(O)-*t*-Bu]$_2$, 88393-52-6; W_2(O-*t*-Bu)$_4$[PhC(O)CHC(O)Me]$_2$, 88393-53-7; Mo_2(O-*i*-Pr)$_6$, 62521-20-4; Mo, 7439-98-7; W, 7440-33-7.

Supplementary Material Available: Complete listings of atomic positional parameters, anisotropic thermal parameters, bond distances, bond angles, and structure factor amplitudes for $Mo_2(OCH_2$-*t*-Bu)$_4$(MeCOCHCOMe)$_2$ (37 pages). Ordering information is given on any current masthead page. The complete structural report, MSC No. 82080, is available from the Indiana University Library, in microfiche form only.

Notes

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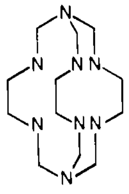
Preparation and Molecular Structure of the Nickel(II) Perchlorate Complex of a Hexadentate Macrobicyclic Ligand, 1,3,6,8,10,13,16,19-Octaazabicyclo[6.6.6]eicosane

Myunghyun Paik Suh,* Whanchul Shin,* Dooseop Kim,
and Sangsoo Kim

Received December 20, 1982

Some macrocyclic ligands render extraordinary stability to metal complexes against ligand substitution or dissociation by effectively encapsulating the metal ions. Typical examples are the compounds classified as cryptates.[1,2] Condensation of amines with formaldehyde has often been employed for the synthesis of macrocyclic ligands.[3,4] We have isolated several Ni(II) complexes with different ligands (**1–3**) by the template condensation of ethylenediamine, formaldehyde, and ammonia.[5] The preparation and the molecular structure of the nickel(II) perchlorate complex of **1** (1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane; trivial name sepulchrate), a hexadentate cryptand-like ligand, are reported here. The Ni(II) complexes of **2** and **3** will be published separately.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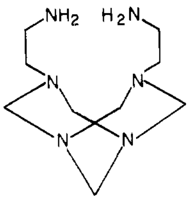
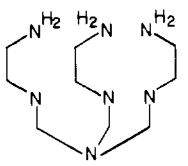


2



3

Experimental Section

Synthesis. The Ni(II) complex of **1**, [Ni(sepulchrate)]$(ClO_4)_2$, was synthesized by refluxing ethylenediamine, formaldehyde, ammonia, and nickel chloride (3:6:2:1 mole ratio) in a 1:1 methanol–water mixture for 48 h, followed by precipitation with lithium perchlorate. The major product of the condensation reaction was the yellow Ni(II) complex of **2** (90% yield), and the second major product isolated was the Ni(II) complex of **3**. The pink title complex was obtained in low yield (<1%) by concentrating the filtrate, followed by fractional recrystallization of the resultant crude precipitates from warm water. Anal. Calcd for $NiC_{12}H_{30}N_8Cl_2O_8$: C, 26.47; H, 5.56; N, 20.61. Found: C, 26.04; H, 5.98; N, 21.08. Crystals of [Ni(**1**)]$(ClO_4)_2$, suitable for X-ray crystallographic work, were obtained by dissolving the pink precipitates in warm water followed by slow evaporation of the solvent.

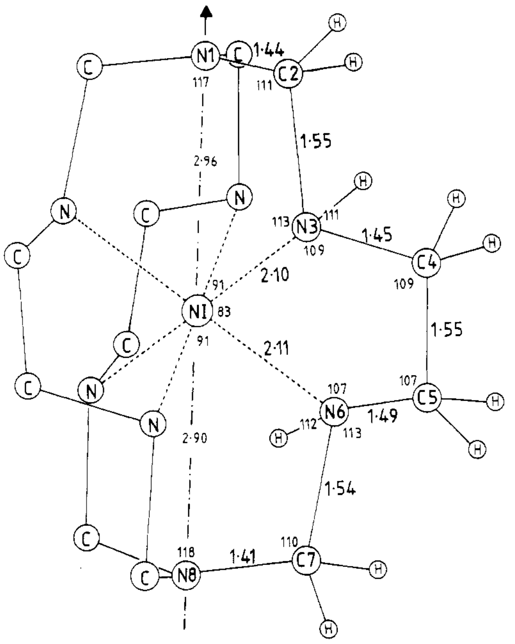


Figure 1. Schematic diagram of [Ni(sepulchrate)]$(ClO_4)_2$ showing the labeling scheme, bond distances (Å), and bond angles (deg). Estimated standard deviations are as follows: Ni–N, 0.01; N–C, C–C, 0.02–0.03; angles, 1–2.

