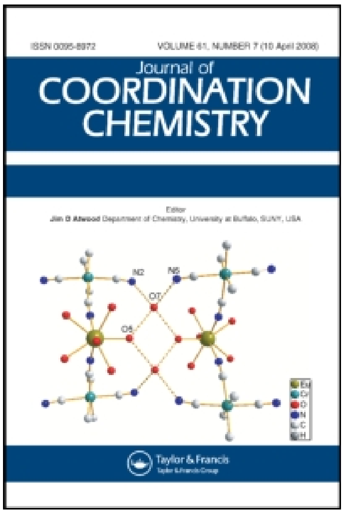


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

COMPLEXES OF THE l,3-BIS(2-ARYLIMINO) BENZ (F) ISOINDOLINE LIGAND INCLUDING THE CRYSTAL STRUCTURE OF THE Cu(II)-ACETATE COMPLEX

D. M. Baird[a]; W. P. Maehlmann[a]; R. D. Bereman[b]; P. Singh[b]
[a] Department of Chemistry, Florida Atlantic University, Boca Raton, FL [b] Department of Chemistry, North Carolina State University, Raleigh, NC

To cite this Article Baird, D. M. , Maehlmann, W. P. , Bereman, R. D. and Singh, P.(1997) 'COMPLEXES OF THE l,3-BIS(2-ARYLIMINO) BENZ (F) ISOINDOLINE LIGAND INCLUDING THE CRYSTAL STRUCTURE OF THE Cu(II)-ACETATE COMPLEX', Journal of Coordination Chemistry, 42: 1, 107 — 126

To link to this Article: DOI: 10.1080/00958979708045284

URL: http://dx.doi.org/10.1080/00958979708045284

J. Coord. Chem., 1997, Vol. 42, pp. 107–126
Reprints available directly from the publisher
Photocopying permitted by license only

COMPLEXES OF THE 1,3-BIS(2-ARYLIMINO) BENZ (F) ISOINDOLINE LIGAND INCLUDING THE CRYSTAL STRUCTURE OF THE Cu(II)-ACETATE COMPLEX

D.M. BAIRD[a], W.P. MAEHLMANN[a], R.D. BEREMAN[b] and P. SINGH[b]

[a]*Department of Chemistry, Florida Atlantic University, Boca Raton, FL 33431;*
[b]*Department of Chemistry, North Carolina State University, Raleigh, NC 27650*

(Received 16 July 1996; Revised 16 September 1996; In final form 21 October 1996)

The new BAII ligand 1,3-bis(2-pyridylimino)benz(f) isoindoline, NBAII, has been synthesized and Zn(II), Ni(II) and Cu(II) complexes with the formula (NBAII)MX (where X = OAc^- for Cu(II) and Ni(II) and X = Cl^- for Pd(II)) have been prepared. The ligand and complexes have been characterized by ^{1}H-NMR spectroscopy, infrared spectroscopy and electronic absorption spectroscopy. The NBAII ligand can accommodate both planar and distorted tetrahedral geometries in these cases. The quadruply-bonded complex $(NBAII)Mo_2(OAc)_3$ has also been prepared. It was found to exhibit an unusual bonding mode for the NBAII ligand. The molecular structure of the Cu(II) compound was determined by single crystal x-ray diffraction techniques: (NBAII)Cu(OAc) crystallizes in the centrosymmetric space group C2/m with $a = 20.256(4)$ Å, $b = 16.166(3)$ Å, $c = 7.915(2)$ Å, $\alpha = 90°$, $\beta = 94.83(2)$ °, $\gamma = 90°$, $V = 2583(1)$ Å^3 and $Z = 4$. The structure of this complex is compared to that of (BAII)Cu(OAc) which has been used as a model for the copper containing enzyme galactose oxidase. The addition of the benzo portion to BAII to give NBAII apparently increases electron density on the Cu(II) ion, disfavoring coordination of water and favoring a coordination number of four.

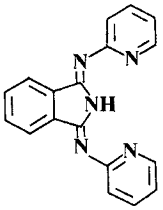
Keywords: isoindoline ligand; BAII; Cu(II) complexes; Zn(II); N(II)

INTRODUCTION

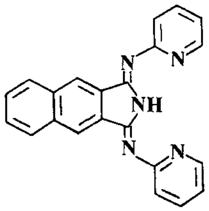
The search for kinetically and thermodynamically stable ligands which are capable of complexing a variety of transition metal ions has been a focus for research in recent years. With more modern characterization techniques, researchers have discovered the utility of complexes that contain large aromatic ligands and the unique properties they possess.

Bis(arylimino)isoindolines (BAIIs) are tridentate ligands capable of occupying three coplanar sites about a metal ion. The ligand can form either 1:1 or 2:1 (ligand:metal) complexes with a metal ion. Numerous BAII complexes have been prepared with first and second-row transition metals. We have also reported the synthesis of dimolybdenum BAII complexes. The dimolybdenum complexes of BAII demonstrate a novel mode of coordination in which one metal atom is coordinated to the isoindoline nitrogen while the other metal atom is bonded to one of the imino nitrogens.

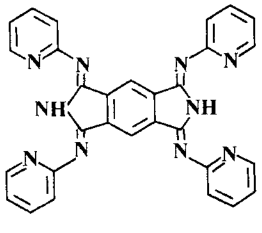
BAII complexes have generated a great deal of interest for several reasons. In general, BAII complexes are easy to prepare, are highly stable and have solubility and donor properties of the BAII ligand that can be easily manipulated to prepare complexes suited to a particular application. BAIIs have been modified by introducing substituents on the aromatic heterocycle or the isoindoline portion of the ligand. Siegl synthesized a variety of BAII ligands and was the first to prepare water-soluble BAIIs.[4,5] In 1977 Siegl synthesized a binucleating analog of BAII capable of chelating two metal ions,[6] 1,3,5,7-tetra (2-pyridylimino) benzodipyrrole (TAII). The TAII ligand was also modified by adding alkyl groups in the 4-position of the pyridyl rings to yield ligands with moderate solubility in organic solvents. When the TAII ligand was developed, there was some hope that the ligand could represent a potential building block for a conjugated polymetal polymer. Marks reported the synthesis of one of the largest compounds, a trinuclear Ru(II) complex.[7] Larger polymetal TAII complexes have not been reported.



