Registry No. $[Ni_2(en)_4Cl_2]Cl_2$, 20647-35-2.

Supplementary Material Available: A listing of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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Contribution from the Departments of Chemistry, University of Virginia, Charlottesville, Virginia 22901, and University of Wollongong, Wollongong, N.S.W., Australia 2500

Properties and Structures of the Five-Coordinate Copper(II) and Six-Coordinate Nickel(II) Complexes $\{[CuL]\cdot 2H_2O\}_\infty$ and $[NiLH_2O]_2$, L = *N,N'*-Bis[(2-hydroxy-5-methylphenyl)(4-methylphenyl)methylene]-3-azahexane-1,6-diamine

DEREK P. FREYBERG,[1a] GARRY M. MOCKLER,[1b] and EKK SINN*[1a]

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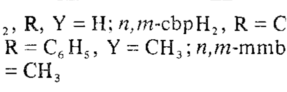
The copper(II) and nickel(II) complexes of the potentially pentadentate ligand (2,3-mmbpN) derived from the Schiff base condensation of 3-azahexane-1,6-diamine and 5,4′-dimethyl-2-hydroxybenzophenone have been synthesized and their crystal structures and magnetic and spectral properties determined. For comparison, the copper and nickel complexes of a series of related ligands have also been synthesized and their magnetic and spectral properties determined. The ligands act as pentadentates, in contrast with the coordination reported for some analogous Schiff base ligands with salicylaldehyde. The structures of both the copper and nickel complexes with 2,3-mmbpN are unexpected. The copper environment is very close to trigonal bipyramidal, with the amine nitrogen bond being only 0.1 Å longer than the imine nitrogen bonds. This amine nitrogen bond, at 2.077 Å, is much shorter than the analogous bond in the related complexes [Cu(3,3-mbpN)] (2.374 Å) and [Cu(3,4-cbpN)] (2.291 Å), and this shortening is ascribed to the steric requirements of the ligand. The nickel environment is close to octahedral, with a molecule of water coordinated to the nickel in a position cis to the amine nitrogen. Such coordination has been previously observed for complexes of cobalt(III) but not for nickel(II). The hydrogen bonding links neighboring molecules to form weakly linked dimers in the nickel complex, $[Ni(2,3\text{-mmbpN})\cdot H_2O]_2$, and infinite chains in the copper complex, $\{[Cu(2,3\text{-mmbpN})]\cdot 2H_2O\}_\infty$. The crystal structures were determined from full-matrix least-squares refinement of counter data: $[Cu(2,3\text{-mmpbN})]\cdot 2H_2O$, space group $C2/c$, $Z = 4$, $a = 29.128$ Å, $b = 8.503$ (2) Å, $c = 13.921$ (5) Å, $\beta = 106.63$ (2)°, $V = 3304$ Å^3, $R = 3.5\%$ for 1718 reflections; $[Ni(2,3\text{-mmbpN})H_2O]$, space group $P\bar{1}$, $Z = 2$, $a = 10.833$ (2) Å, $b = 12.63$ (1) Å, $c = 13.137$ (6) Å, $\alpha = 116.83$ (5)°, $\beta = 91.09$ (4)°, $\gamma = 93.91$ (6)°, $V = 1598$ Å^3, $R = 3.1\%$ for 3118 reflections.

Introduction

A series of bivalent and trivalent metal complexes with pentadentate Schiff base ligands of type **1** have shown an interesting range of structures and properties. In particular, indirect structural studies on the ligand $salXH_2$ (R = H, X = NH, NC_6H_5, S, O, PCH_3, Y = H) have suggested structures in which the donor X was frequently uncoordinated.[2-4] On the other hand, analogous ligands based on substituted *o*-hydroxybenzophenones ($R = C_6H_5$) have to date always yielded complexes in which the ligand acts as a pentadentate, with X coordinated to the metal.[5-10] Comparison of spectral and magnetic properties suggests that in a few specific cases, the salX complexes also have the donor X coordinated. There is in fact no reason why the salicylaldehyde and benzophenone derivatives should behave differently in this respect, except for differences in ligand electronegativities. To date, attempts to obtain X-ray evidence for complexes with the donor atom X uncoordinated have not been successful. Complexes with ligands (**1**) acting as pentadentates have the phenolic oxygen atoms either cis or trans to each other and the mechanism that makes one structure preferred over the other is not yet clear. The differences appear to be small between the ligands of complexes adopting different structural types. In particular, completed and preliminary X-ray studies show that [M(3,3-cbpN)] (M = Ni, Cu, Zn), [M(3,4-cpbN)] (M = Ni,



1: *n,m*-salH_2, R, Y = H; *n,m*-cbpH_2, $R = C_6H_5$, Y = Cl; *n,m*-mbpH_2, $R = C_6H_5$, $Y = CH_3$; *n,m*-mmbpH_2, R = *p*-$CH_3C_6H_4$, $Y = CH_3$

Table I. Analytical Data

		C	H	N
[Cu(2,3-mmbpN)]·2H_2O	calcd	66.60	6.55	6.66
	found	67.03	6.36	6.28
[Ni(2,3-mmbpN)]·2H_2O	calcd	67.11	6.60	6.71
	found	67.14	6.31	6.73
Ni(2,3-cbpN)	calcd	61.73	4.51	6.97
	found	61.54	4.49	7.21
[Cu(2,3-cbpN)]·$^1/_4H_2O$	calcd	60.79	4.53	6.86
	found	60.79	4.54	6.74
[Cu(2,3-mbpN)]·H_2O	calcd	67.73	6.03	7.18
	found	68.05	6.80	6.97
[Ni(2,3-mbpN)]·2H_2O	calcd	66.24	6.23	7.02
	found	66.78	5.80	7.16

Cu), [Zn(3,3-mbpN)], [Cu(3,3-cbpS)], and [M(3,3-cbpS)L] (M = Co, Ni; L = pyridine, 3-methylpyridine), and [Co(3,3-cbpN)NCS] are trans, while [Co(3,3-cbpS)NCS] is cis.[10] All complexes so far studied of bivalent metals with ligands of type **1** are trans.

A further common feature of type **1** ligands has been a close structural similarity between their nickel(II) and copper(II) complexes, except for a dramatic elongation of the Cu–X bond in each case. However, the complexes with 2,3-mmbpH_2 held three surprises in store: the copper and nickel derivatives are not structurally similar either to each other or to any of the analogous complexes previously studied, the Cu–X bond shows little elongation, and the nickel complex has its donor oxygens cis, the first observation of this configuration with nickel.

Experimental Section

2-Hydroxy-4′,5-dimethylbenzophenone, Hmmbp, was prepared by Friedel–Crafts acylation: 133 g (1 mol) of anhydrous $AlCl_3$ was placed in a 1-L round-bottom flask and 155 g (1 mol) *p*-tolyl chloride was added. *p*-Cresol (108 g, 1 mol) was added in portions of about 15 g to the reaction mixture, which rapidly became hot, evolving fumes of HCl. The flask was swirled to encourage mixing of the reactants and was then heated to 180 °C for 30 min. The yellowish brown tarry product mixture was poured, with stirring, into a solution of 300 mL of concentrated HCl dissolved in 1200 mL of water. On cooling of the mixture, a granular precipitate formed, and this was filtered off and washed with water. The Hmmbp was recrystallized from a minimum volume of hot 95% ethanol. The other parent ketones, 3,3′-iminobis(propylamine), and *N*-(2-aminoethyl)-1,3-propanediamine were purchased from the Aldrich Chemical Co., Inc.

The condensation of the ketones with the triamines, to form the Schiff base ligands, and the syntheses of the metal complexes were carried out as previously described.[5] Analytical data for the new complexes are given in Table I. Both of the complexes selected for X-ray study retained water molecules from the reaction mixture, leading to empirical formulas Cu(2,3-mmbpN)·2H_2O and Ni(2,3-mmbpN)·2H_2O. One of the water molecules in the nickel complex is readily lost, but the other is retained in the crystals grown for X-ray study, due to being bonded to the metal atom; both water molecules are retained by the copper complex, presumably due to the hydrogen bonding; vide infra. Both complexes were recrystallized from methanol.

