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Structure of a Tetranuclear Cobalt(II)–Cobalt(III) Complex of Bis(2-hydroxyethyl)amine, $[Co_4\{NH(C_2H_4OH)_2\}_2\{NH(C_2H_4O)_2\}_4](ClO_4)_2$[1]

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The structure of $[Co_4(DetaH_2)_2(Deta)_4](ClO_4)_2$ (where $DetaH_2$ represents bis(2-hydroxyethyl)amine and $Deta^{2-}$ represents the anion formed by removing two protons from bis(2-hydroxyethyl)amine) has been determined crystallographically and consists of tetranuclear cations and perchlorate anions. The compound crystallizes in the monoclinic space group $P2_1/c$ with two formula units in a unit cell of dimensions $a = 8.747$ (2) Å, $b = 17.408$ (4) Å, $c = 13.597$ (3) Å, $\beta = 111.45$ (2)°, $\rho_{exptl} = 1.80$ g/cm^3, and $\rho_{calcd} = 1.82$ g/cm^3. The structure was solved by Patterson methods. Least-squares refinement converged at final values of $R = 0.045$ and $R_w = 0.035$ for 2719 reflections with $I \geq 2\sigma(I)$. The centrosymmetric tetranuclear cation contains two cobalt(III) ions, each coordinated by two tridentate $Deta^{2-}$ ligands in a cis-facial arrangement. These $Co(Deta)_2^-$ units bridge through the three oxygens of one face to the cobalt(II) ions; one oxygen coordinates both cobalt(II) ions, and each of the other two oxygens coordinates one of the cobalt(II) ions. The octahedral coordination of each cobalt(II) ion is completed by a bidentate (N,O) $DetaH_2$ ligand. Cobalt(III)–oxygen distances range from 1.888 (3) to 1.940 (3) Å; cobalt(III)–nitrogen distances are 1.968 (4) and 1.957 (4) Å. Cobalt(II)–oxygen distances range from 2.045 (3) to 2.225 (3) Å, and the cobalt(II)–nitrogen distance is 2.241 (4) Å.

Introduction

Cobalt complexes of bis(2-hydroxyethyl)amine (abbreviated $DetaH_2$ in formulas; $DetaH^-$ and $Deta^{2-}$ will be used for the anions resulting from removal of one and two protons, respectively) were first reported[2] by Hieber and Levy in 1932. Mononuclear and dinuclear structures were proposed for cobalt(II) compounds with formulas $Co(DetaH)(H_2O)X$, $Co_2(DetaH)_3(H_2O)X$, $Co_2(DetaH)(Deta)(H_2O)_4X$, and $Co_2(DetaH)(Deta)(H_2O)X$ (where X = Cl, Br, or I).

More recently, compounds with similar formulas were isolated, and potentiometric analyses for cobalt(II) and for total cobalt indicated that these compounds contained equal amounts of cobalt(II) and cobalt(III). The compounds were formulated as $Co(DetaH_2)(Deta)_2X\cdot H_2O$,[3] $Co_2(Deta)_2X\cdot 4H_2O$[3] (where X = Cl, Br, or I), $Co_2(DetaH_2)(Deta)_2ClO_4\cdot nH_2O$ (n = 1 or 3),[4] and $Co_2(Deta)_2ClO_4\cdot 2H_2O$.[4] Treatment of these compounds with hydroxide bases precipitated cobalt(II) hydroxide and cobalt(III) compounds, $M[Co(Deta)_2]\cdot nH_2O$ (M = Na, n = 8; M = K, n = 7) were isolated. On the basis of spectral studies, a trans-facial arrangement of ligands was proposed for these cobalt(III) complexes. For the mixed-valence compounds, dinuclear structures involving edge-sharing octahedra were proposed.

As part of a continuing investigation of structures of transition-metal complexes of amino alcohols, we have repeated the preparation of $Co_2(DetaH_2)(Deta)_2ClO_4\cdot H_2O$ and have determined the crystal structure for this compound. On the basis of the density of the crystals and the results of the structure study, we formulate this compound as the anhydrous material $[Co_4(DetaH_2)_2(Deta)_4](ClO_4)_2$ rather than as the hydrate.

