

Polynuclear Complexes with Hydrogen-Bonded Bridges. 3.^{1,2} Oxygen–Oxygen Hydrogen Bonding between Tris Chelates of 2-Aminoethanol³

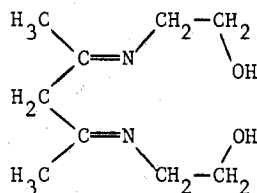
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The structures of $[\text{Co}_2(\text{Eta})_3(\text{EtaH})_3](\text{ClO}_4)_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ and $[\text{Ni}_2(\text{Eta})_2(\text{EtaH})_4](\text{ClO}_4)_2$ (where EtaH represents 2-aminoethanol and Eta represents the anion formed by removing the alcohol proton from 2-aminoethanol) have been determined crystallographically, and both structures contain dinuclear cations made up of tris chelates joined face-to-face by oxygen–hydrogen–oxygen bonds. The nickel cations occupy sites of $\bar{3}$ symmetry, the oxygens form an octahedron with hydrogens on four edges, the oxygen–oxygen distances are 2.68 (5) and 2.73 (2) Å, and the octahedral tris chelates have configurations $\Delta\lambda\lambda\lambda$ and $\Lambda\delta\delta\delta$. The cobalt cations occupy sites of twofold symmetry, the oxygens form a trigonal prism with hydrogens on three edges, the oxygen–oxygen distances are 2.38 (1) and 2.445 (7) Å, and the octahedral tris chelates of one dinuclear unit have the $\Lambda\delta\delta\lambda$ configuration. The compound $[\text{Co}_2(\text{Eta})_3(\text{EtaH})_3](\text{ClO}_4)_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ crystallizes in space group $P2_1/c$ with two formula units in a unit cell of dimensions $a = 12.127$ (4) Å, $b = 8.781$ (3) Å, $c = 16.524$ (6) Å, $\beta = 121.39$ (2)°, $\rho_{\text{exptl}} = 1.740$ g/cm³, and $\rho_{\text{calcd}} = 1.745$ g/cm³. The structure was solved by Patterson methods, and least-squares refinement converged at final values of $R = 0.062$ and $R_w = 0.076$. The compound $[\text{Ni}_2(\text{Eta})_2(\text{EtaH})_4](\text{ClO}_4)_2$ crystallizes in space group $Pa\bar{3}$ with four formula units per unit cell with $a = 13.85$ (1) Å, $\rho_{\text{exptl}} = 1.65$ g/cm³, and $\rho_{\text{calcd}} = 1.67$ g/cm³. The structure was solved by Patterson methods, and least-squares refinement converged at final values of $R = 0.073$ and $R_w = 0.052$.

Introduction

Although dimer formation through cooperative hydrogen bonding is well documented for compounds such as carboxylic acids, there have been few documented examples of transition-metal complexes associated into polynuclear complexes through hydrogen-bonded bridges. The copper(II) and nickel(II) complexes of the diimine I formed by the con-



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densation of 2,4-pentanedione and 2-aminoethanol are examples of dinuclear species in which metal complexes are joined edge-to-edge by oxygen–hydrogen–oxygen bridges.² The oxygen–oxygen distances (2.30 Å) are almost as short as the fluorine–fluorine distance (2.26 Å) in the HF_2^- ion and indicate strong hydrogen bonding. Although the metal–metal distance is 4.98 Å, the copper(II) compound shows significant antiferromagnetic coupling ($J = -93$ cm⁻¹).

Hydrogen bonding into dimers was suggested by Yoneda and Kida⁴ for a series of compounds, $[\text{Co}_2(\text{Eta})_3(\text{EtaH})_3]\text{X}_3$ (where EtaH represents 2-aminoethanol and Eta represents the anion formed by removing a proton from 2-aminoethanol), prepared from cobalt(III) compounds and 2-aminoethanol; they suggested structures ranging from singly bridged corner-to-corner hydrogen bonding to triply bridged face-to-face hydrogen bonding. Recent reports^{5–7} indicate that previously reported⁸ compounds prepared from cobalt(II) compounds are identical with Yoneda and Kida's compounds. Similar compounds with divalent cobalt(II) and nickel(II), $[\text{M}_2(\text{Eta})_2(\text{EtaH})_4](\text{ClO}_4)_2$, have also been reported.⁹ Although structures have not been reported for any of these compounds, a face-to-face hydrogen-bonded structure was found¹ for the compound $[\text{CoNi}(\text{Eta})_3(\text{EtaH})_3]\text{I}_2$. That structure was, however, complicated by disorder problems.

In order to confirm the hydrogen-bonded structures and to further investigate the properties of such species, crystals of the compounds $[\text{Co}_2(\text{Eta})_3(\text{EtaH})_3](\text{ClO}_4)_3$ and $[\text{Ni}_2-$

$(\text{Eta})_2(\text{EtaH})_4](\text{ClO}_4)_2$ were prepared, and the structures and properties of these compounds are reported in this paper.