Magnetic moments were determined by the Gouy method.

Visible and near-infrared solution spectra were measured on a Hitachi EPS-3T recording spectrophotometer and solid-state reflectance spectra on a Zeiss PMQII spectrophotometer with an RA-3 reflectance attachment. The spectral data are given in Table II.

Electron spin resonance spectra were obtained on a Varian E-109 spectrometer with an E-102 microwave bridge, operating at 9 GHz.

Crystal data for [Cu(2,3-mmbpN)]·2H_2O: $CuO_4N_3C_{35}H_{41}$, $M_r = 631$, space group $C2/c$, $a = 29.128$ (6) Å, $b = 8.503$ (2) Å, $c = 13.921$ (5) Å, $\beta = 106.63$ (2)°, $V = 3304$ Å^3, $Z = 4$, $\rho_c = 1.27$ g cm^{-3}, $\rho_o = 1.30$ g cm^{-3}, μ(Mo Kα) = 7.3 cm^{-1}, green crystal, faces (with distances from centroid in mm) (100) 0.08, ($\bar{1}$00) 0.08, (010) 0.14, (0$\bar{1}$0) 0.14, (001) 0.14, (00$\bar{1}$) 0.14.

Crystal data for [Ni(2,3-mmbpN)H_2O]: $NiO_3N_3C_{35}H_{39}$, $M_r = 608$, space group $P\bar{1}$, $a = 10.833$ (2) Å, $b = 12.63$ (1) Å, $c = 13.137$ (6) Å, $\alpha = 116.83$ (5)°, $\beta = 91.09$ (4)°, $\gamma = 93.91$ (6)°, $V = 1598$ Å^3, $Z = 2$, $\rho_c = 1.27$ g cm^{-3}, $\rho_o = 1.25$ g cm^{-3}, μ(Mo Kα) = 6.5 cm^{-1}, green crystal, faces (with distances from centroid in mm) (100) 0.13, ($\bar{1}$00) 0.13, (010) 0.05, (0$\bar{1}$0) 0.05, (01$\bar{1}$) 0.12, (0$\bar{1}$1) 0.12.

For each crystal, the Enraf-Nonius program SEARCH was used to obtain the positions of 15 accurately centered reflections which were then used in the program INDEX to obtain approximate cell dimensions and an orientation matrix for data collection. Refined cell dimensions and their estimated standard deviations were obtained from least-squares refinement of 28 accurately centered reflections. The mosaicity of each crystal was examined by the ω-scan technique and judged to be satisfactory.

Collection and Reduction of the Data. Diffraction data were collected at 292 K on an Enraf-Nonius four-circle CAD-4 diffractometer controlled by a PDP-8/M computer, using Mo Kα radiation from a highly oriented graphite crystal monochromator. The θ–2θ scan technique was used to obtain the intensities of all nonequivalent reflections for which 1° < 2θ <46° for [Cu(2,3-mmbpN)]·2H_2O and 1° < 2θ < 45° for [Ni(2,3-mmbpN)H_2O]. Scan widths (SW) were calculated from the formula SW = $A + B \tan \theta$ where A is estimated from the crystal mosaicity and B allows for the increase in width of peak due to Kα_1–Kα_2 splitting. The values of A and B were 0.80 and 0.30°, respectively, for [Cu(2,3-mmbpN)]·2H_2O and 0.50 and 0.30°, respectively, for [Ni(2,3-mmbpN)H_2O]. The calculated scan angle is extended at each side by 25% for background determination (BG1 and BG2). The net count is then calculated as NC = TOT − 2(BG1 + BG2), where TOT is the integrated peak intensity. Reflection data

Table II. Magnetic and Spectral Data

		freq, cm^{-1}		
	μ,[a] μ_B	solid state	CH_2Cl_2[b]	pyridine[b]
[Cu(3,4-cbpN)]·$^1/_2H_2O$	1.96	17 500 sh, 15 000	16 500 sh, 14 200 (151.5)	16 500 sh, 13 500 (151.5)
Cu(2,3-cbpN)	1.92	12 500	12 800 (194)	12 100 (211)
[Cu(2,3-mbpN)]·H_2O	1.87	12 000	12 800 (216)	12 200 (300)
[Cu(2,3-mmbpN)]·2H_2O	1.89	12 000	12 800 (252)	12 200 (222)
[Ni(3,4-cbpN)]·$^1/_2H_2O$	3.21	16 000, 11 300, 7500 sh, 6800 sh, 5900	16 250 (54.5), 10 400 (14.5), 8200 (18), 5200 (11)	17 500 sh, 10 400 (12)
Ni(2,3-cbpN)	3.22	17 100, 10 500, 8700, 5100	17 500 sh, 11 000 (6), 8200 (9), 5300 (6)	11 200 (15.6)
[Ni(2,3-mbpN)]·2H_2O	3.27	17 500 sh, 11 500 sh, 8100	10 800 (17.5), 7700 (19.8)	11 200 (20.2)
[Ni(2,3-mmbpN)]·2H_2O	3.27	16 800, 11 200, 7900	17 500 sh, 11 000 (>10.5), 8100 (>13)	*c*
Cu(3,3-cbpN)		13 300	14 300 (200)	12 700 (192)
Ni(3,3-cbpN)		17 700, 11 000, 8600, 5400	16 800 (41), 10 400 sh, 8500 (14.5)	11 100 (13.7)
Cu(3,3-mbpN)		13 500 br	14 500 (190)	13 100 (185)
Ni(3,3-mbpN)		17 000 sh, 10 100 sh, 8500	16 800, 10 200 sh, 8300 (27.8)	11 000 (12.2)

[a] Room temperature. [b] Cu complexes, 0.005 M; Ni complexes, 0.01 M. [c] Complex not sufficiently soluble in pyridine.