BAII



NBAII



TAII

Several BAII complexes were employed as redox catalysts. Saussine reported the use of Co(III) alkylperoxy complexes as catalysts in the oxidation of hydrocarbons.[8] Ruthenium BAII complexes were also used to catalyze oxidation of primary and secondary alcohols to aldehydes and ketones.[9] Tolman used bis[bis((3-methyl-2-pyridyl)imino) isoindolinato] cobalt(II) to catalyze the oxidation of cyclohexane.[10]

In addition to catalytic activity, BAII and TAII complexes have been used to investigate biological systems.[12,13] Copper BAII complexes have been used to simulate naturally occurring copper coordination systems. Gagné reacted (4′Me)BAII with CuCl in the presence of triethylamine and carbon monoxide to produce the Cu(I) carbonyl complex.[11] The copper(I) carbonyl complex forms several products when reacted with dioxygen. Investigation of the active sites in copper-containing proteins also prompted Addison to synthesize a five-coordinate copper(II) BAII complex containing dibenzoylmethane.[12]

The copper(II) center of the galactose oxidase enzyme was modeled by several complexes, one of which was the (4′Me-BAII)OAc copper complex reported by Bereman.[13] The goal was to design a system that would exhibit the known reactivity patterns of the metalloenzyme. Anion binding studies were conducted on both the model BAII complex and galactose oxidase. Anions in this study replace the equatorial acetate anion in the Cu(II) model complex. The reactivity of the BAII complex towards NCO^- and SCN^- anions was similar to the reactivity of galactose oxidase. ESR spectra of the BAII complex and galactose oxidase coordinated with CN^- were also obtained. Bereman concluded that galactose oxidase may possess a five-coordinate copper center geometrically similar to the structure of their complex. Thus, the labile axial position may serve as the substrate binding site in the enzyme.

BAII and TAII ligands have also been modified to create new ligands. Substituted BAII ligands have been expanded to form 1,4-disubstituted pyridylaminophthalazines.[14] These aminophthalazines function as quadridentate ligands which can coordinate two metal atoms. The metal centers are only a small distance apart in these complexes and antiferromagnetic exchange between the metal centers in Co, Ni, and Cu complexes has been observed.[14] Bautista synthesized dicopper complexes of these aminophthalazines as a model for active sites in hemocyanin. TAII expanded in identical fashion yielded the octadentate benzodipyridazine ligand.[15] Tetranucleating ligands of this type are rare and complexes of this type may also be applicable in multielectron transfer processes.

The unique properties and wide-ranging applications of BAII and TAII complexes were the inspiration for this work. 1,3-bis(pyridylimino) benz(f)isoindoline (NBAII) was synthesized for possible comparison with complexes of previously reported BAII ligands. NBAII was synthesized from 2,3-dicyanonaphthalene. NBAII ligands are expected to form highly stable complexes which possess useful redox capabilities.

EXPERIMENTAL

Materials and Methods

Chemicals and solvents used for synthetic procedures were reagent grade and were used as received from the manufacturer without further purification unless specified. Certain procedures required dry or air-free solvents or reagents. Dry solvents were degassed by purging with argon for at least ten minutes.

Dimethylformamide was dried over 4 Å molecular sieves for at least one week before use. Dichloromethane was stored over 4 Å molecular sieves and passed through a column of neutral alumina immediately before use. Methanol was dried by distillation over calcium or magnesium sulfate under argon. Benzene and hexane were stored over 4 Å molecular sieves. Diethyl ether was dried by distillation over sodium and benzophenone under argon.

All reactions and preparations that required inert conditions were done in a glove box or by standard Schlenk techniques under argon.

Analyses of products were performed by Atlantic Microlab, Inc. Norcross, Georgia.

Infrared spectra were obtained with a Mattson Instruments 4020 Galaxy Series FT-IR spectrophotometer. Spectra were recorded from 400 to 4000 cm^{-1} as KBr pellets. Electronic spectra were taken using a Shimadzu UV-2100 spectrophotometer scanning from 200 to 900 nm. Air-sensitive samples were prepared in a glovebox using sealed quartz cuvettes. NMR spectra were determined using a General Electric QE-300 spectrometer. Samples were prepared in d_1-chloroform or d_6-dimethylsulfoxide. Air-sensitive samples were prepared and sealed in a glovebox. X-ray crystal data were collected using a R3m/μ diffractometer from Siemens Analytical X-ray Instruments, Inc. Crystallographic calculations and graphics were processed using the SHELXTL program package.

Syntheses

2,3-Dicyanonaphthalene: The procedure outlined by Wheeler was scaled down.[17] 8.44 g. (0.02 mol) of α, α, α′, α′-tetrabromo-o-xylene, 1.56 g. (0.02 mol) of fumaronitrile, and 20.0g of NaI were combined in 140 mL of dry DMF. The reaction flask was fitted with a thermometer and a $CaCl_2$ drying tube. The reaction mixture was stirred for seven hours at 70–80°C then cooled to less than 40°C. The solution was poured into 300 mL of cold water and sodium bisulfite (1 M) was added to the red solution to remove the liberated iodine from the mixture. The tan solid produced was recrystallized in a 2:1

mixture of benzene and petroleum ether yielding 2.72 g (76%, lit. reports 78%) of product: m.p. 252°C(lit. 251°C); IR (KBr) 2227 cm^{-1} (s, CN); ^{1}H NMR ($CDCl_3$) 8.37 (s, 1,4-H), 8.00 (m, 5,8-H), 7.81 (m, 6,7-H).

1,3-Bis (2-pyridylimino) benz (f) isoindoline (NBAII): 1.32 g (0.0074 mol) of 2,3-dicyanonaphthalene, 1.46 g (0.01554 mol) 2-aminopyridine, and 0.082 g (0.00074 mol) calcium chloride were added to 20 mL of 1-butanol. The solution was refluxed for 48 h and a small aliquot was removed and the solvent was evaporated leaving a brown solid. The solid was washed with water to remove 2-aminopyridine. The UV-visible spectrum of the solid was identical to the starting dinitrile so the reaction was continued. After several runs it was determined that a reaction time of 7–10 days was required for nearly all of the starting dinitrile to react. Varying the amount of solvent or catalyst did not decrease the reaction time. After completion, cooling of the reaction mixture precipitated the crude ligand as a yellow brown solid. The solid was filtered and washed with water. Recrystallization in ethanol/water yielded 1.04 g (40%) of ligand, a yellow-brown solid: m.p. 201°C; ^{1}H NMR ($CDCl_3$) 8.64 (d, 2H), 8.64 (s, 2H), 8.08 (q, 2H), 7.80 (m, 2H), 7.63 (q, 2H), 7.55 (d, 2H), 7.15 (m, 2H).

Synthesis of complexes

Preparation of Cu(II), Ni(II), Zn(II) and Pd(II)

Cu(II), Ni(II), Zn(II) and Pd(II) complexes were each prepared in a similar manner using less than 0.001 mol of the NBAII ligand. One equivalent of NBAII and 2 equivalents of the hydrated metal acetate (Cu, Zn, and Ni) or metal chloride (Pd) were added to 10 mL of methanol. The reaction mixture was stirred at ambient temperature for 24 h. The complexes precipitated as colored solids. The solutions were filtered and the solids were washed with methanol. Recrystallization of the Cu(OAc) complex in methanol produced dark green rectangular crystals suitable for x-ray analysis.

(NBAII)Cu(OAc): Yield 74%, dark green solid. *Anal.* Calcd. for $CuC_{24}H_{17}N_5O_2 \cdot 1.5H_2O$: C, 57.88; H, 4.05; N, 14.06. Found: C, 57.05; H, 4.05; N, 13.88.