Crystal Data Collection. Data were obtained at room temperature from a roughly spherical crystal of diameter 0.45 mm on a Rigaku AFC diffractometer equipped with Cu Kα radiation (λ = 1.5418 Å) and a graphite monochromator. The unique cell dimension was refined by a least-squares fit of 2θ angles for 15 accurately centered reflections having $30° \le 2\theta \le 40°$. Crystal data: $NiC_{12}H_{30}N_8 \cdot 2ClO_4$, mol wt 543.7, cubic space group $P2_13$, a = 12.707 (1) Å, V = 2051.9 (4) Å^3, Z = 4, d_{calcd} = 1.76 g cm^{-3}, d_{measd} = 1.74 g cm^{-3} in CH_3I–cyclohexanol, μ(Cu Kα) = 41.21 cm^{-1}. Intensity data were collected by the ω–2θ scan method over a range of $(1.1 + 0.4 \tan \theta)°$ in ω at a scan rate of 4° min^{-1} and by measuring background counts for 10 s at each end of the scan range. All data in the unique region of reciprocal space ($^1/_{24}$ of the reflecting sphere) were measured within $5° \le 2\theta \le 120°$ by keeping l greater than or equal to h and k indices. No decline in the intensities of three periodically remeasured reflections was noted. Of the 532 unique data measured, 497 had $I < 3\sigma(I)$ and were used in the refinement. Background, Lorentz, and polarization corrections were applied.[6] The variations in intensities of reflections near $\chi = 90°$ during ψ scans were less than 5%, and thus no absorption correction was applied.

Structure Determination and Refinement. Systematic absences $h00$ with h odd, $0k0$ with k odd, and $00l$ with l odd limit the space group to either $P2_13$ or $P4_232$. The space group was initially assumed to be $P2_13$ with 12 general positions since there were 4 formula units in the unit cell and both the cation and two anions have the potential for possessing molecular threefold axes that could coincide with

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[5] The preliminary results were reported in: (a) Suh, M. P.; Kim, D. S. "Abstracts of Papers", 45th Meeting of the Korean Chemical Society, 1980; p 214. (b) Shin, W.; Kim. S. S.; Suh, M. P. "Abstracts of Papers", Meeting of the American Crystallographic Association, Aug 1982; p C9.

[6] Data collection and data reduction were performed by using the Rigaku-Denki AFC software system for a PDP-8 computer.

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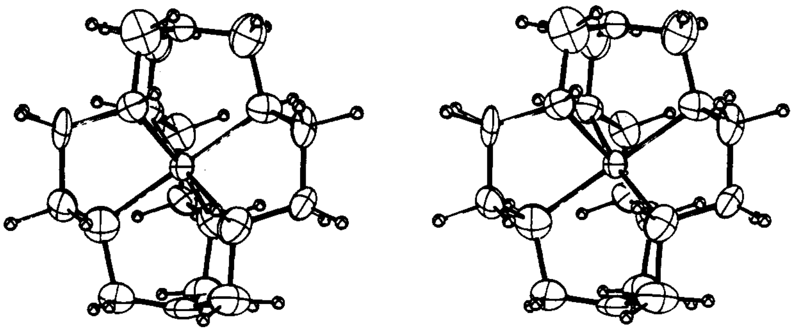

Figure 2. Stereoscopic view of $[Ni(sepulchrate)]^{2+}$.