Table III. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

(A) $[Cu(2,3\text{-mmbpN})]\cdot 2H_2O$

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	0.5000 (0)	0.48446 (6)	0.2500 (0)	2.97 (2)	2.94 (2)	3.91 (2)	0.0000 (0)	0.90 (2)	0.0000 (0)
O(1)	0.51678 (7)	0.3691 (2)	0.3819 (1)	4.03 (9)	3.6 (1)	3.83 (9)	1.08 (8)	1.70 (7)	0.80 (8)
O(3)	0.05068 (8)	0.1371 (3)	0.5063 (2)	5.48 (10)	4.0 (1)	5.36 (11)	−0.76 (9)	2.38 (8)	−0.46 (9)
N(1)	0.56872 (8)	0.4899 (3)	0.2581 (2)	3.14 (9)	3.0 (1)	4.2 (1)	−0.5 (1)	0.87 (8)	0.1 (1)
N(2)	0.50073 (16)	0.7218 (5)	0.2154 (3)	3.41 (20)	2.4 (2)	4.1 (3)	−0.6 (2)	1.66 (21)	−0.1 (2)
C(1)	0.5899 (1)	0.2576 (3)	0.3621 (2)	2.8 (1)	2.8 (1)	3.2 (1)	−0.2 (1)	0.6 (1)	−0.3 (1)
C(2)	0.5500 (1)	0.2574 (3)	0.4012 (2)	3.3 (1)	2.8 (1)	2.8 (1)	−0.3 (1)	0.8 (1)	−0.7 (1)
C(3)	0.5465 (1)	0.1338 (4)	0.4656 (2)	4.1 (1)	3.1 (1)	3.6 (1)	−0.1 (1)	1.3 (1)	0.2 (1)
C(4)	0.5792 (1)	0.0143 (4)	0.4889 (2)	4.9 (1)	3.3 (1)	3.8 (1)	−0.4 (1)	0.9 (1)	0.6 (1)
C(5)	0.6173 (1)	0.0076 (4)	0.4486 (2)	3.9 (1)	3.1 (1)	4.5 (1)	0.2 (1)	0.6 (1)	0.4 (1)
C(6)	0.6223 (1)	0.1288 (4)	0.3871 (2)	3.1 (1)	3.9 (2)	4.7 (2)	0.1 (1)	0.9 (1)	−0.1 (1)
C(7)	0.6007 (1)	0.3871 (3)	0.3020 (2)	2.9 (1)	3.2 (1)	3.5 (1)	−0.3 (1)	0.8 (1)	−0.6 (1)
C(8)	0.6513 (1)	0.3954 (4)	0.2962 (2)	3.1 (1)	3.4 (1)	3.8 (1)	−0.3 (1)	0.9 (1)	−0.1 (1)
C(9)	0.6618 (1)	0.3752 (4)	0.2067 (3)	3.4 (1)	6.0 (2)	4.2 (2)	−0.8 (1)	0.8 (1)	−0.5 (1)
C(10)	0.7089 (1)	0.3682 (5)	0.2046 (3)	4.8 (1)	7.2 (2)	5.5 (2)	−1.2 (2)	2.8 (1)	−1.6 (2)
C(11)	0.7468 (1)	0.3820 (5)	0.2903 (3)	3.4 (1)	6.4 (2)	7.0 (2)	−0.9 (1)	1.6 (1)	−1.5 (2)
C(12)	0.7359 (1)	0.4061 (6)	0.3784 (3)	3.1 (1)	8.8 (2)	5.6 (2)	−1.1 (2)	0.5 (1)	−0.8 (2)
C(13)	0.6890 (1)	0.4136 (5)	0.3819 (3)	3.7 (1)	7.1 (2)	4.4 (2)	−0.6 (2)	1.0 (1)	−0.7 (2)
C(14)	0.6526 (1)	−0.1271 (4)	0.4732 (3)	5.4 (2)	4.3 (2)	7.9 (2)	1.2 (2)	1.5 (2)	1.4 (2)
C(15)	0.7982 (1)	0.3694 (7)	0.2870 (4)	4.1 (2)	13.8 (4)	9.8 (3)	−1.0 (2)	3.1 (2)	−2.9 (3)
C(16)	0.5803 (1)	0.6269 (4)	0.2036 (3)	3.6 (1)	3.4 (2)	5.3 (2)	−0.5 (1)	1.3 (1)	0.7 (1)
C(17)	0.5756 (2)	0.7741 (8)	0.2413 (4)	4.1 (3)	4.0 (3)	4.0 (3)	0.3 (2)	2.3 (2)	0.6 (3)
C(18)	0.5244 (2)	0.8305 (8)	0.2312 (5)	4.7 (3)	3.5 (3)	4.7 (3)	0.9 (2)	2.7 (2)	0.4 (3)
C(17′)	0.5511 (2)	0.7716 (7)	0.2385 (4)	3.9 (2)	3.3 (3)	4.2 (3)	−0.0 (2)	2.4 (2)	−0.3 (2)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
H(201)	0.0442 (10)	0.056 (4)	0.475 (2)	4.8 (8)	H(152)	0.1843 (11)	0.351 (4)	0.148 (2)	7.2 (10)
H(202)	0.0337 (11)	0.140 (4)	0.545 (2)	5.8 (8)	H(153)	0.1954 (12)	0.306 (4)	0.259 (2)	7.3 (9)
H(3)	0.5197 (10)	0.137 (3)	0.495 (2)	4.7 (8)	H(161)	0.6074 (33)	0.601 (11)	0.183 (7)	7.5 (26)
H(4)	0.5735 (9)	−0.063 (3)	0.532 (2)	2.7 (6)	H(162)	0.5530 (32)	0.612 (11)	0.119 (7)	7.9 (26)
H(6)	0.6465 (10)	0.128 (3)	0.354 (2)	4.0 (7)	H(163)	0.5645 (23)	0.607 (8)	0.131 (5)	2.5 (17)
H(9)	0.6362 (10)	0.362 (3)	0.151 (2)	4.5 (7)	H(164)	0.6128 (19)	0.645 (7)	0.225 (4)	2.9 (13)
H(10)	0.7144 (10)	0.360 (4)	0.145 (2)	4.6 (8)	H(171)	0.5852 (28)	0.855 (10)	0.209 (6)	5.4 (22)
H(12)	0.7613 (11)	0.419 (4)	0.438 (2)	5.8 (8)	H(172)	0.5935 (28)	0.768 (11)	0.318 (6)	5.8 (23)
H(13)	0.6827 (9)	0.425 (3)	0.443 (2)	4.0 (7)	H(173)	0.5497 (43)	0.877 (14)	0.200 (9)	8.1 (38)
H(141)	0.1709 (11)	0.375 (4)	0.432 (2)	5.3 (8)	H(174)	0.5670 (22)	0.782 (8)	0.307 (5)	2.6 (16)
H(142)	0.3276 (12)	0.129 (4)	0.447 (3)	7.1 (10)	H(181)	0.5060 (44)	0.860 (15)	0.145 (9)	8.0 (39)
H(143)	0.1355 (11)	0.280 (4)	0.469 (2)	6.3 (9)	H(182)	0.5215 (61)	0.902 (19)	0.274 (16)	9.8 (75)
H(151)	0.3044 (13)	0.958 (5)	0.247 (3)	8.7 (10)					