Experimental Section

Preparation. The compound $[Co_4(DetaH_2)_2(Deta)_4](ClO_4)_2$ was prepared by a slight modification of the published method.[4] A solution of 3.66 g (10 mmol) of $Co(ClO_4)_2\cdot 6H_2O$ in 15 mL of water was mixed with a solution of 6.30 g (60 mmol) of bis(2-hydroxyethyl)amine in 30 mL of methanol. The resulting pink solution was air-oxidized and filtered. After 1 week, dark green, needle-shaped crystals were obtained. Anal. Calcd for $Co_4C_{24}H_{58}N_6O_{20}Cl_2$: C, 27.26; H, 5.53; N, 7.95. Found: C, 26.51; H, 5.76; N, 7.74.

Magnetic Susceptibility. The magnctic susceptibility was determined by the Faraday method using $HgCo(NCS)_4$ as calibrant. Diamagnetic corrections were applied using tabulated values.[5] The experimental moments per gram-atom of cobalt(II) are 5.19 μ_B at 298 K, 5.19 μ_B at 195 K, and 5.07 μ_B at 93 K.

Collection of X-ray Diffraction Data. A dark green needle crystal with approximate dimensions 0.1 × 0.1 × 0.3 mm was mounted on a glass fiber using epoxy cement such that the longest crystal dimension (a^*) 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 Kα radiation at a takeoff angle of 6.75°. Fifteen reflections whose 2θ values ranged from 6.74 to 20.10° were machine-centered and used in least-squares refinement of the lattice parameters and orientation matrix. Unit cell parameters obtained were $a = 8.747$ (2) Å,[6] $b = 17.408$ (4) Å, $c = 13.597$ (3) Å, $\beta = 111.45$ (2)°, and $V = 1926.8$ (8) Å^3. The calculated density of 1.82 g cm^{-3} for 8 cobalts/unit cell agrees with the experimental density of 1.80 g cm^{-3} measured by the flotation method using a mixture of carbon tetrachloride and ethylene dibromide. ω scans of several low 2θ angle reflections gave peak widths at half-height of less than 0.25°, 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 $h0l$ reflections with $l = 2n + 1$ and $0k0$ reflections with $k = 2n + 1$ is consistent only with space group $P2_1/c$ (No. 14).[7]

Intensity data were collected using θ–2θ 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 3.91 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 the total background time equal to scan time. No significant fluctuations were observed in the intensities of three standard reflections (400, 080, 004) monitored every 97 reflections. Intensities were calculated from the total scan count (CT) and background counts by the relationship

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

The intensities were assigned standard deviations according to the formula

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

from a total of 3804 reflections collected in a complete quadrant (h and k positive) of data out to $2\theta = 50°$; 2719 were accepted as statistically above background on the basis that I was greater than $2\sigma(I)$. Lorentz and polarization corrections were made in the usual way, but no corrections were made for absorption.

Solution and Refinement of the Structure. Computations were performed using standard programs;[8] all computations were carried out on the CDC Cyber 74 system. For structure factor calculations, the scattering factors were taken from Cromer and Waber's tabulation[9] for all atoms except hydrogen; Stewart's hydrogen atom scattering factors[10] were used. The scattering factor(s) for cobalt and chlorine were corrected for the real and imaginary anomalous dispersion

