes that have been characterized are the following: $Mn_2TSAB{\cdot}H_2O$ (Calcd. for $Mn_2C_{34}H_{24}N_4O_5$, C: 59.84; H: 3.23; N: 8.22. Found, C: 59.45; H: 3.29; N: 7.80), $Mn_2TSAB{\cdot}Et_3N$ (Calcd. for $Mn_2C_{34}H_{22}N_4O_4{\cdot}Et_3N$, C: 63.09; H: 4.86; N: 9.20. Found, C: 63.62; H: 4.57; N: 8.46), $Ni_2TSAB{\cdot}4H_2O$ (Calcd. for $Ni_2C_{34}H_{22}N_4O_4{\cdot}4H_2O$, C: 55.4; H, 4.06; N: 7.58; Ni: 15.9. Found, C: 56.22; H: 3.79; N: 7.71; Ni: 15.6), $Cu_2TSAB{\cdot}2H_2O$ (Calcd. for $Cu_2C_{34}H_{22}N_4O_4{\cdot}2H_2O$, C: 57.55; H: 3.67; N: 7.90. Found, C: 56.97; H: 3.76; N: 7.95), and a polymeric compound which analyzes for Cu_4TSAB (Calcd. for $Cu_4C_{34}H_{22}N_4O_4$, C: 50.7; H: 2.73; N: 6.96. Found, C: 50.01; H: 2.82; N: 7.00). Several other metal complexes have been formed but based on elemental analysis their purity remains suspect at the moment.

The infrared spectrum of the free ligand shows a strong band at 1610 cm^{-1} and a weaker but still strong band at 1570 cm^{-1}, both bands having pronounced shoulders on them. These bands also appear in all the metal complexes with a fairly broad, strong band at 1610 - 1620 cm^{-1} and a shoulder at between 1585 and 1595 cm^{-1}. The upper band is attributed to the imine stretching frequency which is commonly rather invariant in Schiff Base complexes. The lower band may be attributed to some aromatic C–C stretching or could be part of a complex set of imine vibrations. In any case these two bands remain a prominent feature of the infrared spectra of both the free ligand and its metal complexes.

A band at 1520 - 1525 cm^{-1} is observed in the metal complexes which is probably due to the aromatic ring breathing mode and is rather invariant from compound to compound.

TABLE. Electronic Spectra of Some TSAB Compounds.

Compound	
TSAB[a]	25.6[b] (31,700); 28.3 (35,100); 36.7 (25,400)
$Mn_2TSAB \cdot H_2O$	21.0 (30,200); 28.2 (28,000)
$Cu_2TSAB \cdot 2H_2O$	18.5 (sh); 19.8 (sh); 21.7 (18,800); 27.0 (sh); 29.4 (17,200)
Cu_4TSAB	18.2 (sh); 20.0 (24,200); 21.0 (25,000); 28.9 (17,300); 30.3 (17,300)
$Ni_2TSAB \cdot 4H_2O$	18.9 (sh); 20.0 (sh); 22.0 (4000); 26.0 (3860); 27.8 (sh); 31.4 (3500)

[a] Compounds are all 10^{-5} molar in DMSO. [b] Units are kK.

The values of the bands in the UV–Vis spectra of these deeply colored compounds are shown in the Table. Due to the limited solubility of the compounds only strong absorptions are observed. In general 10^{-5} molar solutions of DMSO were used and the extinction coefficients were on the order of 10^5. The free ligand shows three strong CT bands with extinction coefficients on the order of 30,000. Each of the metal complexes has a band positioned between 28,200 and 29,400 cm^{-1} which corresponds well to the band at 28,300 cm^{-1} in the free ligand. This band must be associated with a ligand to ligand band in the aromatic part of the backbone which is not affected extensively by binding the ligand to the metal.

The metal complexes all show a band in the region of 21,000 to 22,000 cm^{-1} which is most likely due to M→L charge transfer.

The Cu complexes show quite complex spectra with five obvious bands in each. The "polymer" and the monomer show bands with similar peak positions but the spectra are quite different due to the fact that the monomer has bands at approximately 19,800 cm^{-1} and 27,000 cm^{-1} which are definitely strong peaks. The Ni_2TSAB complex shows a spectrum similar to Cu_2TSAB with six bands, five in positions similar to the Cu_2TSAB compound and a sixth at 26.0 kK which is not found in the Cu compound.

Utilizing the method of Soxhlet extraction of the ligand into a solution of $Cu(OAc)_2$, a red-brown polymeric compound that analyses for Cu_4TSAB is obtained. This complex has a room temperature magnetic moment of 2.02 B.M. per Cu^{2+} ion which is typical of Cu^{2+} compounds. This compound is extremely insoluble in all common solvents.

To form a non-polymeric Cu compound, the $Cu(OAc)_2$ solution is dripped slowly into a slurried solution of the ligand in 1,2-dimethoxyethane to prevent excess Cu^{2+} ion in the presence of the ligand which might allow the formation of polymeric species. A preliminary magnetic study of Cu_2TSAB shows that below approximately 40 °K there is quite a large antiferromagnetic interaction between the two Cu^{2+} ions. Above 40 °K both Cu^{2+} ions act individually and follow the normal Curie–Weiss Law giving a magnetic moment of 1.75 B.M. typical of Cu^{2+} compounds. The EPR at both room temperature and at 77 °K show essentially identical spectra with a $g_\perp$ of 2.05 and a $g_\parallel$ of 2.22.

Further studies are being undertaken to try to understand the nature of the interactions between metal ions in this ligand. This is part of an ongoing project to determine the ability of electrons to interact across differing amounts of space utilizing various orbitals for the electron transfer.

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