Experimental Section

Preparation of $[\text{Co}_2(\text{Eta})_3(\text{EtaH})_3](\text{ClO}_4)_3 \cdot \frac{1}{2}\text{H}_2\text{O}$. Cobalt perchlorate hexahydrate (3.66 g, 0.010 mol) was dissolved in 50 mL of methanol, and a solution of 2-aminoethanol (1.83 g, 0.030 mol, in 25 mL of methanol) was added. Concentrated phosphoric acid was added dropwise until a total of 2 mL had been added; the reddish purple solid that formed was filtered, and the filtrate was set aside to crystallize. Red platelets that could be recrystallized from methanol or water were isolated. Anal. Calcd for $[\text{Co}_2(\text{NH}_2\text{CH}_2\text{CH}_2\text{O})_3(\text{NH}_2\text{CH}_2\text{CH}_2\text{OH})_3](\text{ClO}_4)_3 \cdot \frac{1}{2}\text{H}_2\text{O}$: C, 18.27; H, 4.99; N, 10.65; Cl, 13.48. Found: C, 18.19; H, 5.01; N, 10.60; Cl, 13.54.

Preparation of $[\text{Ni}_2(\text{Eta})_2(\text{EtaH})_4](\text{ClO}_4)_2$. The compound was prepared by the reported method.⁹ Solutions of 2.0 g (5.46 mmol) of nickel perchlorate hexahydrate in 30 mL of ethanol and 3.2 g (52.4 mmol) of 2-aminoethanol in 20 mL of ethanol were warmed to 60 °C and mixed. The resulting solution was filtered while hot and set aside to cool slowly in a Dewar flask; well-formed blue octahedral crystals separated and were filtered. Anal. Calcd for $[\text{Ni}_2(\text{NH}_2\text{CH}_2\text{CH}_2\text{O})_2(\text{NH}_2\text{CH}_2\text{CH}_2\text{OH})_4](\text{ClO}_4)_2$: C, 21.17; H, 5.92; N, 12.34. Found: C, 21.24; H, 5.97; N, 12.31.

Magnetic Susceptibility of $[\text{Ni}_2(\text{Eta})_2(\text{EtaH})_4](\text{ClO}_4)_2$. The magnetic susceptibility at different temperatures was determined by the Faraday method with $\text{HgCo}(\text{NCS})_4$ as calibrant. Diamagnetic corrections were made by using tabulated values.¹⁰ The magnetic moments at 298, 195, and 93 K were 3.16, 3.13, and 3.04 μ_B , respectively.

Crystallographic Data Collection for $[\text{Co}_2(\text{Eta})_3(\text{EtaH})_3](\text{ClO}_4)_3 \cdot \frac{1}{2}\text{H}_2\text{O}$. A reddish purple platelet with approximate dimensions 0.2 × 0.4 × 0.5 mm was mounted on a glass fiber with epoxy cement such that the longest crystal dimension (b^*) was approximately parallel to the fiber axis.

Unit cell parameters and the orientation matrix were determined on a Syntex $P2_1$ four-circle diffractometer equipped with a graphite monochromator (Bragg 2θ angle = 12.2°) using Mo $K\alpha$ radiation at a takeoff angle of 6.75°. Fifteen reflections whose 2θ values ranged from 7.39 to 31.57° were machine-centered and used in least-squares refinement of the lattice parameters and orientation matrix. Unit cell parameters obtained are $a = 12.127$ (4) Å,¹¹ $b = 8.781$ (3) Å, $c = 16.524$ (6) Å, $\beta = 121.39$ (2)°, and $V = 1501.9$ (8) Å³. The calculated density of 1.745 g/cm³ for two formula units per unit cell agrees with the experimental density of 1.740 g/cm³ measured by the flotation method in a mixture of carbon tetrachloride and 1,2-dibromoethane. ω scans of several low 2θ angle reflections gave peak widths at half-height of less than 0.26°, indicating a satisfactory mosaic spread for the crystal.

Axial photographs indicated that the crystal belonged to the monoclinic system. Intensity data for zero and upper levels were collected at a rapid scan rate and the intensities examined carefully for systematic absences. The absence of $l = 2n + 1$ for $h0l$ reflections is consistent only with space group $P2_1/c$ (No. 13¹²).

Intensity data were collected by using θ - 2θ scans with X-ray source and monochromator settings identical with those used for determination of the unit cell parameters. A variable scan rate of from 7.32 to 29.30°/min was used, and a scan width of 2.00° 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 a total background to scan time ratio of 1. No significant fluctuations were observed in the intensities of three standard reflections (700, 040, and 008) monitored every 97 reflections. Intensities were calculated from the total scan count (CT) and background counts by the relationship

$$I = CT - (\text{bgd1} + \text{bgd2})$$

The intensities were assigned standard deviations according to the formula

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

From a total of 2875 reflections collected in a complete quadrant ($k \geq 0, l \geq 0$) of data out to $2\theta = 50^\circ$, 2353 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; no corrections were made for absorption ($\mu = 13.7 \text{ cm}^{-1}$).