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Table I. Positional and Thermal Parameters for $[Co_2(Deta)_2(DetaH_2)]_2(ClO_4)_2$[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co1	0.09258 (7)	−0.02618 (3)	0.20073 (4)	3.03 (3)	2.11 (2)	1.77 (2)	0.33 (3)	0.75 (2)	0.04 (3)
Co2	0.14060 (7)	0.06711 (3)	0.02038 (4)	2.63 (3)	2.69 (2)	1.99 (2)	−0.16 (3)	0.92 (2)	−0.03 (2)
Cl	0.4018 (2)	−0.3451 (1)	0.0861 (1)	4.75 (8)	3.9 (1)	2.94 (6)	−0.06 (3)	0.70(4)	0.00 (9)
PO1	0.5667 (7)	−0.3553 (4)	0.1066 (7)	5.47 (2)	9.8 (4)	23.6 (7)	2.0 (5)	4.2 (3)	6.7 (4)
PO2	0.3416 (6)	−0.2830 (3)	0.0157 (3)	7.2 (2)	7.0 (2)	6.7 (3)	1.1 (2)	2.0 (2)	2.9 (2)
PO3	0.3164 (7)	−0.4128 (3)	0.0408 (3)	12.2 (2)	7.0 (2)	5.8 (2)	−4.2 (3)	1.8 (2)	−1.3 (2)
PO4	0.3735 (10)	−0.3332 (3)	0.1796 (4)	21.1 (6)	9.0 (4)	5.4 (3)	4.3 (3)	6.1 (3)	0.7 (2)
O11	−0.0424 (3)	0.0338 (1)	0.0842 (2)	2.6 (1)	2.3 (1)	2.2 (1)	0.3 (1)	1.0 (1)	0.4 (1)
O12	−0.0810 (4)	−0.0624 (2)	0.2460 (2)	4.6 (2)	3.0 (1)	2.6 (1)	−0.7 (1)	1.9 (1)	−0.3 (1)
O21	0.2639 (3)	0.0136 (2)	0.1619 (2)	2.5 (1)	4.1 (1)	2.7 (1)	0.5 (1)	0.7 (1)	0.4 (1)
O22	0.0499 (4)	−0.1097 (2)	0.1059 (2)	4.5 (2)	2.2 (1)	2.4 (1)	0.8 (1)	0.5 (1)	−0.8 (1)
O31	0.3059 (4)	0.0705 (2)	−0.0595 (2)	3.9 (2)	5.0 (1)	3.3 (1)	−1.1 (2)	1.8 (1)	−1.1 (2)
O32	0.1723 (8)	0.2969 (3)	0.1957 (4)	13.2 (4)	4.5 (2)	5.2 (2)	2.2 (2)	0.3 (2)	0.2 (2)
N1	0.0998 (5)	0.0632 (2)	0.2910 (3)	3.7 (2)	2.8 (1)	2.6 (1)	−0.2 (2)	2.1 (2)	−0.6 (2)
N2	0.2599 (5)	−0.0916 (2)	0.3005 (3)	5.2 (2)	3.6 (2)	2.2 (1)	0.9 (2)	1.5 (2)	−1.3 (2)
N3	0.2772 (6)	0.1755 (2)	0.0876 (3)	5.2 (2)	4.1 (2)	3.4 (2)	−1.2 (2)	1.1 (2)	−0.3 (2)
C11	−0.1233 (6)	0.0914 (3)	0.1204 (4)	3.7 (2)	2.4 (2)	3.4 (2)	0.9 (2)	1.9 (2)	0.4 (2)
C12	−0.0028 (7)	0.1251 (3)	0.2221 (4)	5.1 (3)	2.1 (2)	3.4 (3)	0.6 (2)	2.2 (2)	0.1 (2)
C13	0.0358 (7)	0.0360 (3)	0.3736 (3)	5.7 (3)	3.8 (2)	2.0 (2)	−0.1 (2)	1.6 (2)	−0.4 (2)
C14	−0.1145 (7)	−0.0111 (3)	0.3184 (4)	5.8 (3)	3.8 (2)	3.3 (3)	−1.2 (2)	3.2 (2)	−0.5 (2)
C21	0.4125	−0.0247 (4)	0.2114 (5)	3.8 (3)	6.9 (4)	6.3 (3)	3.1 (3)	1.8 (2)	1.9 (3)
C22	0.4182 (8)	−0.0546 (4)	0.3153 (5)	4.1 (3)	5.6 (4)	5.4 (3)	1.4 (3)	−0.5 (2)	1.1 (3)
C23	0.2398 (9)	−0.1697 (3)	0.2546 (4)	8.0 (4)	2.8 (2)	3.7 (3)	1.8 (3)	−0.3 (2)	0.4 (2)
C24	0.1266 (14)	−0.1732 (4)	0.1526 (5)	19.8 (12)	3.9 (4)	5.6 (4)	5.3 (6)	−5.2 (5)	−2.3 (4)
C31	0.4062 (9)	0.1376 (4)	−0.0386 (5)	5.1 (3)	7.4 (4)	4.4 (3)	−3.1 (3)	2.7 (2)	−2.2 (3)
C32	0.4377 (8)	0.1599 (5)	0.0740 (13)	5.1 (3)	7.6 (4)	4.8 (3)	−2.9 (3)	2.1 (2)	−1.8 (3)
C33	0.2149 (10)	0.2515 (4)	0.0452 (5)	10.0 (5)	4.8 (4)	5.1 (3)	−1.8 (3)	1.4 (3)	−0.6 (3)
C34	0.0963 (12)	0.2858 (4)	0.0875 (5)	10.8 (6)	5.1 (4)	4.9 (3)	1.1 (4)	2.1 (4)	0.9 (3)