crystallographic threefold axes in $P2_13$. This choice was found to be correct in the course of structure determination. The Patterson map was interpreted in terms of a Ni position on the threefold axis at $^1/_4$, $^1/_4$, $^1/_4$ and two Cl positions also on the threefold axis. Reflections with all even or all odd indices were generally stronger than the others, and this tendency could be explained by the above arrangement of the three heavy atoms. The R value ($R = \sum||F_o| - |F_c||/\sum|F_o|$) on the basis of these atoms was 0.34, and all of the non-hydrogen atoms were located in a subsequent difference Fourier map. After two cycles of full-matrix least-squares refinement for the parameters of all non-hydrogen atoms (anisotropic) and the geometrically calculated hydrogen positions (fixed isotropic, $U = 0.05$ Å^2), a difference Fourier map revealed the disordered positions for the oxygen atoms in the second perchlorate anion. After several cycles of refinement, the disordered model converged to give site occupancy factors of 0.72 and 0.28 for the major and minor sites, respectively. Throughout the process of refinement, the positions of the hydrogen atoms were refined with the constraint of a fixed X–H (X = C or N) bond distance of 1.08 Å. The function minimized in the least-squares refinement was $\sum w(|F_o| - k|F_c|)^2$, where w was unity in the early stage of refinement and $w = 1.4454/(\sigma^2(F) + 0.0066|F|^2)$ in the last cycle of refinement. The final R value was 0.073, and R_w ($R_w = \sum(w^{1/2}||F_o| - |F_c||)/\sum w^{1/2}|F_o|$) was 0.082. All of the atomic scattering factors including the correction factors for anomalous dispersion were taken from ref 7. The final atomic coordinates are listed in Table I. The anisotropic thermal parameters (Table II) and the final values of $|F_o|$ and $|F_c|$ (Table III) are available as supplementary materials. All of the calculations were performed with the program SHELX-76.[8]

Results and Discussion

The pink title complex was isolated in low yield by the template condensation described in the Experimental Section. Further condensation of the isolated Ni(II) complex of **3** with formaldehyde and ammonia produced the Ni(II) complex of **2** exclusively, rather than that of **1**.

The title complex is extraordinarily stable against ligand substitution with donors such as NCS^-, Me_2SO, H_2O, or CH_3CN. The IR spectrum of the complex (Nujol mull) exhibits an N–H stretching at 3290 cm^{-1} and no bands around 1600 cm^{-1}, indicating the absence of primary amines. The electronic spectrum of the PF_6^- salt of the complex in an acetonitrile solution shows absorption maxima at 19.6×10^3 cm^{-1} ($\epsilon = 8.0$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$) and 31.6×10^3 cm^{-1} ($\epsilon = 11.2$, $^3A_{2g} \rightarrow {}^3T_{1g}(P)$), typical of a Ni–N$_6$ chromophore. The spectrum is quite similar to that of $[Ni(en)_3]^{2+}$, which has absorption maxima at 18.5×10^3 cm^{-1} ($\epsilon = 6.9$) and 30.0×10^3 cm^{-1} ($\epsilon = 9.0$). The shift to shorter wavelengths for the former complex may be attributed to the small increase in ligand field strength caused by macrocyclization.

Results of elemental analysis together with the spectroscopic data suggested that the Ni complex contains the ligand structure of **1**. This was confirmed by the X-ray structure determination of the complex. According to the detailed report published after completion of the present investigation, the Co(III) complex of **1** was also formed by the condensation of $[Co(en)_3]^{3+}$ with ammonia and formaldehyde.[9]

Table I. Atomic Coordinates for $[Ni(sepulchrate)](ClO_4)_2$[a]

atom	x	y	z
Ni	252.8 (2)	252.8 (2)	252.8 (2)
N(1)	388 (1)	388 (1)	388 (1)
C(2)	362 (3)	305 (2)	461 (2)
N(3)	298 (2)	216 (1)	408 (1)
C(4)	204 (2)	190 (1)	468 (1)
C(5)	131 (2)	122 (1)	398 (1)
N(6)	109 (1)	184 (1)	301 (1)
C(7)	59 (2)	116 (2)	213 (2)
N(8)	121 (1)	121 (1)	121 (1)
Cl(1)	−36.1 (3)	−36.1 (3)	−36.1 (3)
O(1)	−101 (1)	−101 (1)	−101 (1)
O(2)	62 (1)	−17 (1)	−88 (1)
Cl(2)	705.7 (3)	705.7 (3)	705.7 (3)
O(3)	643 (2)	643 (2)	643 (2)
O(4)	797 (2)	645 (2)	732 (2)
O(3)′	768 (2)	768 (2)	768 (2)
O(4)′	610 (2)	675 (3)	756 (4)
H(21)	44 (1)	26 (1)	47 (1)
H(22)	29 (1)	34 (1)	51 (1)
H(3)	34 (1)	14 (1)	40 (2)
H(6)	3 (1)	23 (1)	30 (1)
H(41)	21 (1)	16 (1)	55 (1)
H(42)	16 (1)	26 (1)	49 (2)
H(51)	7 (1)	9 (1)	45 (1)
H(52)	16 (1)	4 (1)	40 (1)
H(71)	−1 (1)	17 (1)	20 (2)
H(72)	8 (2)	4 (1)	24 (1)

[a] Fractional coordinates $\times 10^3$ for non-hydrogen atoms and $\times 10^2$ for hydrogen atoms. Standard deviations in parentheses refer to least significant digits. Primed oxygens are for the minor sites (28%).