Crystallographic Data Collection for $[\text{Ni}_2(\text{Eta})_2(\text{EtaH})_4](\text{ClO}_4)_2$. The preparative batch yielded well-formed, blue, square-pyramidal and octahedral crystals. A square-pyramidal crystal having a base edge of 0.50 mm and height of 0.35 mm was mounted parallel to a base diagonal on a glass fiber and attached to a goniometer head. This direction corresponded to one of the cubic axes. Precession photographs of the $hk0$, $hk1$, $h0l$, $h1l$, and $h2l$ levels exhibited Laue symmetry m^3 and the systematic absences $0kl$ ($k = 2n + 1$), $h0l$ ($h = 2n + 1$), and $hk0$ ($h = 2n$). These conditions uniquely define the centrosymmetric cubic space group $Pa\bar{3}$ (T_h^6 - No. 205¹²). The crystal was transferred to a Picker automated diffractometer, and 14 reflections were aligned manually and used to refine the cell parameter by a least-squares procedure. The value obtained is $a = 13.85$ (1) Å. In both the cell refinement and the actual data collection, Zr-filtered Mo K α radiation ($\lambda = 0.70930$ Å) was used. The calculated density, 1.665 g cm⁻³, based on four dinuclear units per cell, agreed well with the observed density, 1.65 g cm⁻³, measured by the flotation method in a mixture of carbon tetrachloride and 1,2-dibromoethane. Symmetry requirements dictate that the dinuclear cations and the perchlorate anions align on the threefold axis, with site symmetries $\bar{3}$ and 3, respectively. Intensity data were collected in the manner previously described² to a 2θ limit of 50°. A takeoff angle of 1.8° was used. Three orthogonal reflections, of the form $[400]$, were monitored after every 150 reflections, and an approximately isotropic decrease of 24% was observed. This factor was taken into account during data processing. The corrected intensities were assigned standard deviations according to the formula¹³

$$\sigma(I) = [CT + 4.5 + (t_c/t_b)^2(\text{bgd1} + \text{bgd2} + 9.0) + (pI)^2]^{1/2}$$

where p , the "ignorance factor", was assigned a value of 0.03, and the values of 4.5 and 9.0 account for uncertainties due to truncation of the last digit by the Picker scalar. After equivalent reflections were averaged, a total of 371 unique reflections were accepted as statistically above background on the basis that $I \geq 3\sigma(I)$. Lorentz and polarization corrections were applied in the usual way.

Solution and Refinement of the Structures. Computations were performed with standard programs;¹⁴ computations for the cobalt structure were carried out on a CDC Cyber 74 system, and computations for the nickel structure were carried out on a Univac 1108 computer. For structure factor calculations the scattering factors were taken from Cromer and Waber's tabulation¹⁵ for all atoms except hydrogen; Stewart's hydrogen atom scattering factors¹⁶ were used. The scattering factors for chlorine, cobalt, and nickel were corrected for the real and imaginary anomalous dispersion components by using the factors given by Cromer.¹⁷ The agreement factors are defined in the usual way as

$$R = (\sum ||F_o| - |F_c||) / (\sum |F_o|)$$

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

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

$[\text{Co}_2(\text{Eta})_3(\text{EtaH})_3](\text{ClO}_4)_3 \cdot 1/2 \text{H}_2\text{O}$. Atomic coordinates for a set of cobalt atoms in general positions were obtained from a three-dimensional Patterson synthesis; the remaining atoms were located by successive least-squares refinements and Fourier syntheses. Full-matrix least-squares refinement, utilizing isotropic temperature factors, for all nonhydrogen atoms except the water oxygen converged with $R = 0.135$ and $R_w = 0.152$. Anisotropic thermal parameters were introduced for cobalt, chlorine, and oxygen atoms, and further refinement reduced R to 0.087 and R_w to 0.098. The water oxygen atom and the 20 hydrogen atoms were located as the principal features on a difference electron density map; in subsequent refinements the hydrogen atoms were included at calculated positions, and the hydrogen thermal parameters were varied isotropically. With a total of 215 parameters varied, the refinement converged with $R = 0.062$ and $R_w = 0.076$. In the final cycle of refinement, the maximum parameter shift was $0.26\sigma(U_{11}$ of O3). Final positional and thermal parameters are given in Table I. A list of calculated and observed structure factors is available.¹⁸

$[\text{Ni}_2(\text{Eta})_2(\text{EtaH})_4](\text{ClO}_4)_2$. Coordinates for the nickel and chlorine atoms were deduced from a three-dimensional Patterson synthesis and refined to give the initial residuals $R = 0.31$ and $R_w = 0.38$. The remaining atoms were located by means of successive Fourier syntheses and least-squares refinement. Refinement with all nonhydrogen atoms, using isotropic temperature factors, converged with $R = 0.161$ and $R_w = 0.130$.

Consideration of larger thermal parameters for the chelate ring atoms and residual electron density in the vicinity of the chelates in difference Fourier maps led to introduction of a disordered model for the structure. Distinct atomic positions supplemental to those initially chosen were evident for oxygen, nitrogen, and one of the two carbon atoms in the chelate group. Isotropic temperature and individual positional parameters were henceforth refined for each of these three additional disordered atoms. A single variable was refined to describe the occupancies (α and $1 - \alpha$) of the disordered ligands. The final occupancies for ligand 1 and ligand 2 were 0.690 (9) and 0.310 (9), respectively. The nature of the disorder is treated in greater detail in the Discussion section. The assumption of individually refined occupancy factors for the disordered atoms did not significantly improve the R factor. Anisotropic thermal parameters and disordered atoms were introduced, and further refinement reduced R to 0.088 and R_w to 0.064.

In the final refinements, the methylene and amine hydrogens were included (but not refined) in calculated positions of C_{2v} symmetry ($C-H = N-H = 0.95$ Å and $X-Y-H = H-Y-H = 109.5^\circ$ where X and Y are carbon or nitrogen atoms). Hydrogens involved in the polynuclear bridge were not located, despite some attempts to do so. The maximum parameter shifts in the final cycle of refinement were $0.03\sigma(z$ coordinate of O2), and the final residuals were $R = 0.073$ and $R_w = 0.052$. The magnitude of the highest feature on a final difference Fourier map, $0.66 \text{ e} \text{ \AA}^{-3}$, may be compared to the value of $2.6 \text{ e} \text{ \AA}^{-3}$ for a typical carbon atom in this structure. Final atomic parameters are tabulated in Table II. A list of calculated and observed structure factors is available.¹⁸

Discussion

Both structures contain dinuclear cations and perchlorate anions; the cobalt structure also contains water of crystallization. Selected interatomic distances and angles are presented in Table III; these are consistent with previous structures of 2-aminoethanol complexes.^{1,19} The dinuclear cations are made up of pairs of octahedral tris chelates joined face-to-face through their oxygen faces by hydrogen bonds. Although they are alike in some ways, there are distinct differences in the cations of the two structures.

