The Crystal and Molecular Structure of the Tetrameric Nickel(II) Complex of 7-Hydroxy-4-methyl-5-azahept-4-en-2-one, [Ni(C₇H₁₁NO₂)(CH₃OH)]₄

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The structure of the green methanolate of the nickel(II) complex of 7-hydroxy-4-methyl-5-azahept-4-en-2-one (the dianion of the ligand is represented by EIA in formulas), Ni(EIA)(CH₃OH), has been determined by a single crystal X-ray diffraction study. The compound crystallizes as orthorhombic crystals (a = 12.319(4) Å, b = 25.91(3) Å, and c = 13.132(4) Å) of space group P2₁2₁2₁ with 16 formula units (monomeric) per unit cell. The structure was solved by direct methods and refined by least-squares methods to R = 0.056 and R_w = 0.049 for 2829 independent, non-zero reflections. The structure consists of tetrameric, cubane-like complexes with alkoxide oxygen atoms and octahedrally-coordinated nickel(II) atoms at the corners of a cube. The cube is slightly distorted with eight short Ni–O distances (2.020–2.055 Å) and two pairs of longer, mutually perpendicular Ni–O distances (2.112–2.130 Å).

Introduction

The reactions of copper(II) and nickel(II) with the dianion of 7-hydroxy-4-methyl-5-azahept-4-en-2-one (abbreviated EIA in formulas) have been investigated [1–4] by several workers and solvated and solvent-free forms of both Cu(EIA) and Ni(EIA) have been reported. Cubane-type structures have been found for α-[Cu(EIA)]₄ [3] (solvent-free) and the benzene solvated β-[Cu(EIA)]₄ [4]; the α- and β-forms, Figure 1, differ in the coordination of copper, the relative orientation of ligands, and in the relative positions of short and long Cu–O distances that form the cube edges. The α- form can be thought of as two dimers with short Cu–O distances within each dimer and longer Cu–O distances joining the two dimers into a cubane-like unit; the coordination of each copper is trigonal-bipyramidal. The β- form is best described as a folded 8-membered ring in a boat-like conformation with short Cu–O distances defining the ring and the longer Cu–O distances defining the approach of the folded portions; the coordination of each copper is square-pyramidal.
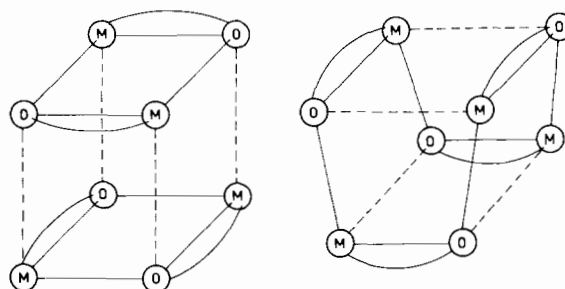

Figure 1. The cubane units of α-(CuEIA)₄ (left) and β-(Cu-EIA)₄ (right). Solid lines indicate short Cu–O distance and dashed lines indicate long Cu–O distances.

The solvent-free form of Ni(EIA) is dimeric [2] with a bent four-membered ring and square-planar coordination about nickel; the compound is red in color and diamagnetic. Crystals of the methanol solvate, Ni(EIA)(CH₃OH), are green in color, paramagnetic, and decompose rapidly in air. A five-coordinate dimeric structure or a cubane-like structure were considered as possibilities.

For compounds with similar properties, a five-coordinate dimeric structure was reported [5] for the nickel complex of N,N-bis-(2-diethylaminoethyl)-2-hydroxyethyl amine and a cubane-like structure was reported [6] for [Ni(Acac)(CH₃O)(CH₃-OH)]₄ (Acac represents the anion of acetylacetone). More recently, dimeric structures with octahedral coordination about nickel have been reported [7] for complexes of the formula [Ni(bsb)(NO₃)-(EtOH)]₂ (bsb represents a bidentate Schiff base).