The atomic numbering scheme, the bond distances, and the bond angles of the title complex are presented in Figure 1. The stereoview of the cation is illustrated in Figure 2. The X-ray structure reveals that the whole cation can be generated by 3-fold rotational symmetry operation, with the 3-fold axis passing through the central Ni ion, N(1), and N(8). Thus, the structure of the ligand can be envisioned as a capsule with tris(methylene)amino caps added to both ends of the tris(ethylenediamine) moiety.

The C(4)–C(5) bond of the ligand tilts 1.7° from the 3-fold axis. Hence, the conformation of the tris(ethylenediamine) portion is *lel*, and its absolute configuration is either $\Delta\lambda\lambda\lambda$ or $\Delta\delta\delta\delta$ although the exact configuration is not determined explicitly by the present analysis. The same *lel* conformation for the tris(ethylenediamine) portion has been observed for the Co(III) complex of **1**.[9,10] There are three pseudo-2-fold

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axes that are perpendicular to the crystallographic 3-fold axis, bisecting the three C(4)–C(5) bonds and directed toward the central Ni(II) ion. The overall symmetry of the cation, therefore, is close to point group D_3. The Ni(II) ion is coordinated to the six nitrogen atoms in a pseudooctahedral arrangement with the average Ni–N bond distance of 2.10 Å. The twist angle between the equilateral triangle (N–N = 2.99 (1) Å) formed by the three N(3) atoms and the one (N–N = 3.00 (1) Å) by the three N(6) atoms is 59°. The Ni(II) ion is 0.004 Å from the best plane formed by the four nitrogen atoms of the octahedron, which are coplanar within ±0.15 Å.

All of the bond distances and angles around the Ni(II) ion are very similar to those of $[Ni(en)_3]^{2+}$.[11-13] The N(3)–C(4)–C(5)–N(6) torsion angle of 57 (1)° and the N(3)–N(6) distance of 2.79 (1) Å also agree well with 58° and 2.786 Å in the oxalate salt of $[Ni(en)_3]^{2+}$, respectively.[13] This indicates that addition of the two tris(methylene)amino groups does not exert significant influence on the coordination geometry around the Ni(II) ion. The average Co(II)–N distance of $[Co(\mathbf{1})]^{2+}$ was almost identical with that of $[Co(NH_3)_6]^{2+}$.[9] Therefore, the encapsulation of Ni(II) by **1** increases the stability of the complex without significant changes in the structural framework as well as ligand field strength compared with the case for $[Ni(en)_3]^{2+}$.

The two tris(methylene)amino groups reveal an interesting structural feature. The N(1) and N(8) atoms in the apexes of the caps are only 0.25 and 0.18 Å, respectively, apart from the best planes formed by three C(2) and three C(7) atoms. Furthermore, the C–N bond distances are 1.41 (2) and 1.44 (2) Å and the C–N–C bond angles are 117 (1) and 118 (1)° (Figure 1). These are indicative of near-sp^2 hybridization of the two tertiary amine nitrogens. The shift from normal sp^3 to near sp^2 is probably due to the long-range interaction of the cap nitrogen with the t_{2g} electrons of the Ni(II) ion. Similar sp^2 hybridization of the tertiary amine nitrogens capping the octahedron has been reported for $[M(trenpy)]^{2+}$ complexes.[14] In the trenpy complexes, the M–N interaction was greatly influenced by the number of t_{2g} electrons of the metal ions. The sp^2 hybridization of the nitrogen atoms of the amino caps was also observed in the Co(II) and Co(III) complexes of **1**.[9]

The large cations are packed in a cubic closest packing (ccp) mode, four nickel ions in the unit cell being near $(^1/_4, ^1/_4, ^1/_4)$, $(^1/_4, ^3/_4, ^3/_4)$, $(^3/_4, ^1/_4, ^3/_4)$, and $(^3/_4, ^3/_4, ^1/_4)$. Two smaller tetrahedral holes and one larger octahedral hole per cation are present in this ccp mode. In the present crystal structure, perchlorate **1** is in one of the tetrahedral holes and **2** in the octahedral hole. Perchlorate **2** might be disordered due to the larger hole size. The Ni–N(1) and Ni–N(8) distances are 2.96 (1) and 2.90 (1) Å, respectively. This asymmetry in distance may be partly attributed to the crystal packing forces, since N(1), N(8), and the two perchlorate Cl atoms are located on the body-diagonal 3-fold axis and the N(1)–Cl(1) distance is only 3.46 (1) Å while the N(8)–Cl(2) distance is 9.97 (1) Å. There is only one type of hydrogen bond in the structure (N(3)–H···O(2) = 3.10(1) Å).

