solely in terms of close-packing considerations either.

The examples in which there is clear metal-metal bonding (Table III) might then be better judged relative to a nonbonding reference ratio $d'/d''$ of ~1.2. Strong metal-metal bonding in this structure appears to put a greater strain on the surrounding matrix, and although bridge angles at the metal open from the ideal 90° by ~4°, those at the bridging halide fall to ~65°. The M-X2 bridging bonds in fact may be under some compression (or the bond order has dropped substantially) since their lengths are now only a few percent larger than those to terminal halogen. The yttrium-zirconium pair suggest that both compression of M-X2 and elongation of the terminal M-X1 bond may occur during the formation of the M-M bond when the observed changes are compared with a reduction in metal size of ~0.17 Å indicated by empirical crystal radii.[31] The closer approach of the bridging iodine atoms to one another (4.01 Å relative to 4.12 Å before) also supports the notion of a compression at the bridging atoms. A substantial shortening of the Cs-I distance between both the AB planes which contain intervening tripositive metal and the AC planes which contain the vacant octahedra are also reflections of the strong metal-metal bonding.

It should be admitted that there are two other factors which might be responsible, at least in part, for the absence of a more significant lengthening of the metal-metal distance in the more polar "nonbonding" examples with the $Cs_3Cr_2Cl_9$ structure. One is the rationale that the $Cs^+$ atoms which lie directly along the metal-metal axis in the next (C) layer resist motion of the M atoms; however, the lack of any apparent response to probable differences in M-X polarity among the $M_2X_9$ groups still remains a problem. A possible restraint from the more or less close-packed $CsI_3$ layers has also been noted. The last two entries in the nonbonding category in Table III suggest these problems may merit further study, the $In_2Cl_9^{3-}$ group in its cesium salt which now occurs in the $Cs_3Tl_2Cl_9$ structure and the $Ti_2Cl_9^-$ ion which is unconstrained by a regular packing (but which also has a higher oxidation state). In the former the dimer units now alternate with the vacant octahedra in a confacial mode so that the outward motion of the trivalent metals might be less restrained. Both of these bioctahedra do exhibit a significant elongation, especially as represented by the $\alpha$ and $\beta$ angles, although the $d'/d''$ ratio changes significantly only ith the higher charged titanium ion. Presumably the restraint of close-packed layers is still significant in the indium phase. The ratio of bridging to terminal M-Cl bond lengths in both remain in a region termed "normal" in the above discussion. Some idea of the effect which packing with even low-field cations can have on what appears to be a "soft" anion in fairly unconstrained circumstances is shown by a 3.1° range of $\alpha$ for $Sb_2Br_9^{3-}$ in its $N(CH_3)_4^+$ and $C_5NH_6^+$ salts[32] even though $d'/d''$ and $d_{M-X_t}/d_{M-X_b}$ are scarcely affected (1.34 and 1.15, respectively; $\bar{\alpha} = 81.8°$).

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**Registry No.** $Cs_3Y_2I_9$, 76173-83-6; $Cs_3Zr_2I_9$, 76173-84-7; CsI, 7789-17-5; $CsI_3$, 12297-72-2; $ZrI_4$, 13986-26-0.

**Supplementary Material Available:** Listings of structure factor amplitudes (3 pages). Ordering information is given on any current masthead page.

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# Stereochemical Perturbations of the Cobalt-Methyl Bond. An X-ray Structural Study of $[Co(d,l(N)\text{-}Me_6[14]4,11\text{-}dieneN_4)(OH_2)CH_3](ClO_4)_2$[1]

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An X-ray structural study has been performed of axial steric interactions in the title compound. The compound crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$. The coordination sphere bond lengths are reasonably typical of a cobalt-methyl complex, but a torsion angle analysis indicates that there is some strain in the equatorial macrocyclic ligand, apparently a consequence of axial $CoOH_2$-geminal methyl repulsive interactions. The unit cell dimensions are $a$ = 11.368 (5) Å, $b$ = 11.611 (4) Å, $c$ = 21.660 (9) Å, $\beta$ = 93.05 (3) °, and $V$ = 2855 (2) Å$^3$. The structure has been refined to final discrepancy factors $R_1$ = 0.050 and $R_2$ = 0.065.

## Introduction

A variety of studies of organocobalt complexes have suggested that the cobalt-carbon bond is very susceptible to stereochemical perturbations.[2-5] Thus bulky alkyl ligands have been shown to have relatively long[2] and easily cleaved[3] Co-C bonds. Further, various stereochemical interactions of adenosylcobalamin with the apoenzyme have been suggested[4,5] as possible means for sufficiently weakening the cobalt-alkyl bond to make thermal homolysis of this bond a feasible mechanistic step in some enzymatic reactions.[6-8]

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[1] Partial support of this research by the National Institutes of Health (Grant AM 14341) is gratefully acknowledged.