atom	x	y	z	atom	x	y	z
HO31	0.236 (6)	0.073 (3)	−0.122 (4)	HA22	0.425 (6)	−0.014 (3)	0.366 (4)
HO32	0.147 (6)	0.331 (3)	0.211 (4)	HB22	0.487 (7)	−0.084 (3)	0.341 (4)
HN1	0.194 (7)	0.087 (3)	0.322 (4)	HA23	0.188 (6)	−0.196 (3)	0.311 (4)
HN2	0.258 (6)	−0.094 (3)	0.366 (4)	HB23	0.309 (7)	−0.192 (3)	0.287 (4)
HN3	0.319 (6)	0.180 (3)	0.163 (4)	HA24	0.057	−0.211	0.146
HA11	−0.229 (7)	0.066 (3)	0.123 (4)	HB24	0.198	−0.186	0.110
HB11	−0.141 (6)	0.128 (3)	0.073 (4)	HA31	0.351 (6)	0.180 (3)	−0.087 (4)
HA12	0.065 (6)	0.161 (3)	0.204 (4)	HB31	0.511 (7)	0.129 (3)	−0.045 (4)
HB12	−0.059 (6)	0.155 (3)	0.259 (4)	HA32	0.522 (7)	0.204 (3)	0.094 (4)
HA13	0.137 (7)	0.008 (3)	0.423 (4)	HB32	0.501 (7)	0.114 (3)	0.125 (4)
HB13	0.013 (6)	0.082 (3)	0.409 (4)	HA33	0.309	0.286	0.063
HA14	−0.211 (7)	0.028 (3)	0.284 (4)	HB33	0.166	0.249	−0.030
HB14	−0.147 (6)	−0.037 (3)	0.367 (4)	HA34	−0.022 (7)	0.240 (3)	0.063 (4)
HA21	0.434 (6)	−0.058 (3)	0.167 (4)	HB34	0.043 (6)	0.336 (3)	0.047 (4)
HB21	0.502	0.013	0.224				

[a] The form of the thermal ellipsoid expression is $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. All hydrogen atoms were assigned isotropic thermal parameters of 5.0. Positional parameters of HB21, HA24, HB24, HA33, and HB33 were not refined.

components by use of the dispersion factors given by Cromer.[11] 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 in calculating R_w and in least-squares refinement.