(NBAII)Ni(OAc): Yield 67%, yellow-green solid. *Anal.* Calcd. for $NiC_{24}H_{17}N_5O_2$: C, 61.84; H, 3.67; N, 15.02. Found: C, 61.65; H, 4.06; N, 14.82.

(NBAII)Zn(OAc): Yield 91%, bright yellow solid; ^{1}H NMR (d_6 DMSO) 8.60 (d, 2H), 8.47 (s, 2H), 8.20 (q, 2H), 7.93 (m, 2H), 7.63 (q, 2H), 7.46 (d, 2H), 7.21 (m, 2H).

(NBAII)PdCl: Yield 75%, red-brown solid; ^{1}H NMR ($CDCl_3$) 9.86 (d, 2H), 8.54 (s, 2H), 8.07 (q, 2H), 7.86 (m, 2H), 7.64 (q, 2H), 7.64 (d, 2H), 7.07 (m, 2H).

IR and electronic spectra of the complexes prepared from the NBAII ligand were also taken and will be discussed in a later section.

Dimolybdenum Complex of NBAII: This synthesis followed that of the dimolybdenum complex of BAII, Mo_2 (BAII) (OAc).[1-3] Molybdenum acetate, 0.399 g. (0.000933 mol), prepared from $Mo(CO)_3$ using the method of Wilkinson and Dori,[18] and 0.326 g (0.000933 mol) of NBAII were placed in a 50 mL vacuum flask. The flask was purged with argon and 10 mL of dry degassed methanol was added. The flask was sealed and stirred in a glovebox for 24 h. During that time, the reaction mixture turned from yellow to dark green and a dark green precipitate formed. The solution was filtered under argon and the dark green solid was washed with hexane and stored under argon. 0.51 g. (77% yield) was obtained. *Anal.* Calcd. for $Mo_2C_{28}H_{23}N_5O_6$: C, 46.88; H, 3.23; N, 9.73. Found: C, 45.68; H, 3.37; N, 9.50. IR and electronic spectra were used to characterize the complex. The complex is extremely unstable in solution and attempts to obtain a ^{1}H NMR spectrum before decomposition were unsuccessful.

X-Ray Analysis of (acetato) [1,3-bis(2-pyridylimino)benz(f)isoindolinato]-copper(II)

The crystal structure of the Cu(OAc) complex of NBAII, $CuC_{24}H_{17}N_5O_2 \cdot 1.5H_2O$, was determined using direct methods and difference Fourier techniques. The structure was refined by blocked-cascade least-squares in the centrosymmetric space group C2/m. Attempts to refine the structure in the alternate non-centrosymmetric space groups, C2 and Cm, were unsuccessful. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms not attached to the water molecules were placed in calculated positions. The molecule is situated on a crystallographic mirror plane which runs through the middle of bonds C(11)-C(11′), C(9)-C(9′) and C(7)-C(7′), and atoms N(3), Cu, O(1), C(12), O(2) and H(13A).

RESULTS

Characterization of NBAII

Pure NBAII is a high melting, yellow-brown solid. The ligand is insoluble in water and soluble in organic solvents. NBAII is stable and can be stored indefinitely as a solid or in solution. The ^{1}H NMR spectrum of NBAII in $CDCl_3$ is shown in Figure 1. Chemical shifts for the NBAII ligand are listed in Table I. The ligand is planar, with two equivalent pyridyl rings bonded to the parent benz(f)isoindoline. The pyridyl hydrogens are shifted downfield in the following order: H5 < H3 < H4 < H6. This shift pattern was observed earlier in the BAII ligand.[4] The single resonance produced by the naphtho-protons on the middle six-membered ring is shifted downfield at 8.64 ppm due to deshielding by the nearby π-electron cloud. The β and α protons are shifted to a lesser extent than the naphtho protons and exhibit a typical α, α′, β, β′ splitting pattern resulting in two quartets. The singlet produced by the naphtho protons overlaps the doublet produced by the H6 pyridyl protons.

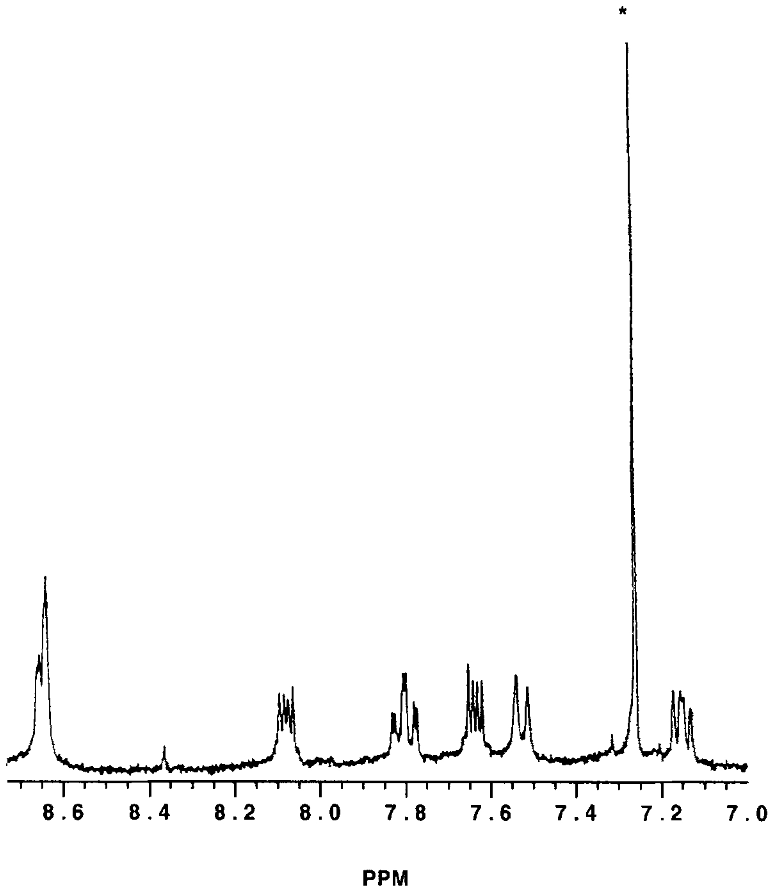


FIGURE 1 ^{1}N-HNMR spectrum of aromatic region for NBAII ligand in $CDCl_3$. Peak marked with an asterisk is from the solvent.

TABLE I Chemical shift data for NBAII ligand, and Pd(II) and Zn(II) complexes

Comp.	*β*	*α*	*benzo*	*H6*	*H5*	*H4*	*H3*
NBAII>(CDCl$_3$)	7.63q	8.08q	8.64s	8.64d	7.15m	7.15m	7.55d
Pd(II)>(CDCl$_3$)	7.64q	8.07q	8.54s	9.86d	7.07m	7.86m	7.64d
NBAII>(d$_6$-DMSO)	7.68q	8.24q	8.63s	8.71d	7.26m	7.89m	7.44d
Zn(II)>(d$_6$-DMSO)	7.63q	8.20q	8.47s	8.60d	7.21m	7.93m	7.46d

A number of ligand vibrations are found in the infrared spectrum. Weak aromatic C-H stretching vibrations occur at 3052 cm^{-1}. The indole N-H stretching vibration appears as a broad band near 3200 cm^{-1}. The imine C=N stretch is a strong band at 1638 cm^{-1}. 2-substituted pyridines show four characteristic absorption bands due to stretching and contracting of bonds in the ring and interaction between these stretching modes.[19] The four pyridyl ring stretching vibrations occur in the 1600–1400 cm^{-1} region of the spectrum. These skeletal bands were assigned using BAII and 2-aminopyridine as references. The imine C-N stretch is a weak band at 1335 cm^{-1}. Pyridine C-H out-of-plane bending and ring-bending vibrations appear at 789 cm^{-1} and 750 cm^{-1}, respectively.