Each cation in $[\text{Co}_2(\text{Eta})_3(\text{EtaH})_3](\text{ClO}_4)_3 \cdot 1/2 \text{H}_2\text{O}$, Figure 1, occupies a site of twofold symmetry. The two tris chelates that form the cation are of the same chirality, and they are oriented so that their oxygen faces form a trigonal prism with one oxygen-oxygen distance of 2.396 (10) Å and two oxy-

Table I. Atomic and Thermal^a Parameters for [Co₂(Eta)₃(EtaH)₃](ClO₄)₃·1/2H₂O

atom	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Co	-0.20362 (5)	0.26568 (7)	0.22286 (4)	0.0302 (5)	0.0316 (4)	0.0332 (4)	0.0002 (2)	0.0194 (3)	0.0004 (2)
Cl1	-0.3057 (2)	0.2088 (2)	0.5026 (1)	0.077 (1)	0.0518 (9)	0.091 (1)	0.0151 (8)	0.062 (1)	0.0107 (7)
Cl2 ^b	-0.50	0.3377 (2)	-0.25	0.051 (1)	0.054 (1)	0.0416 (9)	0.0	0.0249 (8)	0.0
O1	-0.0995 (3)	0.4413 (4)	0.2483 (2)	0.042 (2)	0.029 (2)	0.050 (2)	-0.004 (1)	0.028 (2)	-0.003 (1)
O2	-0.1589 (3)	0.1939 (4)	0.1353 (2)	0.035 (2)	0.039 (2)	0.036 (2)	-0.003 (1)	0.020 (1)	0.002 (1)
O3	-0.0646 (3)	0.1556 (4)	0.3229 (2)	0.039 (2)	0.036 (2)	0.043 (2)	0.006 (1)	0.023 (2)	0.001 (1)
O41	-0.2033 (7)	0.171 (1)	0.4928 (5)	0.098 (5)	0.190 (7)	0.112 (5)	0.056 (5)	0.074 (4)	0.071 (5)
O42	-0.3726 (8)	0.0836 (9)	0.5032 (6)	0.136 (6)	0.094 (5)	0.164 (7)	0.021 (5)	0.074 (6)	-0.032 (5)
O43	-0.385 (1)	0.306 (2)	0.434 (1)	0.141 (7)	0.23 (1)	0.39 (2)	0.23 (1)	0.19 (1)	0.118 (8)
O44	-0.273 (2)	0.281 (2)	-0.418 (1)	0.37 (2)	0.29 (2)	0.31 (2)	-0.21 (2)	0.26 (2)	-0.16 (2)
O51	-0.409 (2)	0.256 (2)	-0.1802 (6)	0.37 (2)	0.37 (2)	0.083 (5)	0.101 (7)	0.123 (8)	0.31 (2)
O52	-0.453 (1)	0.413 (2)	-0.2946 (5)	0.23 (1)	0.36 (2)	0.079 (4)	0.002 (7)	0.049 (6)	-0.22 (1)
O6 ^c	-0.50	-0.077 (2)	-0.25	0.16 (2)	0.08 (1)	0.45 (5)	0.0	0.25 (3)	0.0
N1	-0.2433 (4)	0.3479 (5)	0.3141 (3)	0.043 (2)	0.051 (3)	0.047 (2)	-0.003 (2)	0.029 (2)	0.005 (2)
N2	-0.3439 (4)	0.3727 (5)	0.1152 (3)	0.037 (2)	0.050 (3)	0.042 (2)	0.000 (2)	0.020 (2)	0.006 (2)
N3	-0.3037 (4)	0.0800 (5)	0.1994 (3)	0.047 (3)	0.037 (2)	0.063 (3)	-0.003 (2)	0.034 (2)	-0.11 (2)
C11	-0.1349 (7)	0.4545 (8)	0.3765 (4)	0.069 (4)	0.075 (4)	0.051 (3)	-0.026 (3)	0.036 (3)	-0.10 (3)
C12	-0.1052 (6)	0.5448 (7)	0.3128 (5)	0.060 (4)	0.044 (3)	0.071 (4)	-0.022 (3)	0.040 (3)	-0.004 (3)
C21	-0.3588 (6)	0.3059 (8)	0.0262 (4)	0.055 (3)	0.064 (4)	0.039 (3)	0.000 (3)	0.023 (3)	0.010 (3)
C22	-0.2238 (6)	0.2758 (7)	0.0480 (4)	0.053 (3)	0.066 (4)	0.035 (3)	0.005 (2)	0.025 (3)	0.008 (3)
C31	-0.2310 (7)	-0.0228 (9)	0.2808 (7)	0.066 (4)	0.061 (4)	0.105 (6)	0.028 (4)	0.023 (4)	-0.010 (4)
C32	-0.0929 (7)	-0.0045 (8)	0.3188 (6)	0.061 (4)	0.045 (3)	0.107 (6)	0.033 (4)	0.042 (4)	-0.001 (3)