Coordinates for two sets of cobalt atoms and one set of oxygen atoms were obtained from a three-dimensional Patterson synthesis. Three cycles of full-matrix least-squares refinement of the coordinates and isotropic temperature factors for these atoms resulted in an R of 0.367 and an R_w of 0.39. The remaining oxygen, nitrogen, carbon, and chlorine atoms were located by means of subsequent difference Fourier calculation and least-squares refinement. A refinement using isotropic temperature factors for all nonhydrogen atoms converged with $R = 0.109$ and $R_w = 0.106$. Anisotropic thermal parameters were introduced, and further refinements reduced R to 0.056 and R_w to 0.049. The 29 hydrogen atoms were located as principal features on an electron density map; in subsequent refinements the hydrogen coordinates were varied but the hydrogen thermal parameters were fixed at 5.0. The positional parameters of five hydrogens which are bonded to C21, C24, and C33 did not refine well and were fixed. The refinement converged to final values of $R = 0.045$ and $R_w = 0.035$. In the final cycle of refinement the maximum parameter shift was 0.43σ (x coordinate of HN3). The major feature on a final difference Fourier map was a peak of 0.64 e Å^{-3}, approximately 0.9 Å from Co1; this compares to values of approximately 3.5 and 0.5 e Å^{-3} for typical carbon and hydrogen atoms in this structure. Final atomic parameters are listed in Table I; final calculated and observed structure factors are available.[12] Selected bond distances and bond angles are tabulated in Tables II and III, respectively. The tetranuclear unit is illustrated in Figure 1.

Discussion

The structure of the tetranuclear cation, Figure 1, is similar to that found for several titanium alkoxides[13-16] and corresponds to a tetranuclear fragment of a cadmium chloride layer.[17] The skeleton of the tetranuclear unit, Figure 2, consists of portions of two adjoining cubes in which alternate corners are oxygen and cobalt; there is a center of symmetry on the interface of the two cubes, and two symmetry-related extreme-corner cobalt atoms are removed. There remain four octahedral cobalts related in pairs by inversion symmetry; one pair (Co2 and Co2′) are at the interface, and the other pair (Co1 and Co1′) are at the extreme corners of the two cube fragments. Each of the interface cobalts is coordinated to both μ_3-alkoxide oxygens (O11 and O11′) and to two μ-alkoxide oxygens (O21 and O22′ are coordinated to Co2). Each of the

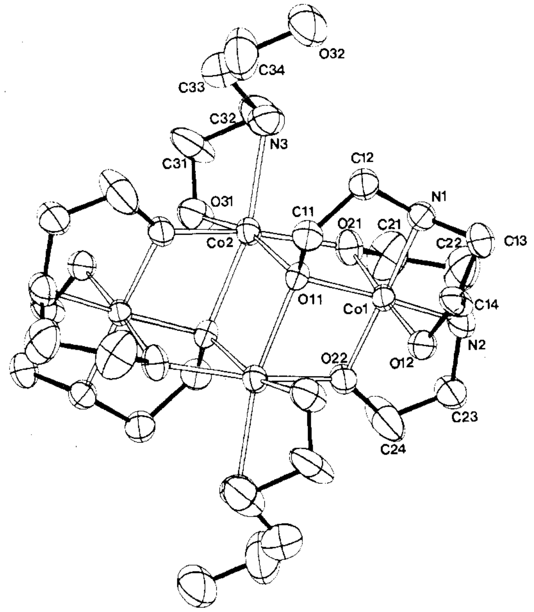

Figure 1. View of the tetranuclear cation $[Co_4(DetaH_2)_2(Deta)_4]^{2+}$. Hydrogen atoms have been omitted.

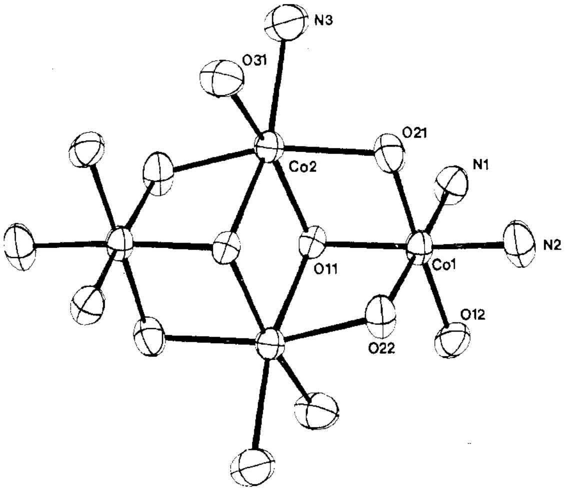

Figure 2. Coordination of the cobalt atoms of the tetranuclear cation.