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A few years ago we prepared a number of cobalt–alkyl complexes containing relatively saturated equatorial ligands.[9] Among the more intriguing of these complexes was $Co(Me_6[14]4,11\text{-dieneN}_4)(OH_2)CH_3^{2+}$.[10] Two isomers of this complex were isolated and, on the basis of $^1H$ NMR evidence, they were assigned as *meso*(*N*) (N–H bonds trans) and *d*,*l*(*N*) (N–H bonds cis). Owing to the axial asymmetry of the aquomethyl complexes, two *d*,*l*(*N*) isomers are possible. However, only one of these isomers has been detected. On the basis of the observation that this isomer was almost quantitatively produced from the *meso*(*N*) isomeric aqueous cyanide solutions, it seemed likely that this isomeric preference had its origin in a repulsive interaction of the cobalt methyl and the geminal methyls. Consequently, it was anticipated, but not established, that the axial methyl groups of the geminal methyl pairs would both be parallel to the Co–OH$_2$ bond in $Co(d,l(N)\text{-}Me_6[14]4,11\text{-dieneN}_4)(OH_2)CH_3^{2+}$.

Both the *meso*(*N*) and *d*,*l*(*N*) isomers of $Co(Me_6[14]\text{-}4,11\text{-dieneN}_4)(OH_2)CH_3^{2+}$ are relatively easily dehydrated.[9] This ease of dehydration is suggestive of a relatively weak $H_2O$–Co–CH$_3$ bonding interaction. Recent studies[11] of Co–CH$_3$ photohomolysis threshold energies and the equilibria between $Co(N_4)(OH_2)CH_3^{2+}$ and $Co(N'_4)(OH_2)_2^{2+}$ complexes have indicated a relatively weak (~150 kJ mol$^{-1}$) Co–CH$_3$ bond in $Co(meso(N)\text{-}Me_6[14]4,11\text{-dieneN}_4)(OH_2)CH_3^{2+}$. These studies have suggested that the geminal methyls destabilize the Co–CH$_3$ bond by 40–45 kJ mol$^{-1}$ in the *meso*(*N*) isomer. To the extent that the $H_2O$–Co–CH$_3$ bonding interaction has a three-center component[12] a related destabilization might be expected in the *d*,*l*(*N*) isomer. The present study was undertaken to explore the structural aspects of axial–equatorial ligand interactions in these complexes.

## Experimental Section

The $[Co(d,l(N)\text{-}Me_6[14]4,11\text{-dieneN}_4)(OH_2)CH_3](ClO_4)_2$ complex was synthesized as described previously.[9,11] Crystals suitable for X-ray investigations were grown by cooling a layered aqueous/saturated $NaClO_4$ solution of $[Co(Me_6[14]4,11\text{-dieneN}_4)(OH_2)CH_3](ClO_4)_2$. $[Co(d,l(N)\text{-}Me_6[14]4,11\text{-dieneN}_4)(OH_2)CH_3](ClO_4)_2\cdot 3H_2O$ crystallizes as orange-red parallelpipeds. Because we anticipated that this complex would be easily dehydrated, the chosen crystal was mounted inside a sealed glass capillary which contained plugs of mother liquor to preserve the atmosphere. The approximate size of the mounted crystal was 0.15 × 0.46 × 0.53 mm.

The crystal was transferred to a Syntex P2$_1$ automated diffractometer (Mo K$\alpha$, $\lambda$ = 0.710669 Å, graphite monochromator) and optically centered. Analysis of 15 intense precisely centered reflections gave the following monoclinic cell constants: $a$ = 11.368 (5) Å, $b$ = 11.611 (4) Å, $c$ = 21.660 (9) Å, $\beta$ = 93.05 (3)°, $V$ = 2855 (2) Å$^3$, $Z$ = 4, $\rho_{calcd}$ = 1.455 g/cm$^3$, $F_{000}$ = 1320. Partial rotation photographs taken about each axis substantiated the monoclinic assignment. A sample data set indicated systematic absences of $0k0$, $k$ odd, and $h0l$, $h + l$ odd, which is consistent with the space group[13] $P2_1/n$. The nonconventional setting with $\beta$ near 90° was used in order to reduce correlations. The lattice constants for the conventional setting, $P2_1/c$, are $a$ = 11.386 Å, $b$ = 11.611 Å, $c$ = 23.920 Å, and $\beta$ = 64.72°.

Intensities were measured for 4363 reflections of the forms $h,k,\pm l$ in the region 2.5° ≤ 2$\theta$ ≤ 45°. From these, 2664 unique observed ($I \geq 2\sigma(I)$) reflections were obtained by averaging. Three standard reflections were monitored between every 97 reflections and showed a 2% variation in intensity, which was random in behavior; therefore no drift correction was applied. Gaussian integration absorption corrections[14] were applied ($\mu$ = 8.451 cm$^{-1}$) with transmission coefficients varying from 1.16 to 1.29. Other details of data collection were as follows: scan method, $\theta/2\theta$; scan rate, 2.0–5.0°/min; scan range, 1.0° below K$\alpha_1$ to 1.0° above K$\alpha_2$ in 2$\theta$; ratio of background/scan time, 0.5.