Because of the continuing interest in cubane-like structures [4, 8] and because of interest in dimer–tetramer equilibria [9], further attempts were made to determine the structure of Ni(EIA)(CH₃OH); in this paper we report the results of those studies.

Experimental

Crystallographic Data Collection

The compound was prepared by the method reported in the literature [1]. A green crystal with

TABLE I. Final Atomic Positional and Thermal Parameters for [Ni(EIA)(CH$_3$OH)]$_4$.

Atom Name	X	Y	Z	B or β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni(1)	0.1786(1)	0.17013(5)	-0.1011(1)	0.0044(1)	0.00116(3)	0.00329(8)	0.00022(5)	0.00022(8)	-0.000006(4)
Ni(2)	0.2134(1)	0.17748(6)	-0.3308(1)	0.0045(1)	0.00100(2)	0.00368(9)	0.00013(5)	0.00046(9)	0.00020(4)
Ni(3)	0.1390(1)	0.07276(5)	-0.2477(1)	0.00456(9)	0.00098(2)	0.00380(9)	-0.00019(5)	-0.0001(1)	0.00006(4)
Ni(4)	0.3674(1)	0.10829(5)	-0.1900(1)	0.0043(1)	0.00100(2)	0.0045(1)	0.00024(5)	0.0000(1)	-0.00008(4)
O(11)	0.0978(6)	0.1517(3)	-0.2328(6)	3.0(2)					
O(21)	0.2674(6)	0.1035(3)	-0.3220(5)	2.7(1)					
O(31)	0.2226(6)	0.0915(3)	-0.1197(5)	2.7(1)					
O(41)	0.3083(5)	0.1809(3)	-0.1970(5)	2.6(1)					
O(13)	0.1640(6)	0.2528(3)	-0.1230(6)	4.2(2)					
C(18)	0.0905(13)	0.2874(7)	-0.0685(12)	6.4(4)					
C(11)	-0.0127(9)	0.1697(5)	-0.2229(8)	3.6(2)					
C(12)	-0.0561(9)	0.1560(5)	-0.1142(9)	3.7(3)					
N(1)	0.0318(8)	0.1647(4)	-0.0384(7)	3.6(2)					
C(14)	0.0123(9)	0.1646(5)	0.0579(8)	3.5(2)					
C(13)	-0.107(1)	0.1541(5)	0.092(1)	4.7(3)					
C(15)	0.0935(9)	0.1733(5)	0.1307(8)	3.7(2)					
C(16)	0.2031(9)	0.1812(5)	0.1197(9)	4.0(3)					
C(17)	0.277(1)	0.1912(5)	0.209(1)	4.9(3)					
O(12)	0.2535(6)	0.1779(3)	0.0312(6)	3.8(2)					
C(28)	0.091(1)	0.1610(6)	-0.556(1)	5.6(3)					
C(23)	0.0839(6)	0.1574(3)	-0.4444(6)	3.8(2)					
C(21)	0.307(1)	0.0894(5)	-0.4221(9)	3.8(3)					
C(22)	0.374(1)	0.1343(5)	-0.4671(9)	3.7(2)					
N(2)	0.3218(7)	0.1831(4)	-0.4411(7)	3.3(2)					
C(24)	0.354(1)	0.2278(5)	-0.4829(9)	3.8(3)					
C(23)	0.445(1)	0.2261(6)	-0.563(1)	5.1(3)					
C(25)	0.306(1)	0.2756(5)	-0.4571(9)	3.9(3)					
C(26)	0.233(1)	0.2855(5)	-0.3872(9)	3.8(2)					
C(27)	0.202(1)	0.3430(5)	-0.360(1)	5.0(3)					
O(22)	0.1819(6)	0.2531(3)	-0.3268(6)	3.8(2)					
O(33)	0.2333(6)	0.0011(3)	-0.2723(6)	3.8(2)					
C(38)	0.208(1)	-0.0510(6)	-0.242(1)	5.7(3)					
C(31)	0.205(1)	0.0529(5)	-0.0450(9)	3.6(2)					
C(32)	0.080(1)	0.0364(5)	-0.048(1)	4.1(3)					
N(3)	0.0409(8)	0.0363(4)	-0.1529(7)	3.3(2)					
C(34)	-0.053(1)	0.0145(5)	-0.177(1)	4.0(3)					
C(33)	-0.120(1)	-0.0129(6)	-0.094(1)	6.8(4)					
C(35)	-0.0930(9)	0.0150(5)	-0.275(1)	4.0(3)					
C(36)	-0.051(1)	0.0390(5)	-0.3633(9)	3.9(3)					
C(37)	-0.114(1)	0.0392(6)	-0.462(1)	5.5(3)					