Characterization of Divalent Metal Complexes

NBAII functions as a uninegative, planar, tridentate ligand in most cases. Divalent metal ions coordinate with the deprotonated NBAII ligand through one indole and two pyridyl nitrogens. In this study, the metal to ligand ratio was 1:1 with an acetate or chloride anion occupying a fourth coordination site. Cu(II) and Ni(II) were expected to form complexes with NBAII which have nearly square-planar geometry. This was indeed the case for the Cu(II) complex whose structure was determined by x-ray diffraction. Large downfield shifts observed in the ^{1}H NMR spectrum of the Ni(II) complex of NBAII suggest that the Ni(II) complex is paramagnetic. Paramagnetic Ni(II) complexes can form when the geometry around the nickel atom deviates from square planar.[20] The possibility of tetrahedral coordination is supported by formation of the Zn(II) complex since Zn(II), which usually prefers tetrahedral coordination, can also complex with the planar NBAII ligand. The flexibility of coordinating pyridine groups and the mobility of the acetate group allow for deviations from planarity in these complexes. Such variations in geometry have been observed in other BAII complexes. Four-coordinate Pd(II) d^8 complexes are almost exclusively square planar because the energy difference between the $d_{x2\text{-}y2}$ and d_{xy} orbitals is greater than in the Ni(II) case. The divalent NBAII complexes were characterized using NMR, IR, and

UV-visible spectroscopy. The crystal structure of the Cu(II)OAc complex was also determined.

^{1}H NMR of Zn(II) and Pd(II) complexes

^{1}H NMR spectra of diamagnetic Zn(II) and Pd(II) complexes were obtained. Because of the low solubility of the Zn(II)OAc complex in chloroform the ^{1}H NMR of the zinc complex was run in d_6-DMSO. Chemical shifts for the aromatic protons in both complexes are listed in Table 1.

The ^{1}H NMR spectrum of the Pd(II) complex is shown in Figure 2. Overlap of the doublet produced by the H3 pyridyl protons with the quartet from the α protons results in a four proton multiplet at 7.64 ppm. Pyridyl protons H6 are shifted downfield from 8.64 ppm in the free ligand to 8.86 ppm in the Pd(II) complex. If the Pd(II) complex is square planar, the H6 protons may be deshielded by the electron rich environment around the coordinated chlorine atom.

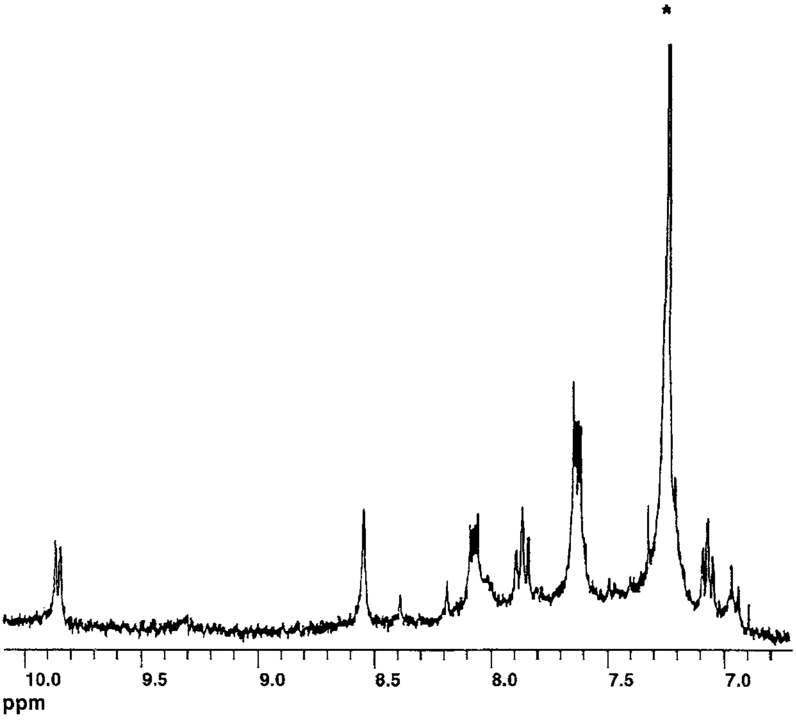


FIGURE 2 ^{1}H-NMR spectrum of aromatic region for (NBAII)PdCl in $CDCl_3$. Solvent peaks marked with an asterisk.

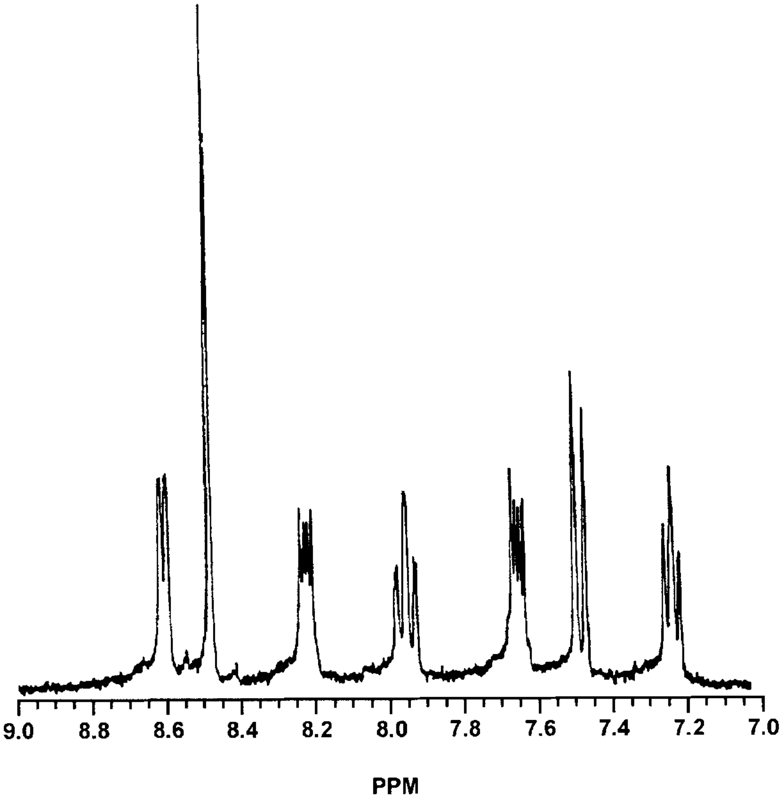


FIGURE 3 ^{1}H-NMR spectrum of aromatic region for (NBAII)Zn(OAc) in d_6-DMSO.