Table II. Interatomic Distances (Å) for $[Co_4(DetaH_2)_2(Deta)_4](ClO_4)_2$[a,b]

Co1–Co2	3.096 (2)	C24–HB24	1.02
Co1–Co2′	3.037 (3)	C31–HA31	0.99 (5)
Co1–Co1′	5.176 (4)	C31–HB31	0.97 (5)
Co2–Co2′	3.289 (3)	C32–HA32	1.03 (5)
Co1–O11	1.904 (3)	C32–HB32	1.08 (5)
Co1–O12	1.940 (3)	C33–HA33	0.98
Co1–O21	1.893 (3)	C33–HB33	0.95
Co1–O22	1.888 (3)	C34–HA34	1.25 (5)
Co1–N1	1.968 (4)	C34–HB34	1.04 (6)
Co1–N2	1.957 (4)	O32–O12″	2.782 (5)
Co2–O11	2.161 (3)	C23–C24	1.380 (7)
Co2–O11′	2.225 (3)	C24–O22	1.328 (7)
Co2–O21	2.053 (3)	O31–C31	1.426 (6)
Co2–O22′	2.045 (3)	C31–C32	1.504 (8)
Co2–O31	2.103 (4)	C32–N3	1.507 (8)
Co2–N3	2.241 (4)	N3–C33	1.466 (8)
O11–C11	1.416 (5)	C33–C34	1.484 (10)
C11–C12	1.517 (7)	C34–O32	1.388 (8)
C12–N1	1.494 (6)	Cl–PO1	1.377 (6)
N1–C13	1.503 (6)	Cl–PO2	1.412 (4)
C13–C14	1.498 (7)	Cl–PO3	1.412 (4)
C14–O12	1.436 (6)	Cl–PO4	1.397 (5)
O21–C21	1.395 (6)	O31–HO31	0.85 (5)
C21–C22	1.489 (9)	O32–HO32	0.69 (5)
C22–N2	1.473 (8)	N1–HN1	0.95 (5)
N2–C3	1.479 (7)	N2–HN2	0.90 (5)
C14–HB14	0.93 (5)	N3–HN3	0.88 (5)
C21–HA21	0.91 (5)	C11–HA11	1.04 (5)
C21–HB21	0.98	C11–HB11	0.88 (5)
C22–HA22	0.97 (5)	C12–HA12	0.95 (5)
C22–HB22	0.77 (5)	C12–HB12	0.98 (5)
C23–HA23	1.13 (5)	C13–HA13	1.02 (5)
C23–HB23	0.71 (5)	C13–HB13	0.99 (5)
C24–HA24	0.88	C14–HA14	1.05 (5)

[a] X and X′ are related by the inversion operation. [b] X and X″ are related by the twofold screw operation.

extreme cobalts is coordinated to one μ_3-alkoxide oxygen and two μ-alkoxide oxygens (O11, O21, and O22 are coordinated to Co1). The octahedral coordination of the Co1 atom is provided by two tridentate bis(2-hydroxyethyl)amine dianions and consists of two amine nitrogen atoms (in cis positions) and four alkoxide oxygen atoms with the nitrogen and two oxygen atoms from each ligand occupying facial positions. The average Co–N distance is 1.962 Å, and the four Co–O distances are between 1.88 and 1.94 Å. The severely distorted octahedral coordination of the Co2 atom consists of one amine nitrogen atom, two μ_3-alkoxide oxygen atoms, two μ-alkoxide oxygen atoms, and one alcohol oxygen atom. The cobalt-coordinating atom distances are a Co–N of 2.241 (4) Å, two Co–O's of 2.161 (3) and 2.225 (3) Å, two Co–O's of 2.053 (3) and 2.045 (3) Å, and a Co–O of 2.103 (4) Å, respectively. All of these bond distances are longer than the corresponding bond distances for Co1 and suggest that Co2 is divalent and Co1 is trivalent. All of the nitrogen and oxygen atoms of two dianionic bis(2-hydroxyethyl)amine ligands are coordinated to Co1, whereas the remaining symmetrically independent