(B) $[Ni(2,3\text{-mmbpN})H_2O]$

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	0.24517 (4)	0.01915 (3)	0.03342 (3)	1.788 (9)	1.747 (7)	8.11 (3)	0.464 (7)	0.06 (1)	1.16 (1)
O(1)	0.3851 (2)	0.1228 (1)	0.0152 (1)	1.84 (5)	2.11 (4)	12.0 (2)	0.16 (4)	−0.54 (9)	2.28 (7)
O(1′)	0.1266 (2)	0.1470 (1)	0.0789 (1)	1.85 (5)	2.03 (4)	9.8 (2)	0.54 (4)	−0.71 (9)	0.97 (7)
O(2)	0.0767 (2)	−0.0808 (2)	0.0628 (2)	1.83 (5)	2.97 (5)	13.4 (2)	−0.00 (5)	−0.74 (10)	2.74 (8)
N(1)	0.2111 (2)	−0.0495 (2)	−0.1411 (2)	1.91 (6)	1.55 (5)	9.2 (2)	0.10 (5)	0.4 (1)	1.37 (8)
N(1′)	0.2977 (2)	0.0850 (2)	0.2036 (2)	1.99 (6)	2.07 (5)	8.8 (2)	0.64 (5)	−0.2 (1)	1.29 (9)
N(3)	0.3498 (2)	−0.1215 (2)	0.0134 (2)	2.13 (7)	1.46 (5)	9.3 (2)	0.27 (5)	0.0 (1)	1.40 (8)
C(1)	0.2658 (3)	0.1431 (2)	−0.1313 (2)	1.72 (8)	1.69 (6)	11.2 (3)	0.18 (6)	0.0 (1)	1.7 (1)
C(2)	0.3456 (3)	0.1893 (2)	−0.0299 (2)	1.58 (7)	1.93 (6)	10.9 (3)	0.23 (6)	0.4 (1)	1.6 (1)
C(3)	0.3826 (3)	0.3123 (2)	0.0201 (3)	2.27 (9)	1.98 (7)	13.5 (4)	−0.04 (7)	−1.0 (2)	1.4 (1)
C(4)	0.3430 (3)	0.3853 (2)	−0.0234 (3)	3.27 (11)	1.52 (7)	17.5 (4)	−0.10 (7)	−0.5 (2)	1.7 (1)
C(5)	0.2643 (3)	0.3409 (2)	−0.1214 (3)	3.19 (10)	1.96 (7)	18.0 (4)	0.23 (7)	−1.2 (2)	2.8 (1)
C(6)	0.2301 (3)	0.2213 (2)	−0.1733 (3)	2.77 (9)	2.12 (7)	13.7 (4)	0.03 (7)	−1.4 (2)	2.4 (1)
C(7)	0.2222 (3)	0.0158 (2)	−0.1927 (2)	1.56 (7)	1.91 (6)	9.8 (3)	0.32 (6)	0.4 (1)	1.7 (1)
C(8)	0.1947 (3)	−0.0337 (2)	−0.3195 (2)	2.34 (8)	1.59 (6)	9.5 (3)	0.20 (6)	−0.1 (1)	1.7 (1)
C(9)	0.0748 (3)	−0.0720 (3)	−0.3680 (2)	2.16 (9)	2.77 (8)	9.8 (3)	0.44 (7)	0.5 (1)	1.7 (1)
C(10)	0.0523 (3)	−0.1173 (3)	−0.4844 (3)	2.28 (9)	2.96 (8)	12.2 (4)	0.33 (7)	−0.8 (2)	2.0 (1)
C(11)	0.1460 (3)	−0.1286 (2)	−0.5566 (2)	3.07 (10)	2.50 (7)	10.2 (3)	0.59 (7)	0.1 (2)	2.6 (1)
C(12)	0.2643 (3)	−0.0909 (3)	−0.5082 (2)	3.04 (10)	3.52 (8)	11.7 (3)	0.45 (8)	1.4 (2)	3.6 (1)
C(13)	0.2887 (3)	−0.0433 (3)	−0.3917 (2)	2.35 (9)	2.93 (8)	11.9 (3)	−0.14 (7)	−0.2 (2)	2.9 (1)
C(16)	0.1813 (3)	−0.1785 (2)	−0.2054 (2)	2.90 (9)	1.65 (6)	8.5 (3)	−0.19 (7)	−0.1 (1)	1.2 (1)
C(17)	0.2833 (3)	−0.2479 (2)	−0.1900 (2)	2.77 (9)	1.59 (7)	11.5 (4)	0.18 (7)	0.9 (2)	0.9 (1)
C(18)	0.2976 (3)	−0.2413 (2)	−0.0728 (2)	2.36 (9)	1.69 (6)	13.8 (4)	0.47 (6)	−0.2 (2)	1.9 (1)
C(14)	0.2197 (5)	0.4217 (3)	−0.1684 (4)	6.92 (17)	2.29 (8)	27.7 (6)	0.15 (10)	−4.8 (3)	4.2 (1)
C(15)	0.1202 (4)	−0.1831 (3)	−0.6841 (3)	4.56 (14)	5.16 (11)	10.8 (4)	0.91 (11)	0.0 (2)	3.5 (1)
C(1′)	0.2049 (3)	0.2738 (2)	0.2745 (2)	1.73 (7)	1.68 (6)	8.8 (3)	0.27 (6)	0.3 (1)	1.1 (1)
C(2′)	0.1395 (3)	0.2508 (2)	0.1708 (2)	1.51 (7)	1.68 (6)	10.7 (3)	0.13 (6)	0.3 (1)	1.3 (1)
C(3′)	0.0809 (3)	0.3462 (2)	0.1681 (2)	2.19 (8)	2.11 (7)	13.4 (4)	0.33 (6)	−0.6 (2)	2.0 (1)
C(4′)	0.0768 (3)	0.4529 (2)	0.2638 (3)	2.51 (9)	1.77 (6)	18.8 (4)	0.53 (6)	0.0 (2)	2.4 (1)
C(5′)	0.1321 (3)	0.4736 (2)	0.3684 (3)	2.42 (9)	1.76 (7)	13.6 (4)	0.37 (7)	0.6 (2)	1.0 (1)
C(6′)	0.1949 (3)	0.3846 (2)	0.3703 (2)	2.17 (8)	2.03 (7)	10.0 (3)	0.09 (7)	0.0 (1)	1.3 (1)
C(7′)	0.2850 (3)	0.1897 (2)	0.2862 (2)	1.71 (8)	1.89 (6)	8.2 (3)	0.01 (6)	0.1 (1)	1.5 (1)
C(8′)	0.3595 (3)	0.2338 (2)	0.3973 (2)	2.06 (8)	1.92 (6)	8.6 (3)	0.22 (6)	0.2 (1)	1.3 (1)

Table III. (*continued*)

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(9′)	0.3275 (3)	0.1955 (3)	0.4773 (2)	3.12 (11)	2.75 (8)	11.2 (3)	−0.57 (8)	−0.6 (2)	2.3 (1)
C(10′)	0.3963 (4)	0.2380 (3)	0.5803 (3)	4.71 (13)	3.48 (9)	9.4 (3)	−0.16 (9)	−0.4 (2)	2.8 (1)
C(11′)	0.4965 (3)	0.3198 (3)	0.6067 (3)	3.73 (11)	2.87 (9)	10.3 (4)	0.49 (8)	−1.3 (2)	1.1 (1)
C(12′)	0.5292 (3)	0.3571 (3)	0.5262 (3)	2.47 (10)	2.59 (8)	15.4 (4)	−0.37 (8)	−1.5 (2)	1.3 (1)
C(13′)	0.4620 (3)	0.3148 (2)	0.4232 (2)	2.34 (9)	2.55 (7)	11.9 (3)	−0.17 (7)	−0.1 (2)	2.5 (1)
C(16′)	0.3909 (3)	0.0106 (2)	0.2165 (2)	2.55 (9)	2.63 (7)	10.7 (3)	0.75 (7)	−0.6 (1)	2.1 (1)
C(17′)	0.3581 (3)	−0.1163 (2)	0.1278 (2)	2.09 (8)	2.20 (7)	12.6 (3)	0.71 (6)	0.4 (1)	2.4 (1)
C(14′)	0.1227 (4)	0.5902 (3)	0.4757 (3)	4.11 (12)	2.13 (8)	17.5 (5)	0.85 (9)	1.0 (2)	0.6 (2)
C(15′)	0.5746 (5)	0.3668 (4)	0.7189 (3)	6.79 (18)	4.49 (13)	12.9 (5)	−0.02 (13)	−4.1 (2)	1.3 (2)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
H(3)	0.439 (3)	0.342 (2)	0.087 (2)	4.5 (7)	H(181)	0.351 (3)	−0.300 (2)	−0.074 (2)	3.8 (7)
H(4)	0.370 (3)	0.471 (2)	0.014 (2)	4.6 (7)	H(182)	0.217 (2)	−0.259 (2)	−0.050 (2)	3.5 (6)
H(6)	0.177 (3)	0.190 (2)	−0.234 (2)	4.3 (7)	H(3′)	0.043 (3)	0.331 (2)	0.092 (2)	4.8 (7)
H(9)	0.015 (3)	−0.069 (2)	−0.325 (2)	4.0 (7)	H(4′)	0.036 (3)	0.514 (2)	0.256 (2)	5.3 (8)
H(10)	−0.033 (2)	−0.145 (2)	−0.511 (2)	4.0 (7)	H(6′)	0.239 (3)	0.399 (2)	0.437 (2)	3.8 (7)
H(12)	0.328 (3)	−0.102 (2)	−0.554 (2)	5.0 (8)	H(9′)	0.257 (3)	0.136 (2)	0.457 (2)	4.6 (7)
H(13)	0.373 (3)	−0.014 (2)	−0.359 (2)	4.9 (7)	H(10′)	0.371 (3)	0.214 (2)	0.634 (2)	6.6 (8)
H(161)	0.102 (3)	−0.202 (2)	−0.174 (2)	4.3 (7)	H(12′)	0.595 (3)	0.417 (2)	0.545 (2)	4.9 (8)
H(162)	0.168 (3)	−0.202 (2)	−0.283 (2)	4.6 (7)	H(13′)	0.483 (3)	0.344 (2)	0.371 (2)	4.2 (7)
H(171)	0.365 (3)	−0.221 (2)	−0.209 (2)	4.6 (7)	H(163)	0.471 (3)	0.040 (2)	0.201 (2)	4.7 (7)
H(172)	0.267 (3)	−0.333 (2)	−0.244 (2)	4.6 (7)	H(164)	0.392 (3)	0.015 (2)	0.292 (2)	5.0 (8)

[a] The form of the anisotropic thermal parameter is $\exp[-(B_{11}a^{2*}h^2 + B_{22}b^{2*}k^2 + B_{33}c^{2*}l^2)/4 + (B_{12}a^*b^*hk + B_{13}a^*c^*hl + B_{23}b^*c^*kl)/2]$.

were considered insignificant if intensities registered less than 5 counts above background on a rapid prescan, such reflections being rejected automatically by the computer.