The ^{1}H NMR spectrum of the Zn(II) complex is shown in Figure 3. The upfield shift of the H6 protons in the Zn(II) complex is due to shielding by the electropositive zinc ion. The naphtho protons of both the Pd(II) and Zn(II) complexes are shifted upfield from the free ligand. The shift may result from loss of electron density in the C═N π-electron cloud to the metal atom. The loss of electron density would reduce the deshielding effect on the naphtho protons.

IR Spectra of Divalent Complexes

The infrared spectra of the divalent OAc complexes and the Pd(II)Cl complex do not differ significantly. Spectra of all the divalent complexes are dominated by ligand bands. Coordinated acetate vibrations are obscured in the Ni(II), Zn(II), and Cu(II) complexes by ligand vibrations in the 1600–1400 cm^{-1}

TABLE II Selected infrared spectroscopic data for NBAII and Cu(II), Ni(II), Pd(II) and Zn(II) complexes

Compound		*Pyridine Ring Stretching Vibrations (cm^{-1})*			*C=N Stretch (Imine) (cm^{-1})*
	I	*II*	*III*	*IV*	
NBAII Ligand	1584s	1557s	1460s	1429s	1638s
Zn(II) Complex	1572s	1532s	1470s	1431s	1634w
Cu(II) Complex	1574s	1527s	1465s	1433s	1636w
Ni(II) Complex	1570s	1526s	1464s	1429s	1640w
Pd(II) Complex	1580s	1533s	1468s	1429s	1634w

region. Lattice water is evident in all four complexes in the 3450-3300 cm^{-1} region. The presence of water was later confirmed in the crystal structure of the Cu(II) (NBAII) complex. Chelation with Cu(II), Zn(II), Ni(II), and Pd(II) causes several changes in the ligand vibrational spectrum.[21] Selected IR spectral data for the free NBAII ligand and each metal complex are listed in Table II. Coordination of NBAII shifts pyridyl skeletal bands I and II to a lower frequency. This shift is due to the electron withdrawing power of the metal cation which reduces electron density in the ring. The same effect is observed in substituted pyridines with electronegative substituents.[19] Chelation also fixes the pyridine rings which causes a decrease in intensity of the C=N imine stretching band in the 1600–1650 cm^{-1} region.[22]

Electronic Spectra of Divalent Complexes

The colored NBAII complexes owe their colors to a combination of strong ligand bands, M→L charge-transfer bands, and metal d-d bands in the visible region. Absorption data are summarized in Table III. The bright yellow Zn(II) complex is dominated by ligand bands at 280 and 395 nm. M→L charge-transfer should take place in the Pd(II), Cu(IHÒ(and Ni(II) complexes.[23,20] The pyridine and indoline π-systems possess empty low-energy orbitals which can accept electrons from higher energy metal *d*-orbitals. The absorption spectra of the diamagnetic Pd(II) complex shows ligand bands at 285 and 402 nm and a M→L charge-transfer band at 456 nm. Dilute solutions of the Cu(II) complex are yellow and show strong ligand bands at 286 and 400 nm. The shoulder at 438 nm was designated as the M→L charge-transfer band in the Cu(II) (NBAII) complex. Concentrated solutions of the Cu(II) (NBAII) complex are dark green

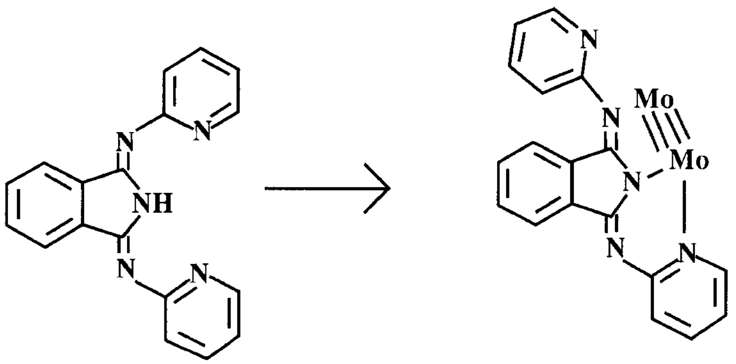
TABLE III Electronic absorption data for NBAII and Cu(II), Ni(II), Pd(II) and Zn(II) complexes

Compound	$\pi \rightarrow \pi^*$ *Ligand Bands*	$M \rightarrow L$ *Charge Transfer*	*d-d Metal Band*
NBAII Ligand	275–381 nm	-----	-----
Zn(II) (NBAII)	280,395 nm	-----	-----
Cu(II) (NBAII)	286,400 nm	438 nm	588 nm
Ni(II) (NBAII)	299,389 nm	453 nm	-----
Pd(II) (NBAII)	285,402 nm	456 nm	-----
Cu(II) (BAII)	312–419 nm	442 nm	635 nm

and a metal *d-d* band is observed at 588 nm. The *d-d* band in the Cu(II) (BAII) complex appears at 635 nm. It is believed that the copper atom is subjected to a stronger ligand field in the NBAII complex since the ligand can donate more electron density to the metal. If this is the case, resulting *d-d* transitions would require more energy. Metal *d-d* bands were not observed in concentrated solutions of the Ni(II) complex, only ligand bands and M→L charge-transfer bands. Highly concentrated solutions of the Ni(II) complex were difficult to prepare because the Ni(II) complex is considerably less soluble than the Cu(II) complex. The yellow-green color of the Ni(II) complex also suggests that the *d-d* bands are much less intense in the Ni(II) complex.

Characterization of Mo_2 $(OAc)_3$ (NBAII)

The dimolybdenum complex of BAII has been previously synthesized.[1-3] In addition to the BAII ligand, the dimolybdenum unit is bridged by three acetate groups. Rotation about one of the imino bonds is accomplished after deprotonation of the free ligand. This allows the dimolybdenum unit to bind to the non-bonding pair of one imino nitrogen instead of the ring nitrogen as in the previously described complexes. The dimolybdenum NBAII complex is expected to have a similar structure.



The NBAII complex was synthesized from equimolar molybdenum acetate and NBAII ligand in methanol. Extreme care was taken to insure that no oxygen or moisture entered the reaction system. When air is present, the reaction mixture turns from emerald green to a green-brown color. The NBAII complex that was isolated is emerald green just like the analogous BAII complex and precipitated readily from solution during the reaction.

The BAII complex was soluble in chloroform and stable enough in solution so that the structure could be verified using NMR spectroscopy. This was not the case with the NBAII complex. While the solid was stable in air for several hours it was very unstable in solution. The NBAII complex was not soluble in chloroform or acetonitrile. It was soluble in DMF and DMSO but decomposed almost immediately even under inert conditions in a glovebox. Solutions of the NBAII complex turned from dark green to brown as the complex decomposed. Decomposition even under inert conditions suggests that the complex is interacting with the solvent and not oxygen or water in the solvent. NMR spectra of the decomposed complex indicated a substantial quantity of the free NBAII ligand and dissociation of the dimolybdenum unit from the ligand. No NMR data could be obtained to confirm the structure of the NBAII complex.