TABLE I. *(Continued)*

Atom Name	X	Y	Z	B or β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(32)	0.0409(6)	0.0625(3)	-0.3670(5)	3.4(2)					
O(43)	0.4293(7)	0.1231(3)	-0.0368(6)	4.1(2)					
C(48)	0.484(1)	0.0827(6)	0.020(1)	6.3(4)					
C(41)	0.3980(8)	0.2157(4)	-0.1853(9)	3.1(2)					
C(42)	0.496(1)	0.1969(4)	-0.243(1)	3.8(2)					
N(4)	0.5036(7)	0.1410(4)	-0.2388(8)	3.3(2)					
C(44)	0.590(1)	0.1157(5)	-0.266(1)	4.3(3)					
C(43)	0.692(1)	0.1466(6)	-0.299(1)	6.8(4)					
C(45)	0.596(1)	0.0594(5)	-0.268(1)	4.8(3)					
C(46)	0.520(1)	0.0262(5)	-0.241(1)	4.3(3)					
C(47)	0.541(1)	-0.0328(6)	-0.257(1)	6.0(3)					
O(42)	0.4227(6)	0.0365(3)	-0.2053(6)	3.7(2)					

approximate dimensions 0.5 × 0.4 × 0.3 mm was coated with epoxy cement and mounted on a glass fiber with epoxy cement such that the long crystal dimension was approximately parallel to the fiber axis.

Unit cell parameters and the orientation matrix were determined on a Syntex P2₁ four-circle diffractometer equipped with a graphite monochromator (Bragg 2θ angle = 12.2°) using MoKα radiation at a takeoff angle of 6.5°. Fifteen reflections whose 2θ values ranged from 4.0° to 15.0° were machine-centered and used in least-square refinement of the lattice parameters and orientation matrix. Axial photographs indicated that the crystal belonged to the orthorhombic system. Intensity data for zero levels of the reciprocal lattice were collected at a rapid scan rate and the intensities examined carefully for systematic absences. The absence of odd reflections along each of the axial rows is consistent with space group P2₁2₁2₁ (No. 19) [10] only. The unit cell parameters obtained were a = 12.319(4) Å, b = 25.91(3) Å, c = 13.132(4) Å, and V = 4191(5) Å³, Z = 16 (based on the monomeric formula). Omega scans of several low 2θ angle reflections gave peak widths at half-height of less than 0.3°, indicating a satisfactory mosaic spread for the crystal.

Intensity data were collected using $\theta-2\theta$ scans with X-ray source and monochromator settings identical to those used for determination of the unit cell parameters. A variable scan rate of from 3.5° to 29.3° min⁻¹ was used and a scan width of 2.0° was sufficient to collect all of the peak intensity. Stationary background counts were measured at the beginning (bgd1) and at the end (bgd2) of each scan with the total background time equal to scan time. No significant flucutations were observed in the intensities of three standard reflections (400, 060, 006) monitored every 97 reflections. Intensities were calculated by subtracting background counts from total scan counts (CT):

$$I = CT - (bgd1 + bgd2)$$

The intensities were assigned standard deviations according to the formula:

$$\sigma(I) = [CT + (bgd1 + bgd2)]^{1/2}$$

From a total of 4220 reflections collected in a complete octant (h, k, and l positive) of data out to 2θ = 50.0°, 2829 were accepted as statistically above background on the basis that $I \geq 3\sigma(I)$. Lorentz and polarization corrections were made in the usual way. Due to the epoxy coating, no attempt was made to correct for absorption (μ = 18.2 cm⁻¹).