The methylenediamine (N–C–N) linkage is easily fragmented unless both of the nitrogen atoms are tertiary.[15] The stability of the ligand in the present complex, however, implies that the N–C–N linkage containing a secondary amine can be stabilized by the coordination of the secondary nitrogen to a metal ion.

Acknowledgment. This work was supported in part by grants from the Korea Science and Engineering Foundation.

Registry No. $[Ni(\mathbf{1})](ClO_4)_2$, 88229-09-8; ethylenediamine, 107-15-3; formaldehyde, 50-00-0; ammonia, 7664-41-7.

Supplementary Material Available: Anisotropic thermal parameters (Table II) and final values of $|F_o|$ and $|F_c|$ (Table III) (4 pages). Ordering information is given on any current masthead page.

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A Centrosymmetric Hydrogen-Bonded Cyclic $(H_2O{\cdot}Br^-)_2$ System. Crystal Structure of 1-Methyl-1,3,5,7-tetraazaadamantan-1-ium Bromide Hydrate

Thomas C. W. Mak

Received June 15, 1983

A recent MNDO study[1] of 1,3,5,7-tetraazaadamantane (commonly known as hexamethylenetetramine), $(CH_2)_6N_4$ (**1**), and related cage molecules has shown that, when a lone pair of **1** is utilized in salt or adduct formation, the C–N$_{\text{quaternary}}$ bonds and adjacent C–N$_{\text{tertiary}}$ bonds become significantly lengthened and shortened, respectively, relative to the remaining six remote C–N bonds. This general trend is in accord with available structural data for $(CH_2)_6N_4{\cdot}BH_3$,[2] $(CH_2)_6N_4O$,[3] and several salts containing the $[(CH_2)_6N_4CH_3]^+$,[4,5] $[(CH_2)_6N_4CH_2C_6H_5]^+$,[6] $[(CH_2)_6N_4CH_2CH{=}CH_2]^+$,[7] and $[(CH_2)_6N_4H]^+$[8] cations. The title compound, $[(CH_2)_6N_4CH_3]Br{\cdot}H_2O$ (**2**), was isolated in the course of our synthetic and structural studies on various heterocyclic cage systems. The mode of hydrogen bonding involving the water molecule seemed intriguing and prompted us to undertake an X-ray crystallographic analysis.

Experimental Section

An equimolar quantity of methyl bromide was chilled to 0 °C and then added dropwise to a solution of **1** in ethanol/water. Slow evaporation of the resulting solution yielded hygroscopic crystals of **2** in the form of thick plates. A selected crystal (0.35 × 0.35 × 0.40 mm) was covered with petroleum jelly, lodged in a 0.5-mm-diameter Lindemann glass capillary, and sealed with epoxy resin. It was then centered on a Nicolet R3m four-circle diffractometer (graphite-monochromatized Mo K$_\alpha$ radiation, λ = 0.71069 Å), and determinations of the crystal class, orientation matrix, and accurate unit-cell parameters were performed according to established procedures.[9]

Crystal Data: $[(CH_2)_6N_4CH_3]Br{\cdot}H_2O$ (**2**), M_r = 253.15, monoclinic, space group $P2_1/c$, a = 6.840 (2) Å, b = 6.898 (2) Å, c = 22.597 (8) Å, β = 94.91 (3)°, V = 1062.3 (6) Å^3, D_{measd} = 1.584 g cm^{-3}, Z = 4, D_{calcd} = 1.583 g cm^{-3}, $F(000)$ = 519.86, μ(Mo K$_\alpha$) = 38.03 cm^{-1}.

Intensities ($h,k,\pm l$; 1577 unique data) were measured at 22 °C by using the ω–2θ variable-scan (2.02–8.37° min^{-1}) technique in the

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