Without NMR evidence or a crystal structure for the dimolybdenum NBAII complex a definite structure cannot be ascertained. Analysis of the NBAII complex for C, H, and N, gave satisfactory results. Percentages were calculated for the complex with three coordinated acetate groups. The visible spectra of both the BAII and NBAII dimolybdenum complexes were compared. The NBAII complex was sufficiently soluble in methylene chloride and the UV-visible spectra could be taken quickly before complete decomposition occurred. A weak band was observed at 649 nm in the NBAII complex. A similar band was observed at 694 nm in the corresponding BAII complex. The absorption spectrum of the NBAII complex is shown in Figure 4. Spectroscopic studies by Baird and Shih showed trends in the BAII complexes that indicated this band was a result of the mixing of a M→L charge-transfer transition with the metal $\delta \rightarrow \delta^*$ transition.[3] The shift of the $\delta \rightarrow \delta^*$ band to higher energy is observed when electron-releasing groups are added to the heterocyclic rings of the BAII ligand. This may explain the shift to higher energy in the NBAII complex. If the addition of a second aromatic ring to the parent isoindoline is considered a substituent effect, the ability of the NBAII to donate additional electron density to the dimolybdenum unit would cause a similar shift in the $\delta \rightarrow \delta^*$ transition. This is consistent with the Cu(II) results although it is difficult to make direct comparisons when the ligand binding mode is so different in the two cases. The dimolybdenum unit being bound to the indoline nitrogen and an imine nitrogen lone pair may result in a substantial electronic interaction between the dimetal unit and the parent isoindoline. Effects

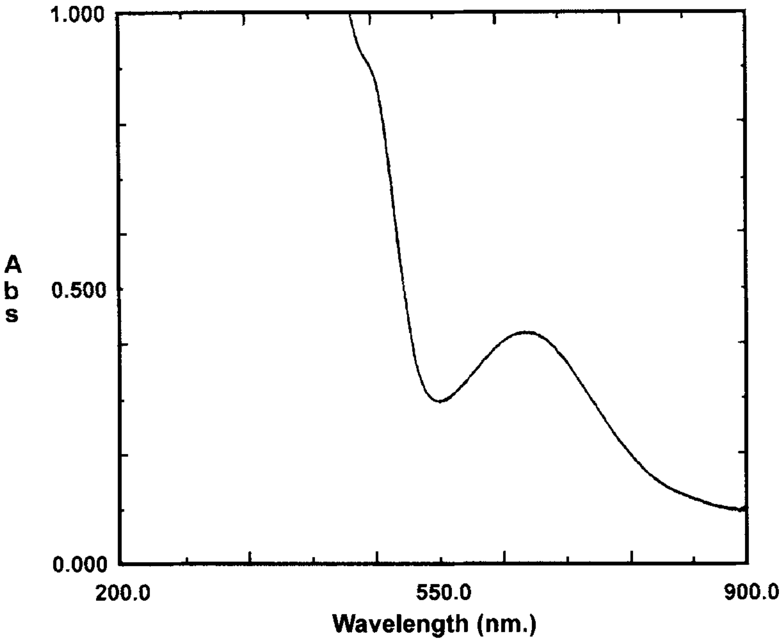


FIGURE 4 Electron absorption spectrum for (NBAII) Mo_2 $(OAc)_3$ in CH_2Cl_2.

of additional substitution to the isoindoline portion of the ligand need to be investigated before any conclusions can be made.

Several indications of complex formation are noted in the spectrum. N-H indole stretching vibrations of the free ligand in the 3200 cm^{-1} region do not appear in the complex spectrum. The coordinated acetate groups produce aliphatic C-H stretching vibrations at 2928 cm^{-1} in addition to the NBAII aromatic C-H stretching vibrations at 3069 cm^{-1}. Acetate COO asymmetric and symmetric stretching vibrations in the 1600-1400 cm^{-1} region are difficult to assign in the complex since pyridyl ring stretching vibrations appear in the same area of the spectrum. Bands at 1466 and 1429 cm^{-1} are assigned to the ligand vibrations since they appear consistently in earlier complexes. Acetate stretching vibrations are either shifted from their positions at 1518 and 1441 cm^{-1} in molybdenum acetate or obscured by ligand bands. However, the OCO scissoring vibration can be clearly assigned in the complex spectrum at 677 cm^{-1}. This band appears at 675 cm^{-1} in molybdenum acetate. A decrease in the imine C=N stretching vibration which was characteristic in the divalent metal complexes also occurs in the dimolybdenum complex at 1633 cm^{-1}.

The electronic and infrared spectral evidence of complex formation can only suggest that certain groups are present in the complex. The visible spectrum of the NBAII complex confirms the existence of the dimolybdenum unit. Elemental analysis suggests the dimolybdenum unit is coordinated to three acetate groups. The infrared spectrum does not confirm the existence of bridging acetate groups but does show evidence of NBAII chelation. Obviously, x-ray analysis of a suitable crystal is needed to confirm the structure. The limited stability of the complex in solution has made crystal growth difficult.

Crystal Structure of Cu(II) OAc(NBAII)

Dark green rectangular crystals of the (NBAII) CuOAc complex were grown in methanol over a two week period. As mentioned in the introduction, recent studies of similar Cu(II) centers prompted interest in the Cu(II) complex of NBAII.[13,24] The physical data and data collection parameters are listed in Table IV. The ORTEP drawing of the Cu(II) complex is shown in Figure 5. Atomic coordinates and isotropic thermal parameters are listed in Table V. Bond distances and angles are included in Table VI. Structure factor tables for the (NBAII) CuOAc complex are provided in the Appendix.

TABLE IV Crytallographic data for $CuC_{24}H_{17}N_5O_2 \cdot 1.5H_2O$

param	*data*
formula	$CuC_{24}H_{17}N_5O_2 \cdot 1.5H_2O$
form. wt.	498.0
cryst. system	centrosymmetric
space group	C2/m
a, Å	20.256(4)
b, Å	16.166(3)
c, Å	7.915(2)
α, deg	90
β, deg	94.83(2)
γ, deg	90
v, Å^3,	2583(1)
D_{calc}, g cm^{-3}	1.28
Temp., K	298
Z	4
cryst. dim, mm	0.43 × 0.32 × 0.25
radiation, Å	0.71069
Scan type	omega
Scan range	2° + dispersion
Scan speed, deg. min^{-1}	variable between 4 & 27
Standards	2 standards/48 meas.
Number of reflections	3043
No. used	2186 with $I \geq 3\sigma(I)$
μ, cm^{-1}	8.7
R,^{b}	0.084
R_w,^{a}	0.106

$^a R = \Sigma||Fo|-|Fc||/\Sigma|Fo|$ $^b R_w = [(\Sigma w(|Fo|-|Fc|)^2/\Sigma wFo^2)]^{1/2}$