*Solution and Refinement of the Structure*

Computations were performed using standard programs [12]; all computations were carried out on the CDC Cyber 74 system. For structure factor cal-

TABLE II. Distances and Angles.

Atoms n =	1	2	3	4	Avg.
			Interatomic Distances		
Ni(n)–O(n1)	2.051(8)	2.032(7)	2.030(7)	2.020(7)	2.033(11)
Ni(n)–O(n2)	1.978(8)	1.998(8)	1.996(7)	1.991(8)	1.991(8)
Ni(n)–N(n)	1.93(1)	1.98(1)	1.98(1)	1.99(1)	1.97(2)
Ni(n)–O(n3)	2.17(8)	2.245(8)	2.215(8)	2.186(8)	2.21(3)
O(n1)–C(n1)	1.45(1)	1.45(1)	1.42(1)	1.43(1)	1.44(1)
O(n2)–C(n6)	1.32(1)	1.31(1)	1.28(1)	1.32(1)	1.31(2)
O(n3)–C(n8)	1.46(2)	1.47(2)	1.44(2)	1.45(2)	1.45(1)
N(n)–C(n2)	1.49(1)	1.46(1)	1.46(1)	1.45(1)	1.47(2)
N(n)–C(n4)	1.29(1)	1.34(1)	1.33(1)	1.30(1)	1.32(2)
C(n1)–C(n2)	1.57(2)	1.54(2)	1.60(2)	1.50(2)	1.55(4)
C(n4)–C(n5)	1.40(2)	1.41(2)	1.38(2)	1.46(2)	1.41(3)
C(n5)–C(n6)	1.37(2)	1.32(2)	1.42(2)	1.31(2)	1.36(4)
C(n3)–C(n4)	1.56(2)	1.54(2)	1.54(2)	1.55(2)	1.55(1)
C(n6)–C(n7)	1.50(2)	1.58(2)	1.51(2)	1.56(2)	1.54(3)
Ni(1)–Ni(n)		3.052(3)	3.210(2)	3.056(2)	
Ni(2)–Ni(n)			3.065(2)	3.198(2)	
Ni(3)–Ni(n)				3.056(3)	

Atoms n,n' =	1,4	2,1	3,2	4,3	Avg.
Ni(n)–O(n'1)	2.054(7)	2.032(7)	2.023(7)	2.055(7)	2.037(13)
Ni(n)–O(n''1)	2.122(7)	2.112(7)	2.115(7)	2.130(7)	2.120(7)

Atoms n =	1	2	3	4	Avg.
			Angles About Ni		
O(n2)–Ni(n)–O(n3)	93.1(3)	93.5(3)	95.2(3)	74.8(4)	93.9(9)
O(n2)–Ni(n)–N(n)	93.9(3)	94.5(4)	93.5(3)	94.4(4)	94.1(4)
O(n3)–Ni(n)–N(n)	92.8(3)	70.5(4)	90.7(3)	89.3(4)	91(1)
O(n1)–Ni(n)–O(n3)	94.5(3)	94.4(3)	93.1(3)	113.3(3)	94.0(6)
O(n1)–Ni(n)–O(n2)	172.1(3)	170.8(3)	171.4(3)	171.6(3)	171.5(5)
O(n1)–Ni(n)–N(n)	83.8(3)	83.7(3)	84.4(4)	83.8(3)	83.9(3)

Atoms n,n' =	1,4	2,1	3,2	4,3	Avg.
N(n)–Ni(n)–O(n'1)	165.8(3)	164.1(4)	166.1(3)	165.6(3)	165.4(8)
O(n2)–Ni(n)–O(n'1)	99.3(3)	99.8(3)	98.5(3)	98.3(3)	99.0(6)
O(n1)–Ni(n)–O(n'1)	83.8(3)	83.3(3)	84.7(3)	84.6(3)	84.1(6)
O(n3)–Ni(n)–O(n'1)	81.3(3)	101.6(3)	81.3(3)	87.6(4)	83(3)