The intensities of four standard reflections, monitored for each crystal at 100 reflection intervals, showed no greater fluctuations during the data collection from those expected from Poisson statistics. The raw intensity data were corrected for Lorentz–polarization effects (including the polarization effect of the crystal monochromator) and then for absorption. After averaging of the intensities of equivalent reflections, the data were reduced to 2241 independent intensities for [Cu(2,3-mmbpN)]·2H_2O and 3614 for [Ni(2,3-mmbpN)H_2O], of which 1718 and 3118, respectively, had $F_o^2 > 3\sigma(F_o^2)$ and were considered "observed", where $\sigma(F_o^2)$ was estimated from counting statistics.[11] All "observed" data were used in the final refinement of the structural parameters.

Determination and Refinement of the Structures. Copper. The structure was solved by use of the MULTAN74[12] program series, using 180 E values. All but one of the nonhydrogen atoms in the parent molecule were located from the solution with the highest figure of merit, and subsequent refinement and a three-dimensional Fourier synthesis revealed the location of the remaining atom and the unique water molecule.

Nickel. The nickel atom was located from a three-dimensional Patterson synthesis, using all data. The intensity data were phased sufficiently well by these positional coordinates to permit location of the remaining nonhydrogen atoms from Fourier difference functions.

Full-matrix least-squares refinement was based on F, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The weights w were then taken as $[2F_o/\sigma(F_o^2)]^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The atomic scattering factors for nonhydrogen atoms were taken from Cromer and Waber[13] and those for hydrogen from Stewart et al.[14] The effects of anomalous dispersion were included in F_c for all nonhydrogen atoms using the values of Cromer and Ibers[15] for $\Delta f'$ and $\Delta f''$. Agreement factors are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Anisotropic temperature factors were introduced for all nonhydrogen atoms. Further Fourier difference functions permitted location of the hydrogen atoms, which were included in the refinement for three cycles of least squares and then held fixed. The models converged with $R = 3.5\%$, $R_w = 4.0\%$ for [Cu(2,3-mmbpN)]·2H_2O and $R = 3.1\%$, $R_w = 3.6\%$ for [Ni(2,3-mmbpN)H_2O]. The copper atom in [Cu(2,3-mmbpN)]·2H_2O lies on a twofold axis, so that only half the molecule is crystallographically independent, the other half being determined by the axial symmetry. Strictly, this should be chemically impossible owing to the asymmetry of the alkyl chains between the nitrogen atoms. The molecule achieves twofold symmetry with 50% occupancy of an ethylene chain and 50% occupancy of a trimethylene chain between the amine atom on the twofold axis and the imino nitrogen near the axis. A parallel calculation of the structure solution was carried out in the acentric space group *Cc*, but the twofold disorder of the methylene chains persisted and the model produced no significant improvement[16,17] in correlation in either of the two possible absolute configurations. Thus the acentric model was abandoned in favor of space group *C*2/*c*.

A structure factor calculation with all observed and unobserved reflections included (no refinement) gave $R = 4.3$ and 4.0% for the two complexes respectively; on this basis it was decided that careful measurement of the unobserved reflections, rejected automatically during the data collection, would not be warranted. A final Fourier difference function was featureless. The error in an observation of unit weight was 1.75 and 1.49 for the two complexes, respectively. Tables of the observed and calculated structure factors are available.[18] The principal programs used were as previously described.[6]

Results and Discussion

Final positional and thermal parameters for [Cu(2,3-mmbpN)]·2H_2O and [Ni(2,3-mmbpN)H_2O] are given in Table III. Tables IV and V contain the bond lengths and angles. The digits in parentheses in the tables are the estimated standard deviations in the least significant figures quoted and were derived from the inverse matrix in the course of least-squares refinement calculations. Figures 1 and 2 are views of [Cu(2,3-mmbpN)]·2H_2O and [Ni(2,3-mmbpN)H_2O], respectively.

The crystallographic twofold symmetry in the copper complex requires statistical disorder in the $-(CH_2)_2-$ and $-(CH_2)_3-$ chains with equal distribution on either side of the twofold axis. The two different types of alkyl chains are shown on the two sides of the amino nitrogen N(2) in the figures, since in any given molecule only one such alkyl chain, and not an average of the two types, must exist between the pair of nitrogen atoms. The nickel complex requires no such disorder.

Although both complexes consist of neutral molecules, they are dramatically different in that the nickel complex has achieved octahedral coordination about the metal atom. Figures 3 and 4 show the coordination about the copper and nickel atoms in the two complexes and give bond distances and angles.

The environment about the copper atom in [Cu(2,3-mmbpN)]·2H_2O approaches trigonal bipyramidal more closely than it does in any other of the five-coordinate Schiff base complexes we have studied. In particular, the Cu–N(2) bond, at 2.077 Å, is only 0.062 Å longer than the Cu–O(1) bonds and 0.104 Å longer than the Cu–N(1) bonds. Also, the O(1)–Cu–O(1′) angle is 121.7°—very close to the ideal trigonal angle of 120°. These distances and angles should be

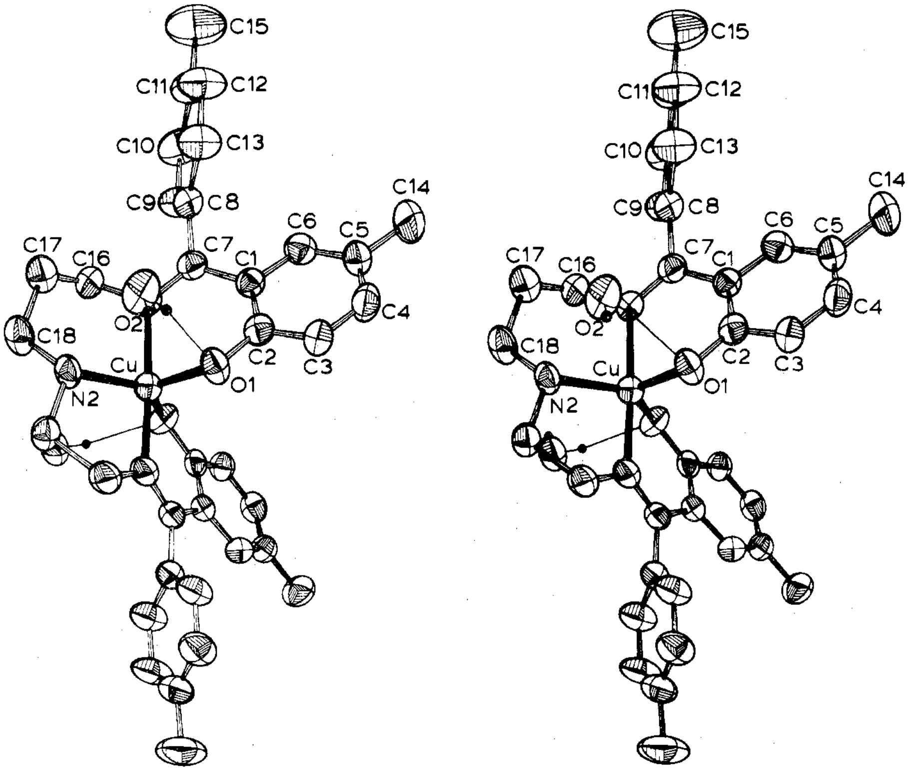


Figure 1. Stereoview of [Cu(2,3-mmbpN)]·$2H_2O$.