TABLE V Atomic coordinates (×10^4 Å) and isotropic thermal parameters (Å×10^3) for $CuC_{24}H_{17}N_5O_2 \cdot 1.5\ H_2O$

	X	*Y*	*Z*	*U**
Cu	2191(1)	5000	5663(2)	56(1)
C(5)	1627(4)	3283(4)	5600(8)	53(2)
N(1)	2140(3)	3787(4)	6153(7)	58(2)
C(1)	2625(4)	3467(5)	7260(10)	69(3)
C(2)	2627(4)	2675(6)	7838(11)	75(3)
C(3)	2127(4)	2167(5)	7247(12)	86(4)
C(4)	1628(5)	2463(5)	6130(11)	74(3)
N(2)	1099(3)	3534(4)	4509(7)	51(2)
C(6)	961(3)	4308(4)	4167(7)	43(2)
C(7)	354(3)	4569(4)	3090(7)	42(2)
C(8)	−144(3)	4124(4)	2245(8)	49(2)
C(9)	−674(3)	4568(4)	1359(7)	47(2)
C(10)	−1205(3)	4144(5)	471(9)	60(3)
C(11)	−1713(3)	4574(5)	−367(9)	68(3)
N(3)	1300(3)	5000	4715(9)	43(2)
O(1)	3153(4)	5000	6010(13)	96(4)
C(12)	3400(5)	5000	4584(21)	82(5)
O(2)	3048(4)	5000	3210(15)	101(4)
C(13)	4139(6)	5000	4590(24)	113(7)
$O_W(1)$	277(6)	2094(7)	3429(19)	102(6)
$O_W(2)$	1320(12)	0	−164(28)	117(15)
H(1)	2987	3819	7653	72
H(2)	2976	2480	8631	81
H(3)	2120	1603	7626	88
H(4)	1275	2102	5713	83
H(8)	−161	3537	2330	41
H(10)	−1218	3531	436	59
H(11)	−2079	4271	−996	70
H(13A)	4290	5000	3557	157
H(13)	4303	4515	5275	157

* Equivalent isotropic U defined as one third of the trace of the orthoganonalised U_{ij} tensor.

TABLE VI Bond distances and angles for Cu (NBAII) OAc

Distances (a)					
atom	*atom*	*distance*	*atom*	*atom*	*distance*
Cu	N(1)	2.003(6)	C(1)	C(12)	1.272(19)
Cu	O(1)	1.945(8)	C(12)	C(13)	1.498(17)
C(5)	N(1)	1.363(9)	Cu	N(3)	1.895(7)
C(5)	N(2)	1.378(8)	Cu	N(1′)	2.003(6)
C(1)	C(2)	1.358(13)	C(S)	C(4)	1.391(11)
C(3)	C(4)	1.372(12)	N(1)	C(1)	1.362(9)
C(6)	C(7)	1.497(8)	C(2)	C(3)	1.356(13)
C(7)	C(8)	1.367(9)	N(2)	C(6)	1.305(9)
C(8)	C(9)	1.425(9)	C9	C12	1.3
C(9)	C(9′)	1.398(14)	C10	C11	1.392(9)
C(11)	C(11′)	1.376(17)			

Angles (b)							
atom	*atom*	*atom*	*angle*	*atom*	*atom*	*atom*	*angle*
N(1)	Cu	N(3)	90.8(2)	O(1)	Cu	N(1′)	92.3(2)
N(3)	Cu	O(1)	164.9(4)	N(1)	C(5)	N(2)	123.8(6)

TABLE VI (*Continued*)

			Angles (b)				
atom	*atom*	*atom*	*angle*	*atom*	*atom*	*atom*	*angle*
N(3)	Cu	N(1′)	90.8(2)	Cu	N(1)	C(5)	124.9(5)
N(1)	C(5)	C(4)	119.4(6)	C(5)	N(1)	C(1)	117.9(6)
C(4)	C(5)	N(2)	116.8(6)	C(1)	C(2)	C(3)	118.3(8)
Cu	N(1)	C(1)	116.8(5)	C(5)	C(4)	C(3)	120.6(8)
N(1)	C(1)	C(2)	123.8(7)	N(2)	C(6)	C(7)	122.6(5)
C(2)	C(3)	C(4)	119.9(8)	C(7)	C(6)	N(3)	108.4(5)
C(5)	N(2)	C(6)	123.6(6)	C(6)	C(7)	C(7′)	106.4(3)
N(2)	C(6)	N(3)	128.9(5)	C(7)	C(8)	C(9)	118.1(6)
C(6)	C(7)	C(8)	131.9(6)	C(8)	C(9)	C(9′)	120.2(4)
C(8)	C(7)	C(7′)	121.7(4)	C(9)	C(10)	C(11)	120.4(7)
C(8)	C(9)	C(10)	120.8(6)	Cu	N(3)	C(6)	124.2(3)
C(10)	C(9)	C(9′)	119.0(4)	C(6)	N(3)	C(6′)	110.3(7)
C(10)	C(11)	C(11′)	120.6(5)	O(1)	C(12)	O(2)	122.3(10)
Cu	N(3)	C(6′)	124.2(3)	O(2)	C(12)	C(13)	120.0(14)
Cu	O(1)	C(12)	109.8(8)	O(1)	C(12)	C(13)	117.7(13)
N(1)	Cu	O(1)	119.5(2)	N(1)	Cu	N(1′)	156.4(3)

Distances are in armstroms. Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

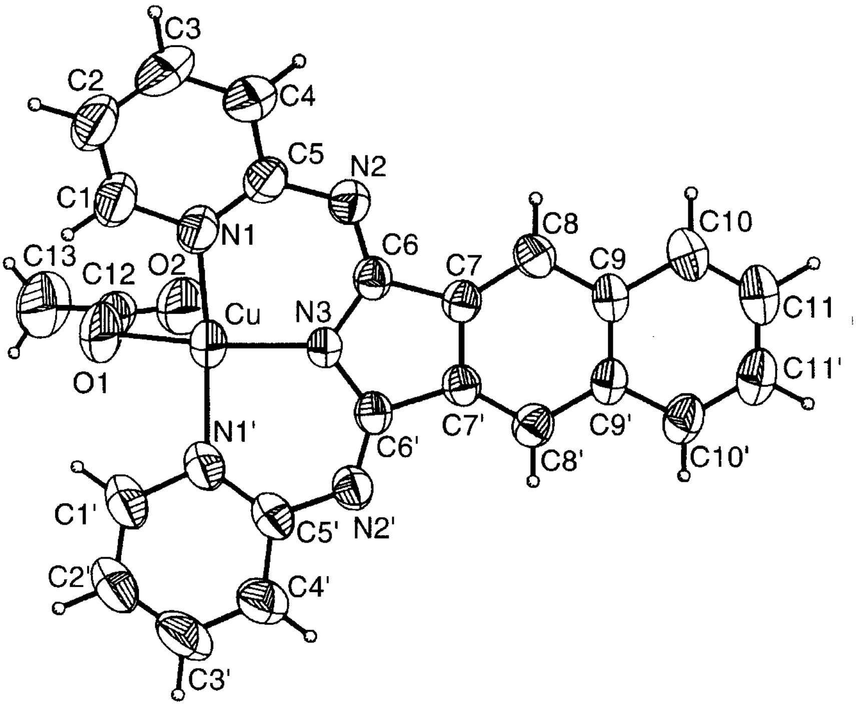


FIGURE 5 Molecular structure and crystallographic numbering scheme for (NBAII) Cu (OAc).