Atoms n, n', n'' =	1,4,3	2,1,4	3,2,1	4,3,2	Avg.
O(n'1)–Ni(n)–O(n''1)	82.9(3)	82.8(3)	81.5(3)	81.5(3)	82.0(5)
O(n1)–Ni(n)–O(n''1)	78.6(3)	79.1(3)	79.3(3)	79.0(3)	79.0(3)
O(n3)–Ni(n)–O(n''1)	162.6(3)	171.8(3)	161.8(3)	162.7(3)	165(4)
N(n)–Ni(n)–O(n''1)	102.2(3)	103.5(3)	105.0(3)	104.5(4)	104(1)
O(n2)–Ni(n)–O(n''1)	94.6(3)	92.5(3)	93.2(3)	93.5(3)	93.5(8)

Atoms n =	1	2	3	4	Avg.
			Ligand Angles		
Ni(n)–O(n1)–C(n1)	107.8(6)	107.3(6)	108.9(6)	107.6(5)	107.9(6)
O(n1)–C(n1)–C(n2)	109.3(9)	109.8(9)	108.9(9)	111.2(8)	109.8(9)
C(n1)–C(n2)–N(n)	109.1(9)	109.3(9)	110(1)	111(1)	110(1)

TABLE II. *(Continued)*

Atoms n =	1	2	3	4	Avg.
			Ligand Angles		
N(n)–C(n4)–C(n3)	117(1)	118(1)	120(1)	119(1)	118(1)
N(n)–C(n4)–C(n5)	122(1)	123(1)	122(1)	123(1)	122(1)
C(n4)–C(n5)–C(n6)	131(1)	129(1)	130(1)	128(1)	130(1)
C(n5)–C(n6)–C(n7)	123(1)	120(1)	121(1)	119(1)	121(1)
C(n5)–C(n6)–O(n2)	123(1)	129(1)	124(1)	127(1)	126(2)
C(n6)–O(n2)–Ni(n)	124.1(7)	121.3(7)	124.5(7)	122.5(8)	123(1)
Ni(n)–O(n3)–C(n8)	126.3(8)	127.2(8)	129.2(7)	120.6(8)	126(3)
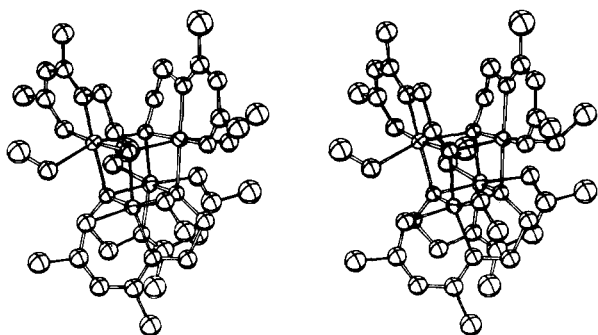
Figure 2. A stereoview of the molecular unit of [Ni(EIA)-(CH$_3$OH)]$_4$.

culations the scattering factors were taken from Cromer and Waber's tabulation [13]. The scattering factors were corrected for the real and imaginary anomalous dispersion components using the dispersion factors given by Cromer [14]. The agreement factors are defined in the usual way as

$$R = (\Sigma \, ||F_o| - |F_c \, ||)/(\Sigma \, |F_o|)$$

and

$$R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|\, F_o|)^2 \,]^{1/2}$$

In all least-squares refinements, the quantity minimized was $w(|F_o| - |F_c|)^2$. A weighting scheme based on counting statistics ($w = 4I/\sigma^2(I)^2$) was employed for calculating R_w and in least-squares refinement.

The structure was solved by direct methods using the program MULTAN; the program was allowed to choose origin-defining reflections and the correct solution was apparent from the Figure-of-Merit index. Positions of all nickel atoms were obtained from the initial E-map and all other non-hydrogen atoms were located in successive difference fourier calculations. Full-matrix least-squares refinement, using anisotropic thermal parameters for nickel atoms and isotropic thermal parameters for all other atoms, converged to

$R = 0.056$ and $R_w = 0.049$. The greatest shift on the final cycle of refinement was less than 0.02 standard deviations and a final difference Fourier had no significant features.