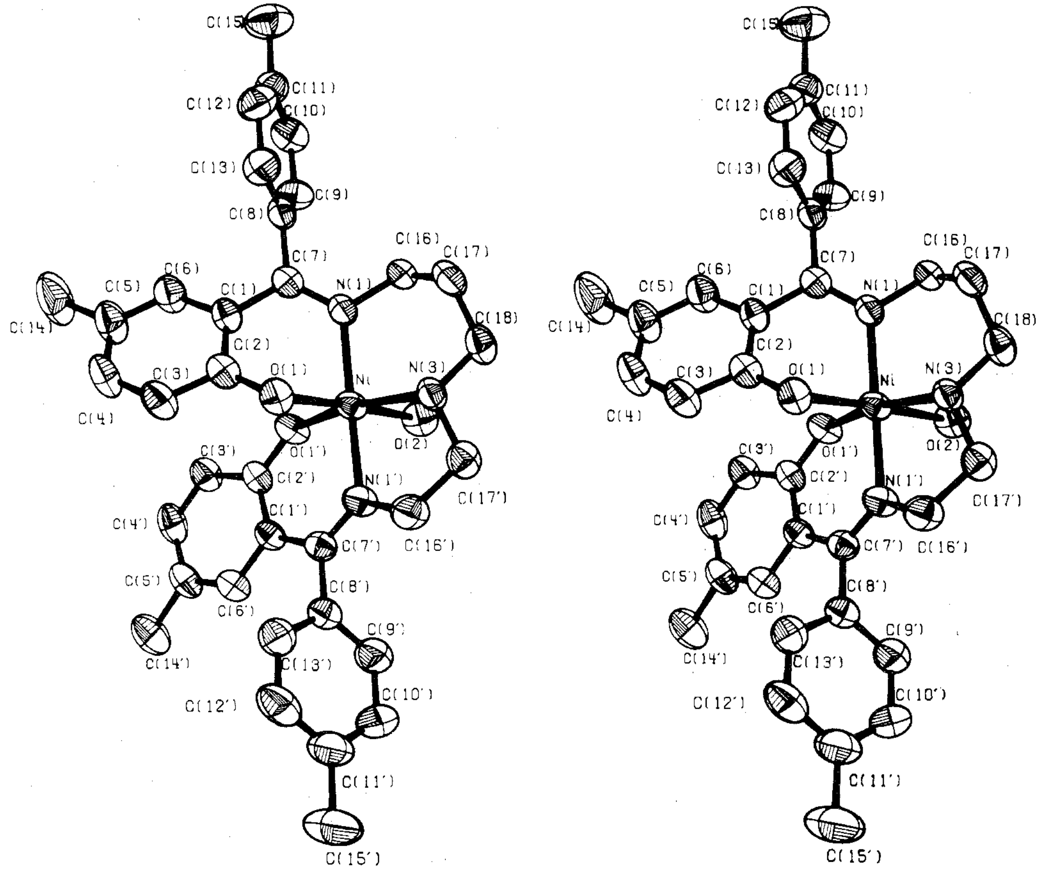


Figure 2. Stereoview of [Ni(2,3-mmbpN)H_2O].

compared with those of [Cu(3,3-mbpN)][5] (where δ_1, the difference between Cu–N(3) and Cu–O(1), is 0.43 Å and δ_2, the difference between Cu–N(3) and Cu–N(1), is 0.40 Å, and the O–Cu–O′ angle is 152.2°) and [Cu(3,4-cbpN)][10] (where δ_1 is 0.249 Å, δ_2 is 0.285 Å and O–Cu–O′ is 173.7°). It seems most probable that the short bond length and the smaller than expected bond angle for [Cu(2,3-mmbpN)]·$2H_2O$ are directly due to the steric requirements of the ligand, while the longer

Table IV

Bond Lengths (Å) for [M(2,3-mmbp)]

	M = Cu	M = Ni		M = Cu	M = Ni
M–O(1)	2.015 (2)	2.023 (2)	C(10)–C(11)	1.380 (4)	1.373 (4)
M–O(1′)	2.015 (2)	2.014 (2)	C(11)–C(12)	1.368 (4)	1.373 (4)
M–O(2)		2.286 (2)			
M–N(1)	1.973 (2)	2.067 (2)	C(11)–C(15)	1.513 (4)	1.508 (4)
M–N(1′)	1.973 (2)	2.054 (2)	C(12)–C(13)	1.382 (4)	1.380 (4)
M–N(2)	2.077 (4)	2.091 (2)	C(16)–C(17)	1.38 (1)	1.522 (4)
O(1)–C(2)	1.327 (3)	1.316 (3)	C(17)–C(18)	1.533 (8)	1.508 (4)
N(1)–C(7)	1.296 (3)	1.285 (3)	O(1′)–C(2′)		1.318 (3)
N(1)–C(16)	1.481 (3)	1.465 (3)	N(1′)–C(7′)		1.296 (3)
N(2)–C(17)	2.152 (9)		N(1′)–C(16′)		1.482 (3)
N(2)–C(18)	1.502 (7)	1.485 (3)	C(1′)–C(2′)		1.422 (3)
N(2)–C(17′)	1.470 (9)	1.475 (3)	C(1′)–C(6′)		1.410 (3)
C(1)–C(2)	1.416 (3)	1.430 (3)	C(1′)–C(7′)		1.474 (3)
C(1)–C(6)	1.423 (3)	1.402 (3)	C(2′)–C(3′)		1.413 (3)
C(1)–C(7)	1.471 (3)	1.473 (3)	C(3′)–C(4′)		1.371 (4)
C(2)–C(3)	1.404 (3)	1.411 (3)	C(4′)–C(5′)		1.392 (4)
C(3)–C(4)	1.367 (3)	1.371 (4)	C(5′)–C(6′)		1.362 (3)
C(4)–C(5)	1.381 (3)	1.393 (4)	C(5′)–C(14′)		1.523 (4)
C(5)–C(6)	1.375 (3)	1.366 (4)	C(7′)–C(8′)		1.500 (3)
C(5)–C(14)	1.510 (4)	1.511 (4)	C(8′)–C(9′)		1.382 (4)
C(7)–C(8)	1.501 (3)	1.507 (3)	C(8′)–C(13′)		1.382 (4)
C(8)–C(9)	1.376 (4)	1.390 (3)	C(9′)–C(10′)		1.388 (4)
C(8)–C(13)	1.380 (4)	1.379 (4)	C(10′)–C(11′)		1.370 (4)
C(9)–C(10)	1.381 (4)	1.380 (4)	C(11′)–C(12′)		1.380 (4)
C(12′)–C(13′)		1.379 (4)	C(11′)–C(15′)		1.527 (4)
C(16′)–C(17′)		1.508 (4)			

Hydrogen Bonded Contacts (Å)

M = Cu			M = Ni		
O(1)	O(2)	2.836 (2)	O(1′)	O(2)	2.68 (2)
O(1)	O(2)	2.862 (2)	H(02)	O(2)	0.74 (2)
H(201)	O(2)	0.81 (1)	H(02)	O(1′)	1.81 (1)
H(201)	O(1)	2.06 (2)			
H(202)	O(2)	0.83 (1)			
H(202)	O(1)	2.01 (1)			

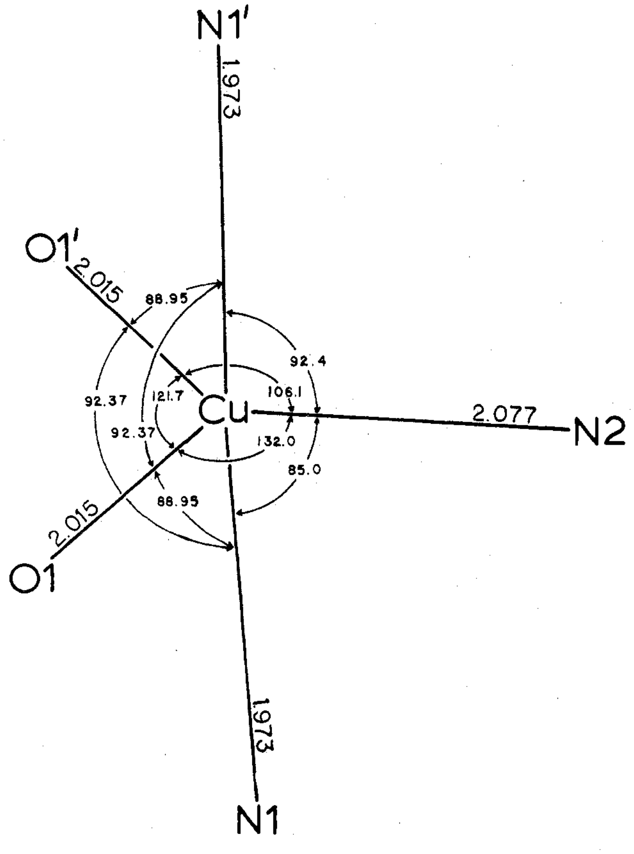


Figure 3. Coordination about the copper atom in [Cu(2,3-mmbpN)]·$2H_2O$.