The structure of the complex can be described as one in which the three-coordinate NBAII ligand together with an oxygen from the acetate form a distorted square-planar geometry with the acetate ion raised out of the plane formed by the three coordinated nitrogen atoms. This occurs so that O(1) can avoid contact with pyridyl hydrogens bonded to C(1) and C(1′). The copper atom is also raised above the plane of the three nitrogen atoms in both the BAII and NBAII complexes. There are 1.5 molecules of water per molecule of the copper complex in the crystal lattice; these are not associated with the complex itself. This is in contrast to the earlier reported (BAII) Cu (OAc) complex in which a water molecule occupies a fifth labile coordination site at a distance of 2.466(7) Å. The geometry around the copper atom in that complex is approximately square pyramidal. Square pyramidal geometry is not observed in the crystal structure of the NBAII analogue. Since both complexes were crystallized in methanol under similar conditions it is unlikely that crystal packing forces account for the difference in structure.

Initially, when the synthesis of these naphthalene-based ligand systems began it was believed that the larger aromatic system in NBAII ligands would further stabilize the metal ion. This is observed in macrocyclic systems where the ligand acts as an ‘electron sink’ which can stabilize a metal in an unusually high or low oxidation state.[25] If the electron density around the copper atom in the NBAII complex is greater than in the BAII complex, the ability to coordinate with a fifth ligand may be reduced. Bond lengths in the coordination spheres of both complexes are almost identical with only a slight reduction in the Cu—O(1) bond length in the NBAII complex.

DISCUSSION

The new ligand 1,3-Bis(2-pyridylimino)benz(f) isoindoline, NBAII has been synthesized and compared to the more common BAII ligand. Several aspects of the new ligand are similar to those of the BAII systems. Both act as tridentate uninegative ligands which can accommodate square-planar or tetrahedral geometries in complexes of divalent metals of formulae (NBAII)MX. Both can form complexes with dimolybdenum in which an unusual coordination mode is observed for the ligand with one molybdenum bonding to the isoindoline nitrogen while the other binds to one of the imino nitrogens. This coordination mode arises by rotation of one of the pyridine rings out of the plane of the ligand.

Some differences between the behavior of BAII and NBAII were also observed. The most significant difference appears to be that addition of the benzo portion generates a more electron-rich environment around the metal; the NBAII ligand seems to be a higher field ligand than the BAII ligand. This difference is supported by shifts to higher energy in the *d-d* band in the Cu(II) complex and the $\delta \rightarrow \delta^*$ band in the dimolybdenum complex of the NBAII ligand.

In addition, the increased electron density about the Cu(II) ion causes a subtle, but important, difference in the structures of the two compounds. The BAII-Cu complex is five coordinate with a labile water molecule attached to the metal atom. This environment for the copper agrees with that found in the enzyme galactose oxidase. In the NBAII-Cu complex no water is present in the coordination sphere of the metal. Thus a small difference in the acidity of the copper in an enzyme may cause a change in the coordination chemistry of the metal with important ramifications in biological activity.

Acknowledgments

Acknowledgment is made to the Donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

References

[1] D.M. Baird, R. Hassan and W.K. Kim, *Inorg. Chem. Acta*, **130**, 39 (1987).
[2] D.M. Baird, K.Y. Shih, J.H. Welch and R.D. Bereman, *Polyhedron*, **8**, 2359 (1989).
[3] D.M. Baird and K.Y. Shih, *Polyhedron*, **10**, 229 (1991).
[4] W.O. Siegl, *J. Org. Chem.*, **42**, 1872 (1977).
[5] W.O. Siegl, *J. Heterocycl. Chem.*, **18**, 1613 (1981).
[6] W.O. Siegl, *Inorg. Chem. Acta*, **25**, L65 (1977).
[7] D.N. Marks, W.O. Siegl and R.R. Gagne, *Inorg. Chem.* **21**, 3140 (1982).
[8] L. Saussine, E. Brazi, A. Robine, H. Mimoun, J. Fischer and R. Weiss, *J. Amer. Chem. Soc.*, **107**, 3534 (1985).
[9] R.R. Gagne and D.N. Marks, *Inorg. Chem.*, **23**, 65 (1984).
[10] C.A. Tolman, J.D. Druliner, P.J. Krusic, M.J. Nappa, W.C. Seidel, I.D. Williams and S.D. Ittel, *J. Mol. Catal.* **48**, 129 (1988).
[11] R.R. Gagne, R.S. Gall, G.C. Lisensky, R.E. Marsh and L.M. Speltz, *Inorg. Chem.*, **18**, 771 (1979).
[12] A.W. Addison, P.J. Burke, P.J. Henrick and K. Henrick, *Inorg. Chem.*, **21**, 60 (1982).
[13] R.D. Bereman, G.D. Shields, J.R. Dorfman and J. Bordner, *J. Inorg. Biochem.*, **19**, 75 (1983).
[14] D.V. Bautista, G. Bullock, F.W. Hartstock and L.K. Thompson, *J. Heterocyclic Chem.*, **20**, 345 (1983).
[15] D.V. Bautista, J.C. Dewan, J.C. Thompson and L.K. Thompson, *Can. J. Chem.*, **60**, 2583 (1982).
[16] S.S. Tandon, S.K. Mandal, L.K. Thompson and R.C. Hynes, *Inorg. Chem.*, **31**, 2215 (1992).
[17] B.L. Wheeler, G. Nagasubramanian, A.J. Bard, L.A. Schechtman, D.R. Dininny and M.E. Kenney, *J. Am. Chem. Soc.*, **106**, 7404 (1984).
[18] G. Wilkinson and Z. Duri, *Inorg. Syn.*, **87**, 1872 (1969).
[19] L.J. Bellamy, "The Infrared Spectra of Complex Molecules" (University Press: Cambridge, Great Britain, 1975) Vol. I.
[20] C.J. Ballhausen, "Introduction to Ligand Field Theory" (McGraw-Hill: New York, 1962).

[21] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds" (John Wiley & Sons: New York, 1963).
[22] R.R. Gagne, W.A. Marritt and D.N. Marks, *Inorg. Chem.* (1981) **20**, 3260 (1981).
[23] F.A. Cotton, G. Wilkinson, "Advanced Inorganic Chemistry" (John Wiley & Sons: New York, 1980).
[24] J.R. Dorfman, Ph.D. Dissertation, North Carolina State University, Raleigh, NC, 1982.
[25] L.F. Lindoy, "The Chemistry of Macrocyclic Ligand Complexes" (Cambridge University Press: New York, 1989).