Final atomic positions and thermal parameters appear in Table I. A table of calculated and observed structure amplitudes is available from the Editor.

Description of the Structure and Discussion

The structure consists of discrete, tetrameric, cubane-like molecules. A stereoview of the molecule is shown in Figure 2 and selected intramolecular distances and angles are presented in Table II. Although each nickel atom of the tetramer is crystallographically independent, the coordination arrangement around each is very similar. Each nickel atom is coordinated to an EIA ligand through the nitrogen and two oxygen atoms of the ligand. In addition,
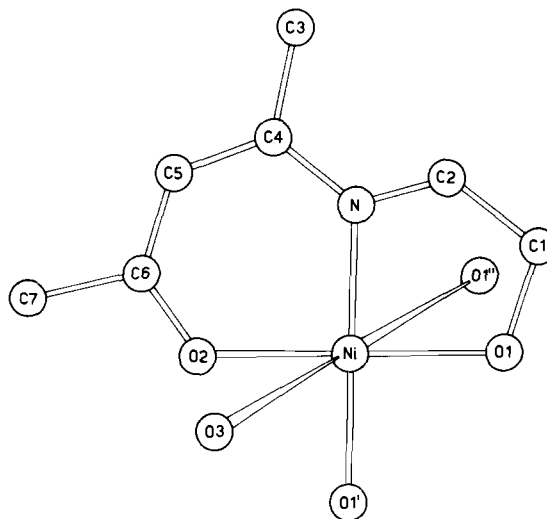

Figure 3. The coordination about nickel and the ligand numbering scheme.
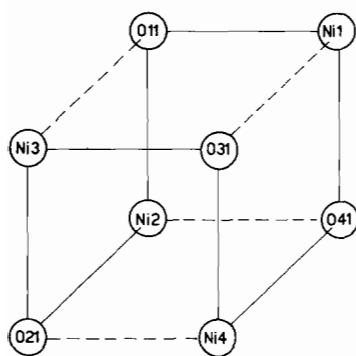
Figure 4. The Ni_4O_4 cubane unit.

each nickel atom is coordinated to a methanol oxygen and to the alkoxide oxygen atoms, O1, of two adjacent ligands. The arrangement about nickel, the atomic numbering scheme, and average bond lengths are illustrated in Figure 3.

The coordination about each nickel is a tetragonally-distorted octahedron. The three donor atoms of the coordinated ligand and one bridging alkoxide from an adjacent ligand form the basal plane with short distances (1.93–2.06 Å). The methanol oxygen and the other alkoxide oxygen occupy the axial positions with longer distances (2.11–2.25 Å). The methanol coordinated to Ni(2) is bent toward the nitrogen to give an angle of 70.5(4)° compared to an average angle of 91° for the other three groups. The methanol coordinated to Ni(4) is bent toward O2 to give an angle of 74.8(4)° compared to an average angle of 93.9(9)° for the other three groups.

The nickel atoms and alkoxide oxygen atoms complete a distorted cube, Figure 4. The cube is distorted, but to a lesser extent than either form of [Cu(EIA)]₄. On the basis of the ease of desolvating [Ni(EIA)(CH₃OH)]₄ to dimeric [Ni(EIA)]₂, a

structure formally built up from two dimeric moieties, similar to α-[Cu(EIA)]$_4$, was expected. However, the cubane unit is distorted in the same manner as β-[Cu(EIA)]$_4$ with two pairs of long, mutually perpendicular Ni–O bonds. The difference between short (2.020–2.055 Å, Avg 2.04(1)Å) and long (2.112–2.130 Å, Avg 2.12(1) Å) metal–oxygen distances is significant but is much smaller than the difference for either the α- form (1.99–2.32 Å) or the β-form (1.97–2.41 Å) of [Cu(EIA)]$_4$.

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