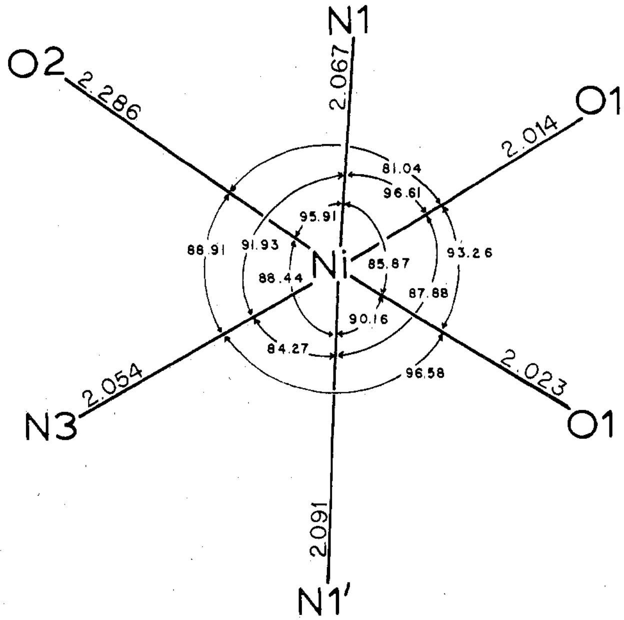


Figure 4. Coordination about the nickel atom in [Ni(2,3-mmbpN)H_2O].

bond and greater O–Cu–O′ angle of the other two complexes reflect the coordination preference of the Cu(II) ion better. This preference for SP stereochemistry is also confirmed by the structures of [Cu(3,3-cbpS)][9] and [Cu(3,3-cbpO)],[10] where the Cu–X bond is significantly longer than the Cu–N bond of the analogous [Cu(3,3-mbpN)]. Despite the forced trigonal-bipyramidal stereochemistry, however, both the oxygen

Table V. Bond Angles (deg) for [M(2,3-mmbp)]

	M = Cu	M = Ni
O(1)–M–O(1′)	121.7 (1)	93.26 (7)
O(1)–M–N(1)	88.95 (7)	85.87 (7)
O(1)–M–N(1′)	92.37 (7)	90.16 (8)
O(1)–M–N(2)	132.0 (1)	96.58 (7)
O(1′)–M–N(1)	92.37 (7)	96.61 (7)
O(1′)–M–N(1′)	88.95 (7)	87.88 (7)
O(1′)–M–N(2)	106.1 (1)	167.41 (8)
N(1)–M–N(1′)	177.3 (1)	174.16 (8)
N(1)–M–N(2)	85.0 (1)	91.93 (8)
N(1′)–M–N(2)	92.4 (1)	84.27 (8)
M–O(1)–C(2)	120.4 (1)	112.1 (1)
M–O(1′)–C(2′)		125.8 (1)
M–N(1)–C(7)	126.3 (1)	122.1 (2)
M–N(1)–C(16)	111.5 (2)	117.0 (2)
C(7)–N(1)–C(16)	122.2 (2)	120.8 (2)
M–N(1′)–C(7′)		128.5 (2)
M–N(1′)–C(16′)		109.0 (2)
C(7′)–N(1′)–C(16′)		119.9 (2)
M–N(2)–C(17)	103.8 (4)	
M–N(2)–C(18)	116.4 (3)	115.3 (1)
M–N(2)–C(17)	107.7 (4)	104.6 (1)
C(17)–N(2)–C(18)	113.9 (5)	
C(18)–N(2)–C(17)	108.2 (6)	110.4 (2)
C(2)–C(1)–C(6)	117.8 (2)	118.8 (2)
N(1)–C(16)–C(17)	117.2 (4)	112.0 (2)
N(1)–C(16)–C(17′)	102.9 (4)	
C(16)–C(17)–C(18)	116.7 (7)	115.3 (2)
N(2)–C(18)–C(17)	111.2 (6)	111.6 (2)
N(2)–C(17′)–C(16)	106.8 (6)	
C(2′)–C(1′)–C(6′)		117.9 (2)
C(2′)–C(1′)–C(7′)		123.5 (2)
C(6′)–C(1′)–C(7′)		118.5 (2)
O(1′)–C(2′)–C(1′)		125.0 (2)
O(1′)–C(2′)–C(3′)		118.0 (2)
C(1′)–C(2′)–C(3′)		117.0 (2)
C(2′)–C(3′)–C(4′)		121.9 (3)
C(3′)–C(4′)–C(5′)		121.6 (3)
C(4′)–C(5′)–C(6′)		116.9 (2)
C(4′)–C(5′)–C(14′)		121.6 (3)
C(6′)–C(5′)–C(14′)		121.5 (3)
C(1′)–C(6′)–C(5′)		124.3 (3)
N(1′)–C(7′)–C(1′)		122.8 (2)
N(1′)–C(7′)–C(8′)		120.4 (2)
C(1′)–C(7′)–C(8′)		116.7 (2)
C(7′)–C(8′)–C(9′)		121.1 (2)
C(7′)–C(8′)–C(13′)		121.0 (2)
C(9′)–C(8′)–C(13′)		117.8 (2)
C(8′)–C(9′)–C(10′)		120.6 (3)
C(2)–C(1)–C(7)	123.5 (2)	121.6 (2)
C(6)–C(1)–C(7)	118.6 (2)	119.7 (2)
O(1)–C(2)–C(1)	123.5 (2)	123.2 (2)
O(1)–C(2)–C(3)	118.9 (2)	120.5 (2)
C(1)–C(2)–C(3)	117.6 (2)	116.3 (2)
C(2)–C(3)–C(4)	122.3 (2)	122.6 (2)
C(3)–C(4)–C(5)	121.5 (2)	121.3 (2)
C(4)–C(5)–C(6)	117.5 (2)	117.2 (3)
C(4)–C(5)–C(14)	120.9 (2)	121.2 (3)
C(6)–C(5)–C(14)	121.6 (2)	121.7 (3)
C(1)–C(6)–C(5)	123.2 (2)	123.9 (3)
N(1)–C(7)–C(1)		121.6 (2)
N(1)–C(7)–C(8)		122.1 (2)
C(1)–C(7)–C(8)	116.1 (2)	116.3 (2)
C(7)–C(8)–C(9)	121.3 (2)	121.6 (2)
C(7)–C(8)–C(13)	120.6 (2)	120.7 (2)
C(9)–C(8)–C(13)	118.0 (2)	117.7 (2)
C(8)–C(9)–C(10)	120.2 (3)	120.4 (3)
C(9)–C(10)–C(11)	122.2 (3)	122.0 (3)
C(10)–C(11)–C(12)	117.0 (3)	117.4 (3)
C(10)–C(11)–C(15)	121.5 (3)	121.2 (3)
C(12)–C(11)–C(15)	121.5 (3)	121.5 (3)
C(11)–C(12)–C(13)	121.6 (3)	121.6 (3)
C(8)–C(13)–C(12)	121.0 (3)	121.0 (3)
C(9′)–C(10′)–C(11′)		121.4 (3)
C(10′)–C(11′)–C(12′)		117.9 (3)
C(10′)–C(11′)–C(15′)		122.4 (3)
C(12′)–C(11′)–C(15′)		119.7 (3)
C(11′)–C(12′)–C(13′)		121.1 (3)
C(8′)–C(13′)–C(12′)		121.1 (3)
N(1′)–C(16′)–C(17′)		108.0 (2)
N(2)–C(17′)–C(16′)		109.5 (2)
O(1)–M–O(2)		174.17 (7)
O(1′)–M–O(2)		81.04 (7)
O(2)–M–N(1)		95.93 (7)
O(2)–M–N(1′)		88.44 (7)
O(2)–M–N(2)		88.91 (7)

donor atoms and the imine nitrogen atoms are trans, as has been commonly found for both the five- and six-coordinate complexes of these pentadentate Schiff base ligands.