atom	x	y	z	U, Å ²	atom	x	y	z	U, Å ²
HO1 ^b	0.00	0.428 (7)	0.25	0.02 (2)	HC12	-0.0135 (6)	0.6020 (7)	0.3547 (5)	0.07 (2)
HO2	-0.068 (8)	0.171 (9)	0.155 (5)	0.08 (2)	HC12	-0.1802 (6)	0.6281 (7)	0.2739 (5)	0.07 (2)
HN1	-0.2490 (4)	0.2572 (5)	0.3558 (3)	0.07 (2)	HC21	-0.4133 (6)	0.2012 (8)	0.0080 (4)	0.10 (3)
HN1	-0.3339 (4)	0.4088 (5)	0.2779 (3)	0.08 (2)	HC21	-0.4072 (6)	0.3856 (8)	-0.0318 (4)	0.10 (2)
HN2	-0.3213 (4)	0.4925 (5)	0.1194 (3)	0.08 (2)	HC22	-0.1746 (6)	0.3820 (7)	0.0550 (4)	0.07 (2)
HN2	-0.4324 (4)	0.3581 (5)	0.1151 (3)	0.09 (2)	HC22	-0.2267 (6)	0.2086 (7)	-0.0078 (4)	0.05 (2)
HN3	-0.3190 (4)	0.0256 (5)	0.1357 (3)	0.08 (2)	HC31	-0.2588 (7)	-0.1392 (9)	0.2582 (7)	0.4 (1)
HN3	-0.3959 (4)	0.1071 (5)	0.1911 (3)	0.13 (3)	HC31	-0.2521 (7)	0.0049 (9)	0.3350 (7)	0.27 (9)
HC11	-0.1640 (7)	0.5299 (8)	0.4136 (4)	0.06 (2)	HC32	-0.0667 (7)	-0.0617 (8)	0.2733 (6)	0.19 (6)
HC11	-0.0508 (7)	0.3906 (8)	0.4272 (4)	0.09 (2)	HC32	-0.0388 (7)	-0.0529 (8)	0.3891 (6)	0.10 (3)

^a The form of the anisotropic thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{12}hka^{*}b^{*} + U_{13}hla^{*}c^{*} + U_{23}klb^{*}c^{*})]$.

^b Occupancy factors for atoms Cl2 and HO1 in special positions were set at 0.5. ^c Occupancy factor for the water oxygen O6 was set at 0.25.

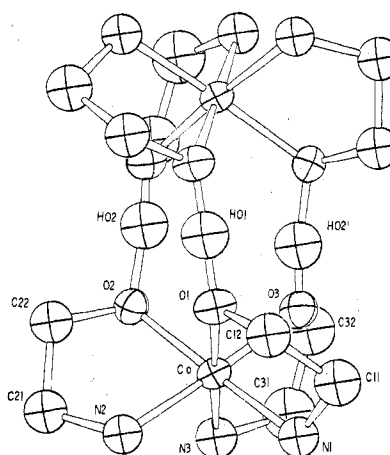


Figure 1. Perspective view of the dinuclear cobalt(III) cation [Co₂(Eta)₃(EtaH)₃]³⁺. A twofold axis perpendicular to the plane of the page and through HO1 relates the two tris chelates (HO2' is related to HO2 by the twofold rotation). Hydrogen atoms bonded to carbon and to nitrogen have been omitted.

gen-oxygen distances of 2.442 (7) Å; the hydrogen atoms are located very close to the edges of the trigonal prism. Although each cation is optically active, the two cations in the unit cell are related to each other by inversion, and the crystal is, thus, racemic.

The cations in [Ni₂(Eta)₂(EtaH)₄](ClO₄)₂, Figure 2, occupy sites of $\bar{3}$ symmetry and, thus, correspond to the meso isomer. The disorder observed for ligand positions could result from a mixture of optically active isomers, but such a model should refine to occupancy factors of 0.5 regardless of the ratio of the two isomers. The refinement of occupancy factors to 0.69

and 0.31 is only consistent with a disorder in the orientation of the meso isomer. Considering the cation whose center occupies the origin of the unit cell, one observes that the nickel with positive coordinates can have either the Δ or the Λ ligand configuration, giving rise to two distinct and disordered sets of ligand coordinates. Because of the $\bar{3}$ symmetry of the cation, the two tris chelates are oriented so that their oxygen faces form an octahedron. With four alcohol groups and two alkoxide groups, each alkoxide group can form two hydrogen bonds. It is not possible to locate the actual hydrogen positions since symmetry requires the six oxygen-oxygen distances corresponding to octahedron edges to be equivalent; these are 2.68 Å for one ligand and 2.73 Å for the alternate (disordered) ligand. Construction of molecular models indicates that the best configuration would place the alkoxide groups in trans positions.

The cations of the two structures also differ in the conformation of chelate rings (Figure 3). In all cases, the five-membered rings achieve the unstrained gauche configuration, but for the nickel tris chelate the configuration is $\Delta\delta\delta\delta$ or $\Delta\lambda\lambda\lambda$, and for the cobalt tris chelate the configuration is $\Lambda\delta\delta\lambda$ or $\Delta\lambda\lambda\delta$. The configuration of the nickel tris chelate corresponds to the conformation calculated to be lowest in energy for a tris chelate of ethylenediamine.²⁰ However, the hydrogen bonding in the present complexes could easily change the relative stabilities; hydrogen bonding was suggested²¹ as an explanation for other configurations of tris(ethylenediamine)chromium(III) observed in crystal structures.

