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# Octahedral Complexes Derived from a Hexaaza-18-crown-6 Ligand: 3,6,12,15-Tetramethyl-18{[N(2,6)-pyridino,N-1.2.1]$_2$-coronand-6}

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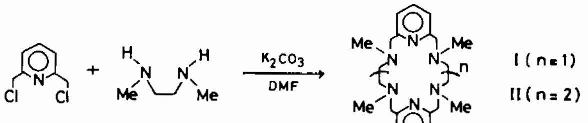
Over the years, many research endeavors have been directed towards the design and synthesis of macrocyclic ligands which are capable of selective metal ion complexation [1]. Crown ethers and cryptands that encapsulate alkali metal ions are common; however, hexaaza analogs of crown ethers capable of coordinatively saturating the relatively 'softer' transition metal ions are less numerous [2], and structurally well-characterized complexes of these ligands are rare. The inability to transform macrocyclic imines to N-alkyl amines has prevented application of Schiff base chemistry to the synthesis of N-alkyl hexaaza analogs of crown ethers capable of a continuous octahedral wrap around transition metals. Model building indicated that I should be the smallest non-imino macrocycle with subheterocyclic rings capable of encapsulating a transition metal ion in an octahedral wrap. We herein report a simple procedure for the synthesis of I, preparation of Co(II) and Cu(II) complex-salts, and the definitive characterization of these complexes by X-ray diffraction.



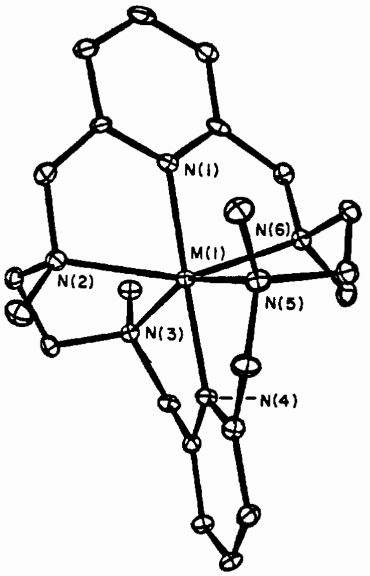
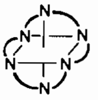


Fig. 1. Structure of the complexes III and IV. Distances and angles in the coordination sphere for the cobalt {copper} complex are: M(1)–N(1) 2.050(5) {1.987(5)}, M(1)–N(2) 2.234(6) {2.307(6)}, M(1)–N(3) 2.237(5) {2.244(6)}, M(1)–N(4) 2.054(5) {1.983(5)}, M(1)–N(5) 2.225(5) {2.214(6)}, M(1)–N(6) 2.235(5) {2.289(5)} Å. N(1)–M(1)–N(4) 178.4(2) {178.2(2)}, N(1)–M(1)–N(2) 76.8(2) {77.5(2)}, N(1)–M(1)–N(6) 76.7(2) {77.7(2)}, N(4)–M(1)–N(3) 76.6(2) {78.0(2)}, N(4)–M(1)–N(5) 77.1(2) {77.8(2)}, N(2)–M(1)–N(6) 153.5(2) {155.1(2)}, N(3)–M(1)–N(5) 153.7(2)° {155.7(2)°}. The cobalt complex is illustrated.

Ligand I was prepared by the treatment of 2,6-bis(chloromethyl)pyridine (10 mmol) with N,N'-dimethylethylenediamine (10 mmol) in N,N-dimethylformamide [3] (600 ml) with anhydrous $K_2CO_3$ (20 mmol), as base, under high-dilution conditions [4]. Chromatography on alumina afforded I** [3%, m.p. 80–81 °C; $^1$H NMR, $\delta$(ppm): 2.39 (s, N–$CH_3$, 12H), 2.48 (s, N–$CH_2$, 8H), 3.57 (s, Py–$CH_2$, 8H), 7.15 (d, 3,5-PyH, J = 7.6 Hz, 4H), 7.45 (t, 4-PyH, J = 7.6 Hz, 2H); MS: m/e 382 ($M^+$, 24.6), 149 (*100*)], an oily 3:3 macrocycle II** and numerous open-chained products. The use of $Cs_2CO_3$ greatly enhances the formation of desired smaller macrocycles [5].

Treatment of I in methanol with either Co(II) or Cu(II) chloride afforded the green complexes III** [m.p. > 300 °C] and IV** [m.p. > 300 °C], respectively. Two modes of complexation (A or B) are possible for an octahedral host wrap. Examination of CPK models indicated that configuration A was less likely, due to the rigidity imposed by the directed pyridine nitrogen atoms. In order to confirm hexacoordination to a single metal ion and the configuration of complexes III and IV, crystals suitable for X-ray analysis were obtained by slow evaporation of respective methanolic solutions.