The average C–H distances were found to be 0.95 Å and 0.98 Å, respectively, for [Ni(2,3-mmbpN)] and [Cu(2,3-mmbpN)], in good agreement with accurate literature determinations for such bond lengths.[19,20]

The nickel atom coordination in [Ni(2,3-mmbpN)H_2O] is unusual in that it represents the first case of (a) coordination of water to one of these Schiff base complexes and (b) cis geometry for the ligand oxygen atoms in a nickel(II) complex. While nickel(II) shows a much greater preference for octahedral coordination than does copper(II), as evidenced by the formation of adducts with heterocyclic bases,[7] no previous complex has had water coordinated to the metal atom. Further, the cis geometry of the ligand oxygens has been previously observed only for Co(III) complexes, such as [Co(3,3-cbpS)NCS][10] and [Co(3,3-sal)O]$_2$·$CH_3C_6H_5$[21] and not for complexes with uncharged ligands. The reason for the cis coordination *in this case* is considered to be the steric requirements of the ligand. In the copper complex, which will not accept a sixth ligand atom, the Schiff base ligand forces the metal into trigonal-bipyramidal coordination, with all metal–ligand distances approximately equal; while in the nickel case, the ligand steric requirements can presumably best be met by approximately square-pyramidal coordination of the Schiff base, the sixth position being filled by water.

Each complex exhibits intermolecular hydrogen bonding via the hydrogen atoms of H_2O molecules. In [Ni(2,3-mmbpN)H_2O], one hydrogen atom, H(O(2)), of the coordinated water molecule is hydrogen bonded to one of the donor oxygen atoms, O(1′), of the ligand of the adjacent molecule. Taking this hydrogen bonding into account, we may view the complex as a weakly linked dimer, [Ni(2,3-mmbpN)H_2O]$_2$. In {[Cu(2,3-mmbpN)]·$2H_2O$}$_\infty$ the water molecules link ligand oxygen atoms of adjacent molecules to one another to form infinite polymeric chains.

The optical spectra of the various nickel complexes are usually similar in the solid state and in dichloromethane solution, indicating that similar structures are likely in both states. The spectra change markedly in pyridine solution, presumably due to chemical reaction to form pyridine adducts. The spectra of the copper complexes show little dependence on the medium. This behavior parallels the failure to form pyridine adducts in related copper complexes.[7]

The powder ESR spectrum of {[Cu(2,3-mmbpN)]·$2H_2O$}$_\infty$ was very broad and anisotropic, with $g \simeq 2.10$. The powder spectrum of the analogous [Cu(2,3-cbpN)] was essentially identical, with $g \simeq 2.09$. The solution spectrum ($CHCl_3$) showed $g^* = 2.122$ and $A^* = 64$ G, while the spectrum in frozen chloroform solution had $g_{\parallel} = 2.214$ and $A_{\parallel} = 184$ G, with $g_{\perp} \simeq 2.030$. No hyperfine $A_{\perp}$ was observed, and a calculation shows that it would be only 4 G. The spectra of [Cu(2,3-cbpN)] are again similar.

Registry No. Cu(2,3-mmbpN)·$2H_2O$, 68876-55-1; Ni(2,3-mmbpN)·H_2O, 68876-56-2; Cu(2,3-cbpN), 68876-57-3; Ni(2,3-cbpN), 68876-58-4; Cu(2,3-mbpN), 68876-59-5; Ni(2,3-mbpN), 68876-60-8; Cu(3,4-cbpN), 68876-61-9; Ni(3,4-cbpN), 68876-62-0; Cu(3,3-cbpN), 56861-98-4; Ni(3,3-cbpN), 56861-99-5; Cu(3,3-mbpN), 56811-15-5; Ni(3,3-mbpN), 56811-16-6; Hmnbp, 26880-95-5.

Supplementary Material Available: Listings of structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

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Contribution from The Evans Chemical Laboratory,
The Ohio State University, Columbus, Ohio 43210

Synthesis and Structure of the Acetone Adduct of the Macrocyclic Complex (Tetrabenzo[*b,f,j,n*][1,5,9,13]tetraazacyclohexadecine)nickel(II)

B. KAMENAR,[1] B. KAITNER,[1] V. KATOVIC,[1,2] and D. H. BUSCH*[2]

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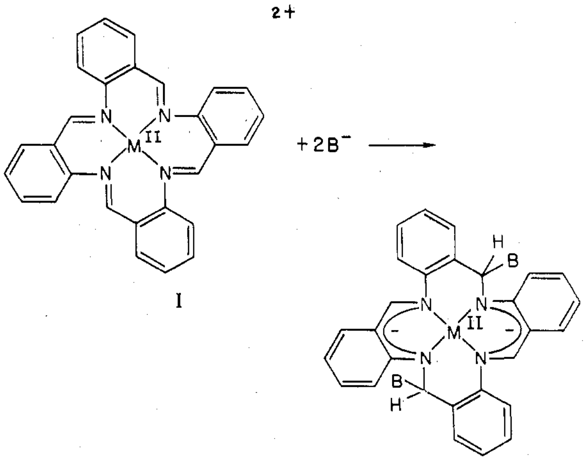
New derivatives of the macrocyclic ligand TAAB, tetrabenzo[*b,f,j,n*][1,3,5,9]tetraazacyclohexadecine, have been prepared in which the substituents are bound by C–C linkages. They are produced by the displacement of diethylamide groups from the azomethine carbon atoms of TAAB with the enolate of acetone. The new compounds have the composition $M^{II}(TAAB)(CH_2COCH_3)_2$. An X-ray structure determination (Ni^{2+} complex) shows the crystals to be triclinic, $\rho_o = 1.37$ g cm^{-3} (flotation), $\rho_c = 1.363$ g cm^{-3}, space group $P\bar{1}$, Mo Kα, λ 0.7107 Å. The structure refined to $R = 0.061$ and $R_w = 0.081$. The two enolate groups have added to trans imine-carbon atoms but the substituents are on the same side of the approximate NiN_4 plane. The overall conformation of the macrocycle is saddle shaped and bond distances confirm the general electronic structures assigned to this class of nucleophilic ligand adducts of TAAB.

Introduction

The incorporation of substituent groups on macrocyclic ligands is of considerable interest because of the possibility of using such materials either as models for biological systems or as precursors for the development of such models.[3] Examples are especially abundant in the area of porphyrin chemistry, e.g., the picket fence porphyrins,[4] capped porphyrin,[5] and strapped porphyrins.[6,7] Earlier studies have shown that the nickel(II) and copper(II) complexes of the anhydrotetramer of *o*-aminobenzaldehyde[8] will add nucleophiles to two of the azomethine groups, thereby forming neutral complexes,[9-11] structures I and II, eq 1. Alkoxides and amides have been found to react in this manner and the first examples of "strapped" macrocyclic complexes were the adducts of $Cu(TAAB)^{2+}$ and $Ni(TAAB)^{2+}$ with $RN(CH_2CH_2O^-)_2$, R = H, CH_3, and $S(CH_2CH_2O^-)_2$.[10,11] The results presented here are significant in two general ways. First, examples of adducts are reported in which the substituent is attached to the ring through carbon–carbon bonds. This opens the possibility of producing acid-stable derivatives and should greatly extend the applicability of TAAB complexes to model systems. Secondly, an X-ray crystal structure determination on the bis(acetone) adduct of $Ni(TAAB)^{2+}$ establishes the detailed structures of this class of compounds.



I

II

(1)

Experimental Section

Preparation of $Ni(TAAB)(CH_2COCH_3)_2$. This compound was prepared by the reaction of the diethylamine adduct $Ni(TAAB)(NEt_2)_2$ with acetone. The latter was prepared by the method previously reported.[11] One gram of $Ni(TAAB)(NEt_2)_2$ was dissolved in 200 mL of acetone. A few milliliters of water was added and the

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