The different arrangements of oxygen atoms in the two structures is also interesting. In an earlier structure, Co₃(Eta)₆²⁺, the trigonal-prismatic arrangement of oxygens was attributed¹⁹ to steric interactions between hydrogens on the α -carbon atoms. For [Co₂(Eta)₃(EtaH)₃]³⁺ we have generated

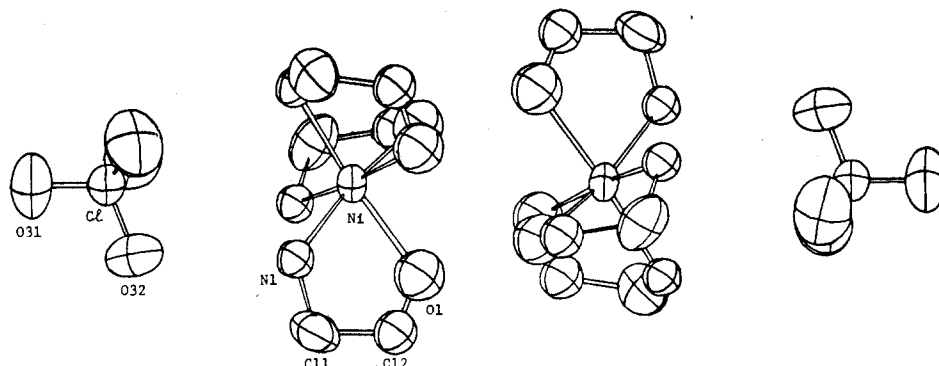


Figure 2. Perspective view of the dinuclear nickel(II) cation (with hydrogens omitted) and the perchlorate anions along a threefold axis. The threefold axis is horizontal in the plane of the page and passes through O31, Cl, and Ni. An inversion center on the threefold axis relates the left half of the figure to the right half.

Table II. Atomic and Thermal^a Parameters for $[\text{Ni}_2(\text{Eta})_2(\text{EtaH})_4](\text{ClO}_4)_2$

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	0.0955 (1)	0.0955	0.0955	0.0103 (2)	0.0103	0.0103	-0.0015 (2)	-0.0015	-0.0015
C11	0.287 (1)	0.043 (1)	-0.044 (1)	0.013 (2)	0.029 (2)	0.018 (2)	-0.002 (2)	-0.002 (2)	-0.002 (2)
Cl	0.2821 (2)	0.2821	0.2821	0.0126 (2)	0.0126	0.0126	-0.0013 (4)	-0.0013	-0.0013
O31	0.3392 (7)	0.3392	0.3392	0.026 (1)	0.026	0.026	-0.006 (2)	-0.006	-0.006
O32	0.3348 (7)	0.2127 (8)	0.2348 (9)	0.022 (2)	0.032 (2)	0.034 (2)	0.010 (2)	-0.001 (2)	-0.012 (2)

atom	x	y	z	$U, \text{\AA}^2$	atom	x	y	z	$U, \text{\AA}^2$
O1 ^b	0.136 (1)	-0.035 (1)	0.034 (1)	0.087 (5)	N2	0.229 (2)	0.050 (2)	0.143 (2)	0.049 (4)
O2	0.141 (2)	0.012 (2)	-0.023 (2)	0.087 (5)	C12	0.222 (2)	-0.031 (1)	-0.002 (2)	0.065 (5)
N1	0.234 (1)	0.133 (1)	0.051 (1)	0.049 (4)	C22	0.236 (4)	-0.006 (3)	-0.030 (3)	0.065 (5)

^a The form of the anisotropic thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{12}hka^*b^* + U_{13}hla^*c^* + U_{23}klb^*c^*)]$.

^b The occupancy factor, α , for disordered atoms O1, C12, and N1 refined to the value 0.690 (9). The corresponding value, $1 - \alpha$, for atoms O2, C22, and N2 is 0.310 (9).

Table III. Selected Interatomic Distances and Angles

	M = Ni		M = Co		
	n = 1	n = 2	n = 1	n = 2	n = 3
Interatomic Distances (Å) within the Cations					
M-M'	4.582 (2)		4.538 (2)		
M-Nn	2.08 (1)	2.05 (3)	1.944 (4)	1.946 (4)	1.947 (3)
Nn-Cn1	1.45 (2)	1.58 (3)	1.502 (8)	1.503 (7)	1.472 (9)
Cn1-Cn2	1.50 (2)	1.42 (5)	1.50 (1)	1.506 (9)	1.46 (1)
Cn2-On	1.29 (2)	1.34 (5)	1.429 (6)	1.427 (7)	1.441 (7)
On-M	2.07 (1)	2.10 (3)	1.897 (3)	1.898 (3)	1.900 (3)
On1-On1''	2.73 (2)	2.68 (5)	2.38 (1)	2.445 (7)	
Interatomic Angles (deg) within the Cations					
On-M-Nn	81.2 (5)	79 (1)	86.1 (2)	85.7 (2)	85.7 (2)
M-Nn-Cn1	106 (1)	102 (1)	106.4 (3)	108.0 (3)	108.4 (4)
Nn-Cn1-Cn2	96 (1)	113 (2)	107.0 (5)	105.9 (4)	109.5 (6)
Cn1-Cn2-On	115 (2)	110 (4)	108.0 (5)	106.8 (5)	108.5 (6)
Cn2-On-M	112 (1)	117 (3)	113.4 (3)	112.1 (3)	112.0 (4)
Interatomic Distances (Å) within the Perchlorate Anions					
	M = Ni	M = Co			
	n = 3	n = 4	n = 5		
Cln-On1	1.37 (2)	1.372 (6)	1.318 (8)		
Cln-On2	1.37 (1)	1.369 (7)	1.318 (7)		
Cln-On3		1.342 (9)			
Cln-On4		1.32 (1)			