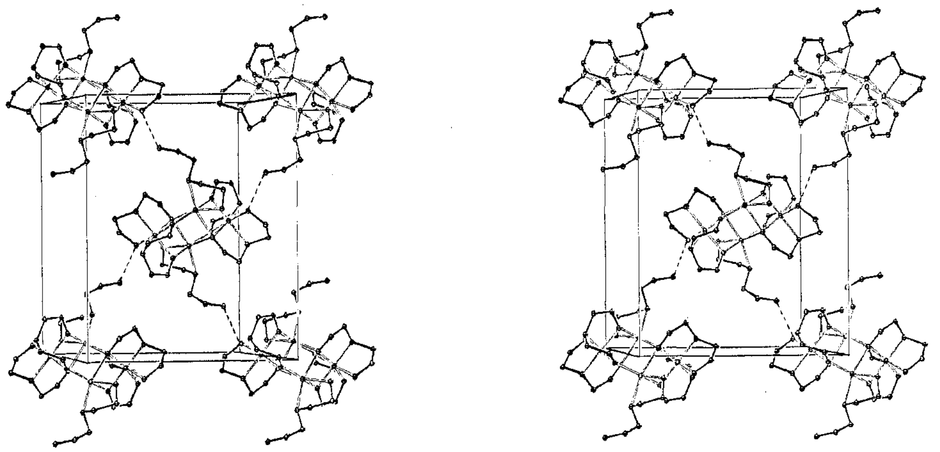

Figure 3. Stereoview of the packing of the tetranuclear cations in the unit cell showing the network of hydrogen bonds (dashed lines). Perchlorate anions and hydrogen atoms have been omitted. The view is approximately along *a*, with *b* vertical and *c* horizontal in the plane of the page.

Table III. Interatomic Angles (deg) for $[Co_4(DetaH_2)_2(Deta)_4](ClO_4)_2$[a,b]

O11–Co1–O12	97.1 (1)	C31–C32–N3	109.8 (5)
O11–Co1–O21	83.1 (1)	N3–C33–C34	115.0 (6)
O11–Co1–O22	86.9 (1)	C33–C34–O32	109.5 (7)
O11–Co1–N1	87.4 (1)	O21–Co2–N3	88.9 (2)
O11–Co1–N2	167.2 (2)	O22′–Co2–O31	93.4 (2)
O12–Co1–O21	176.9 (1)	O22′–Co2–N3	100.7 (2)
O12–Co1–O22	89.1 (1)	O31–Co2–N3	79.8 (2)
O12–Co1–N1	84.8 (1)	Co1–O11–Co2	99.0 (1)
O12–Co1–N2	93.7 (2)	Co1–O11–Co2′	94.4 (1)
O21–Co1–O22	94.0 (1)	Co1–O11–C11	109.7 (2)
O21–Co1–N1	92.1 (2)	Co2–O11–Co2′	97.2 (1)
O21–Co1–N2	86.5 (2)	Co2–O11–C11	119.2 (3)
O22–Co1–N1	171.1 (2)	Co2′–O11–C11	131.0 (3)
O22–Co1–N2	86.3 (2)	Co1–O12–C14	113.3 (3)
N1–Co1–N2	100.5 (2)	Co1–O21–Co2	103.3 (2)
O11–Co2–O11′	82.8 (1)	Co1–O21–C21	109.7 (3)
O11–Co2–O21	73.4 (1)	Co2–O21–C21	112.5 (3)
O11–Co2–O22′	86.5 (1)	Co1–O22–Co2′	103.3 (1)
O11–Co2–O31	164.9 (1)	Co1–O22–C24	112.0 (3)
O11–Co2–N3	115.1 (1)	Co2′–O22–C24	144.8 (4)
O11′–Co2–O21	100.9 (1)	Co2–O31–C31	114.2 (3)
O11′–Co2–O22′	75.2 (1)	Co1–N1–C12	107.7 (3)
O11′–Co2–O31	82.5 (1)	Co1–N1–C13	106.4 (3)
O11′–Co2–N3	100.7 (2)	C12–N1–C13	113.1 (4)
O21–Co2–O22′	159.9 (1)	Co1–N2–C22	105.5 (3)
O21–Co2–O31	105.8 (1)	Co1–N2–C23	107.4 (3)
C32–N3–C33	110.1 (5)	C22–N2–C23	114.9 (5)
O11–C11–C12	108.8 (4)	Co2–N3–32	100.4 (4)
C11–C12–N1	110.5 (4)	Co2–N3–C33	122.2 (4)
N1–C13–C14	107.2 (4)	PO1–Cl–PO2	109.9 (3)
C13–C14–O12	108.8 (4)	PO1–Cl–PO3	109.2 (4)
O21–C21–C22	109.1 (5)	PO1–Cl–PO4	110.9 (5)
C21–C22–N2	108.6 (5)	PO2–Cl–PO3	109.7 (3)
N2–C23–C24	113.3 (4)	PO2–Cl–PO4	111.0 (3)
C23–C24–O22	119.7 (5)	PO3–Cl–PO4	106.2 (4)
O31–C31–C32	106.5 (5)	O32–HO32–O12″	176 (6)