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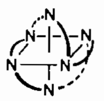

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**Satisfactory analytical (±0.3%) and spectral data were obtained.

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TABLE I. Coordinates for Nonhydrogen Atoms, Co Complex III.

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Co1 | 0.2486(1) | 0.03589(7) | 0.73464(6) |
| Co2 | 0.2732(1) | 0.22860(7) | 0.09918(8) |
| Cl1 | 0.3863(2) | 0.2056(1) | 0.2239(1) |
| Cl2 | 0.4116(2) | 0.2000(1) | −0.0020(1) |
| Cl3 | 0.7188(3) | 0.1423(2) | 0.5951(2) |
| Cl4 | 0.5839(3) | 0.3456(2) | 0.5877(2) |
| N1 | 0.4231(6) | 0.0926(4) | 0.7737(4) |
| N2 | 0.2603(7) | 0.1317(4) | 0.6432(4) |
| N3 | 0.3147(6) | −0.0358(4) | 0.6308(4) |
| N4 | 0.0770(6) | −0.0234(4) | 0.6944(4) |
| N5 | 0.0966(7) | 0.0805(4) | 0.8161(4) |
| N6 | 0.3217(6) | −0.0300(4) | 0.8472(4) |
| C1 | 0.5087(8) | 0.0599(5) | 0.8320(5) |
| C2 | 0.6234(8) | 0.0986(6) | 0.8604(6) |
| C3 | 0.6499(9) | 0.1703(6) | 0.8283(6) |
| C4 | 0.5644(8) | 0.2031(5) | 0.7695(5) |
| C5 | 0.4482(8) | 0.1623(5) | 0.7438(5) |
| C6 | 0.3431(9) | 0.1936(5) | 0.6831(6) |
| C7 | 0.1303(9) | 0.1653(6) | 0.6069(6) |
| C8 | 0.3349(9) | 0.0959(5) | 0.5773(5) |
| C9 | 0.2857(9) | 0.0152(5) | 0.5591(5) |
| C10 | 0.4572(10) | −0.0613(6) | 0.6332(6) |
| C11 | 0.2243(9) | −0.1063(5) | 0.6224(6) |
| C12 | 0.0853(9) | −0.0846(5) | 0.6451(5) |
| C13 | −0.0287(9) | −0.1263(5) | 0.6189(5) |
| C14 | −0.1491(10) | −0.1047(6) | 0.6470(6) |
| C15 | −0.1582(9) | −0.0416(6) | 0.6987(6) |
| C16 | −0.0425(8) | −0.0018(5) | 0.7213(5) |
| C17 | −0.0373(8) | 0.0704(6) | 0.7731(6) |
| C18 | 0.1141(10) | 0.1618(5) | 0.8456(6) |
| C19 | 0.1097(8) | 0.0273(5) | 0.8884(5) |
| C20 | 0.2559(8) | 0.0097(5) | 0.9129(5) |
| C21 | 0.2879(10) | −0.1140(5) | 0.8497(6) |
| C22 | 0.4708(8) | −0.0201(5) | 0.8582(5) |

TABLE II. Coordinates for Nonhydrogen Atoms, Cu Complex IV.

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Cu1 | 0.74878(5) | 0.20120(8) | 0.59292(4) |
| Cu2 | 0.69917(6) | 0.69059(9) | 0.39724(5) |
| Cl1 | 0.6679(2) | 0.7088(2) | 0.5148(1) |
| Cl2 | 0.6061(1) | 0.5401(2) | 0.3507(1) |
| Cl3 | 0.6684(1) | 0.8058(2) | 0.2877(1) |
| Cl4 | 0.1494(1) | 0.2930(2) | 0.5640(1) |
| O1 | 0.1904(5) | 0.2769(7) | 0.3153(4) |
| O2 | 0.0942(5) | 0.4228(7) | 0.1767(5) |
| N1 | 0.6603(3) | 0.1959(5) | 0.4853(3) |
| N2 | 0.8183(4) | 0.0774(5) | 0.5234(3) |
| N3 | 0.8532(4) | 0.3277(5) | 0.5748(4) |
| N4 | 0.8385(4) | 0.2015(5) | 0.6997(3) |
| N5 | 0.6863(4) | 0.0799(5) | 0.6616(3) |
| N6 | 0.6378(3) | 0.3259(5) | 0.6075(3) |
| C1 | 0.5926(4) | 0.2728(6) | 0.4656(4) |
| C2 | 0.5295(4) | 0.2685(7) | 0.3907(4) |
| C3 | 0.5376(4) | 0.1828(7) | 0.3379(4) |
| C4 | 0.6061(5) | 0.1039(7) | 0.3587(4) |
| C5 | 0.6683(4) | 0.1097(7) | 0.4325(4) |
| C6 | 0.7448(5) | 0.0260(8) | 0.4616(4) |
| C7 | 0.8797(6) | −0.0141(8) | 0.5683(5) |
| C8 | 0.8688(5) | 0.1624(7) | 0.4882(4) |
| C9 | 0.9173(5) | 0.2509(8) | 0.5476(4) |
| C10 | 0.8219(6) | 0.4251(8) | 0.5182(5) |
| C11 | 0.8986(5) | 0.3749(8) | 0.6542(6) |
| C12 | 0.9044(5) | 0.2808(7) | 0.7170(5) |
| C13 | 0.9724(6) | 0.2782(9) | 0.7866(5) |
| C14 | 0.9700(6) | 0.1910(10) | 0.8402(5) |
| C15 | 0.9029(5) | 0.1087(8) | 0.8244(4) |
| C16 | 0.8353(5) | 0.1165(7) | 0.7514(4) |
| C17 | 0.7626(5) | 0.0293(7) | 0.7252(4) |
| C18 | 0.6309(6) | −0.0177(8) | 0.6172(6) |
| C19 | 0.6321(5) | 0.1591(7) | 0.6953(5) |
| C20 | 0.5774(5) | 0.2446(7) | 0.6345(4) |
| C21 | 0.6626(6) | 0.4269(8) | 0.6619(4) |
| C22 | 0.5909(5) | 0.3679(6) | 0.5262(4) |