the Δ - Λ octahedral, Δ - Δ octahedral, and Δ - Λ trigonal-prismatic isomers, assuming no change in Co-Co distance and no change in ligand conformation, and have compared the hydrogen-hydrogen interactions in these isomers to those observed in the Δ - Δ trigonal-prismatic isomer. Several hydrogen-hydrogen distances in the Δ - Λ trigonal-prismatic and the Δ - Δ octahedral isomers were less than twice the van der Waals radius of hydrogen (2.2 Å); on the other hand, all hydrogen-hydrogen distances for the Δ - Δ trigonal-prismatic

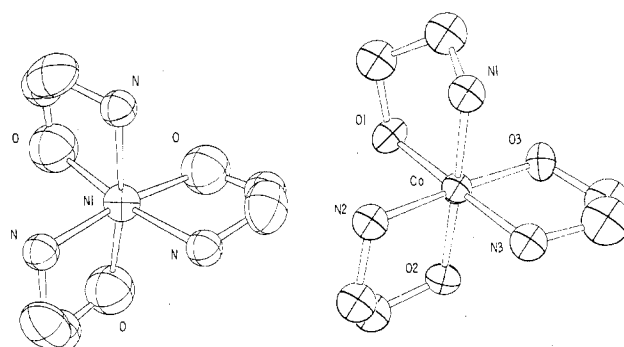


Figure 3. Projection of the cobalt(III) and nickel(II) tris chelates, viewed down the threefold axis, showing the conformation of chelate rings. In the $\Delta\delta\delta$ nickel(II) complex, the carbon-carbon axes of all three chelate rings are approximately parallel to the threefold axis; in the $\Delta\delta\delta\lambda$ cobalt(III) complex, the carbon-carbon axis of one chelate (N1, O1) makes an angle of $\sim 60^\circ$ with the threefold axis.

isomer and the Δ - Λ octahedral isomer are longer than 2.6 Å.

Registry No. $[\text{Co}_2(\text{Eta})_3(\text{EtaH})_3](\text{ClO}_4)_3 \cdot 1/2\text{H}_2\text{O}$, 70623-46-0; $[\text{Ni}_2(\text{Eta})_2(\text{EtaH})_4](\text{ClO}_4)_2$, 70748-79-7.

Supplementary Material Available: Listings of structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) Part 1: Bertrand, J. A.; Howard, W. J.; Kalyanaraman, A. R. *Chem. Commun.* **1971**, 437.
- (2) Part 2: Bertrand, J. A.; Black, T. D.; Eller, P. G.; Helm, F. T.; Mahmood, R. *Inorg. Chem.* **1976**, *15*, 2965.
- (3) Taken in part from the Ph.D. thesis of Etsuko Fujita, Georgia Institute of Technology, 1976.
- (4) Yoneda, H.; Kida, S. *J. Am. Chem. Soc.* **1960**, *82*, 2139.

- (5) Evreev, V. N. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1967**, *12*, 1112.
 (6) Evreev, V. N.; Petrun'kin, V. E. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1968**, *13*, 1552.
 (7) Gerasenkova, A. N.; Udovenko, V. V. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1968**, *13*, 1551.
 (8) Hieber, W.; Levy, E. *Z. Anorg. Allg. Chem.* **1934**, *219*, 225.
 (9) Kida, S. *Nippon Kagaku Zasshi* **1964**, *85*, 32.
 (10) Figgis, B. N.; Lewis, J. "Modern Coordination Chemistry"; J. Lewis and R. G. Wilkins, Eds.; Interscience: New York, 1960.
 (11) Numbers in parentheses here and elsewhere in this paper indicate estimated standard deviations in the least significant digit(s).
 (12) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1952; Vol. I.
 (13) Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197.
 (14) Programs utilized were Zalkin's FORDAP Fourier summation program, Ibers' NUCLS modification of the Busing-Martin-Levy least-squares program, Doeden's RBANG rigid group orientation program, Stewart's ABSORB absorption correction program from the X-Ray 72 system, and Johnson's ORTEP program.
 (15) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.
 (16) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.
 (17) Cromer, D. T. *Acta Crystallogr.* **1965**, *18*, 17.
 (18) Supplementary material.
 (19) Bertrand, J. A.; Kelley, J. A.; Vassian, E. G. *J. Am. Chem. Soc.* **1969**, *91*, 2394.
 (20) Corey, E. J.; Bailar, J. C. *J. Am. Chem. Soc.* **1959**, *81*, 2620.
 (21) Raymond, K. N.; Corfield, P. W. R.; Ibers, J. A. *Inorg. Chem.* **1968**, *7*, 842.