[a] X and X′ are related by the inversion operation. [b] X and X″ are related by the twofold screw operation.

bis(2-hydroxyethyl)amine ligand coordinated to Co2 has one uncoordinated alcohol oxygen atom. This alcohol oxygen atom is associated with one of the coordinated alkoxide oxygens, O12″ (X and X″ are related by twofold screw operation), by a weak hydrogen bond. The O32–O12″ and O32–HO32 distances are 2.782 (5) and 0.69 (5) Å. The O32–HO32–O12″ angle is 176 (6)°. As indicated by the packing diagram, Figure 3, the tetramers are connected into a network approximately parallel to the *bc* plane by this type of hydrogen bond.

On the assumption that the cobalt(III) ions are diamagnetic, the room temperature magnetic moment per gram-atom of cobalt, 5.19 μ_B, is in the normal range for octahedral coordination. The moment shows a slight change with temperature, decreasing to 5.07 μ_B at 93 K, which may be indicative of weak antiferromagnetic coupling. A tetranuclear cobalt(II)–cobalt(III) compound reported[17] earlier, $[Co_4(CH_3O)_4(C_5H_7O_2)_4(C_2H_3O_2)_2]$, showed a larger change in moment with temperature. Additional bridging by the acetate ion in that structure may have provided an additional coupling pathway.

In reviewing the other cobalt compounds of bis(2-hydroxyethyl)amine that have been reported, it is reasonable to assume that the halide salts of the formula $Co_2(DetaH_2)(Deta)_2X\cdot H_2O$ contain the same tetranuclear cation as the perchlorate salt. Furthermore, since treatment of the halide and perchlorate salts with water produces $Co_2(Deta)_2X\cdot 4H_2O$ and $Co_2(Deta)_2ClO_4\cdot 2H_2O$, respectively, it appears that the bidentate ligand on cobalt(II) can be replaced by two water molecules to give a similar tetranuclear cation, $[Co_4(Deta)_4(H_2O)_4]^{2+}$. It is probable that heterometallic compounds such as $[Cu\{Co(DetaH)(Deta)\}_3]X_2\cdot 6H_2O$[18] contain similar polynuclear species, and these are being investigated.

Registry No. $[Co_4(DetaH_2)_2(Deta)_4](ClO_4)_2$, 68630-18-2.

Supplementary Material Available: Listing of structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

References and Notes

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