*Crystal Data:* III $[CoC_{22}H_{34}N_6][CoCl_4]$, *FW* = 642.2, monoclinic space group $P2_1/n$, $a = 9.944(3)$, $b = 17.214(4)$, $c = 16.347(4)$ Å, $\beta = 94.32(2)°$, $Z = 4$, $d_c = 1.529$ g cm$^{-3}$, $\mu(MoK_\alpha) = 16.0$ cm$^{-1}$, $R = 0.041$ for 1738 observed data.

*Crystal Data:* IV $[CuC_{22}H_{34}N_6][CuCl_4]\cdot 2H_2O$, *FW* = 687.5, monoclinic space group $P2_1/c$, $a = 15.467(4)$, $b = 11.287(9)$, $c = 17.459(5)$ Å, $\beta = 106.45(2)°$, $Z = 4$, $d_c = 1.562$ g cm$^{-3}$, $\mu(MoK_\alpha) = 19.1$ cm$^{-1}$, $R = 0.037$ for 1827 observed data.

Both complexes have approximate $D_2$ symmetry in the crystal and exist in configuration B, in which the pyridine N atoms occupy the central positions of the meridional span. In complex III, the Co–N(Py) distances [*av.* 2.052(4) Å] are identical and the equatorial Co–N distances [*av.* 2.233(3) Å] are likewise equal (Fig. 1). Distortion from perfect octahedral geometry may be envisioned as a two stage process: 1) bending of the Co–N bonds *cis* to pyridine towards the pyridine, due to the meridional spanning and 2) twisting of the two meridional NNN planes away from a dihedral angle of 90°, due to the chelate rings joining them. The dihedral angle in the Co complex is 79.1°.

The Cu complex IV is more distorted from perfect octahedral geometry than III. The Cu–N(Py) distances [*av.* 1.985(4) Å] are identical; however, the remaining Cu–N distances range from 2.214(6) to 2.307(6) Å. The dihedral angle between the two meridional planes is 78.7°. The expected Jahn-Teller distortion is manifested in the elongation of 3° amine Cu–N bonds to N(2) and N(6), with pyridino groups in the equatorial positions.

Equatorial Cu–N bonds average 2.107 Å, while axial Cu–N bonds average 2.298 Å.

The $CoCl_4^{2-}$ counterion is a nearly perfect tetrahedron with Co–Cl bond distances of averaging 2.282(7) Å; whereas, the $CuCl_4^{2-}$ counterion is a flattened tetrahedron with Cu–Cl distances ranging from 2.226(2) to 2.254(2) Å.

Data were collected on an Enraf-Nonius CAD4 diffractometer equipped with Mo$K_\alpha$ radiation ($\lambda$ = 0.71073 Å) and a graphite monochromator, employing $\theta$–$2\theta$ scans of variable speed. Theta limits were $1° < \theta < 21.5°$ for the III and $1° < \theta < 23°$ for IV. Data reduction included absorption corrections based upon $\psi$ scans. Minimum relative transmission factors were 0.885 for complex III and 0.908 for complex IV. Structures were solved by standard heavy atom techniques and refined by weighted full matrix least squares procedures using data for which $F_o > 3\sigma(F_o)$. Hydrogen atoms, including those of solvent molecules, were located on difference maps, but were not refined. Difference maps computed after refinements contained no significant features. Refined coordinates for III are given in Table I and those for IV are given in Table II.

## Acknowledgement

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