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Structure of a Methylidiazido Complex of Tungsten, $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2(\text{N}_2\text{CH}_3)$, at Low Temperature

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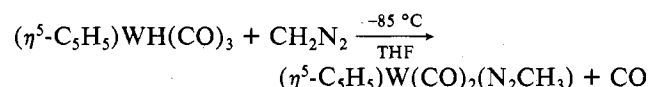
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The structure of the methylidiazido complex $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2(\text{N}_2\text{CH}_3)$ has been determined at -140°C by using X-ray diffraction techniques. The complex, prepared by the action of CH_2N_2 on $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{H}$, appears to have a normal methyl group attached in a singly bent fashion to the $\text{N}(2)\text{-N}(1)\text{-W}$ linkage with $\text{W-N}(1) = 1.856(3) \text{ \AA}$, $\text{N}(1)\text{-N}(2) = 1.215(5) \text{ \AA}$, $\text{W-N}(1)\text{-N}(2) = 173.3(3)^\circ$ and $\text{N}(1)\text{-N}(2)\text{-C}(8) = 116.5(4)^\circ$. The complex is monomeric and has the expected "three-legged" stool geometry about the metal. As compared to the CO groups, the methylidiazido ligand exerts a trans shortening influence on part of the C_5H_5 group, causing a shortening of the $\text{W-C}(7)$ bond by about 0.03 \AA . The title complex crystallized in space group $P1$ with $a = 7.003(2) \text{ \AA}$, $b = 10.988(3) \text{ \AA}$, $c = 6.542(2) \text{ \AA}$, $\alpha = 104.56(1)^\circ$, $\beta = 107.16(1)^\circ$, $\gamma = 86.76(2)^\circ$, and $Z = 2$. On the basis of 2059 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ the structure was refined by using full-matrix, least-squares methods to $R(F) = 0.019$ and $R_w(F) = 0.033$.

Introduction

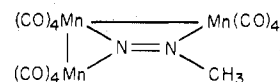
There has been considerable interest in organodiazido complexes because they are intermediates in the metal-assisted reduction of dinitrogen to organic amines and because analogous species are postulated intermediates in the synthetic reduction of dinitrogen to ammonia using $\text{W}(0)$ and $\text{Mo}(0)$ complexes.^{1,2} Organodiazido ligands and the nitrosyl ligand are isoelectronic, and the structural properties of aryldiazido complexes seem to parallel those of their nitrosyl analogues although there are some marked differences in the reactions of the coordinated ligands. Because very little structural data were known for alkyldiazido ligands, we undertook the present structural study in order to determine if there are any important differences between aryl- and alkyldiazido ligands in similar coordination environments.

It is noteworthy that there are far fewer aryldiazido complexes than analogous nitrosyl complexes and that there are far fewer yet alkyldiazido complexes. Furthermore, the only known terminal alkyldiazido complexes contain molybdenum or tungsten. Alkylhydrazines are used to produce $\text{Mo}(\text{N}_2\text{R})\text{-}(\text{S}_2\text{CNET}_2)_3$ ³ and $\text{Mo}(\text{N}_2\text{R})_2(\text{S}_2\text{CNET}_2)_2$,⁴ alkylation of dinitrogen complexes yields $\text{MoI}(\text{N}_2\text{R})(\text{diphos})_2$ ⁵ and $\text{WBr}(\text{N}_2\text{R})(\text{diphos})_2$,⁶ the action of diazoalkanes on metal hydride complexes gave the first reported alkyldiazido complexes $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{N}_2\text{R})$ and $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2(\text{N}_2\text{R})$.^{7,8}



We now report an improved synthesis for $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2(\text{N}_2\text{CH}_3)$ and its structure using single-crystal X-ray

diffraction techniques. Low temperatures were used in order to improve the final structural precision, reduce unwanted thermal motion, and avoid thermal decomposition. The only previously reported structure of a terminal alkyldiazido complex is $\text{MoI}(\text{N}_2\text{R})(\text{diphos})_2$ where R is cyclohexyl; although the general structural features of the cyclohexyldiazido group were determined, accurate metrical parameters for the diazo ligand could not be obtained.⁹ The structure of a three-coordinate, bridging methylidiazido ligand is also known.¹⁰



Experimental Section

Improved Preparation of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2(\text{N}_2\text{CH}_3)$. The title complex was synthesized by the following improved and scaled-up procedure with the usual Schlenk techniques (N_2 as inert gas; rigorously dried, nitrogen-saturated solvents). A magnetically stirred solution of 10.02 g (30 mmol) of resublimed $(\eta^5\text{-C}_5\text{H}_5)\text{WH}(\text{CO})_3$ ¹¹ in 250 mL of tetrahydrofuran was treated at -85°C with 70 mmol of diazomethane¹² (0.10 M ethanol-free solution in diethyl ether) by dropwise addition. The slow addition of the diazomethane solution took about 40 min. Under these conditions it was not necessary to precool the diazomethane solution lower than 0°C . After the addition of diazomethane was complete, the reaction mixture was allowed to slowly warm up to room temperature (ca. 2 h). For completion of the reaction, the mixture was stirred another 2 h at room temperature. After volatile byproducts and the solvents were removed under vacuum, the oily, dark red residue was chromatographed on a silica column ($l = 85 \text{ cm}$, $\phi = 3 \text{ cm}$; column temperature ca. $+10^\circ\text{C}$; silica 60, act. II-III, 70-230 mesh ASTM, Merck 7734) with benzene as eluant. A small amount of $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3(\text{CH}_3)$ was eluted as a fast-moving yellow band, while the desired product was obtained by eluting the dark red band. The solvent was removed, and the remaining oily residue was crystallized twice from pentane-diethyl ether solutions

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