Table I. Atomic Coordinates[a]

| | | | |
|---|---|---|---|
| Co | 0.127 00 (6) | 0.196 82 (6) | 0.128 84 (3) |
| Cl(1) | 0.053 76 (18) | 0.210 34 (21) | 0.400 73 (10) |
| Cl(2) | 0.024 96 (16) | 0.412 01 (17) | −0.217 14 (9) |
| O(1) | 0.062 93 (32) | 0.085 67 (32) | 0.057 37 (16) |
| N(1) | 0.090 02 (37) | 0.080 91 (38) | 0.187 94 (20) |
| N(8) | −0.028 19 (37) | 0.275 18 (36) | 0.130 16 (21) |
| N(11) | 0.160 54 (40) | 0.310 01 (37) | 0.067 32 (20) |
| N(18) | 0.283 00 (36) | 0.121 26 (38) | 0.128 13 (20) |
| C(1) | 0.189 05 (55) | 0.299 74 (50) | 0.195 18 (27) |
| O(21) | 0.022 16 (64) | 0.446 57 (58) | −0.156 78 (28) |
| O(22) | 0.126 91 (63) | 0.360 53 (75) | −0.226 27 (36) |
| O(23) | −0.064 83 (75) | 0.339 75 (81) | −0.233 69 (41) |
| O(24) | 0.016 72 (80) | 0.512 01 (58) | −0.255 96 (36) |
| O(11) | 0.128 47 (56) | 0.195 23 (67) | 0.353 63 (29) |
| O(12) | −0.031 11 (71) | 0.295 66 (74) | 0.378 86 (49) |
| O(13) | −0.003 69 (92) | 0.112 46 (71) | 0.414 95 (41) |
| O(14) | 0.118 69 (59) | 0.254 32 (69) | 0.452 05 (30) |
| C(2) | 0.003 34 (52) | 0.076 58 (53) | 0.222 79 (26) |
| C(3) | −0.015 33 (63) | −0.018 64 (62) | 0.267 55 (34) |
| C(4) | −0.085 40 (55) | 0.172 24 (57) | 0.222 60 (30) |
| C(5) | −0.131 68 (48) | 0.219 33 (53) | 0.159 30 (30) |
| C(6) | −0.225 90 (58) | 0.309 35 (60) | 0.169 99 (37) |
| C(7) | −0.184 75 (49) | 0.120 85 (57) | 0.119 88 (32) |
| C(9) | −0.053 08 (52) | 0.318 92 (52) | 0.066 62 (30) |
| C(10) | 0.055 51 (57) | 0.376 89 (48) | 0.046 23 (28) |
| C(12) | 0.261 56 (58) | 0.337 96 (52) | 0.047 62 (29) |
| C(13) | 0.276 47 (70) | 0.435 47 (62) | 0.003 13 (39) |
| C(14) | 0.371 39 (56) | 0.278 15 (58) | 0.070 46 (31) |
| C(15) | 0.366 65 (49) | 0.147 99 (56) | 0.078 31 (27) |
| C(16) | 0.327 97 (54) | 0.089 54 (59) | 0.016 48 (28) |
| C(17) | 0.489 66 (53) | 0.104 68 (65) | 0.097 47 (32) |
| C(19) | 0.261 40 (48) | −0.002 20 (52) | 0.140 73 (28) |
| C(20) | 0.182 51 (52) | −0.010 00 (51) | 0.193 83 (29) |
| O(91) | 0.030 17 (38) | 0.132 53 (35) | −0.065 89 (18) |
| O(92) | 0.371 28 (49) | 0.195 81 (49) | 0.414 93 (27) |
| O(93) | 0.216 65 (59) | 0.193 79 (58) | −0.134 22 (33) |

[a] The esd's are given in parentheses.

A Patterson map was computed which indicated the position of the cobalt atom. All other nonhydrogen atoms were located from a series of Fourier maps, and their positions were refined[15] by least-squares techniques. This model yielded a conventional $R$ factor[16] of 0.11 by using isotropic temperature factors for each atom. The chemical identity of the methyl group was distinguished from that of the coordinated water on the basis of peak heights on a Fourier map. The hydrogen atoms of the two ammine groups, the coordinated methyl group, and the water molecules were placed according to peaks on a difference Fourier map. Remaining hydrogen atoms were placed in calculated positions (C–H = 0.97 Å, tetrahedral geometry) and given isotropic temperature factors of 4.0 Å$^2$. Full-matrix least-squares calculations were continued with use of our usual weighting scheme,[17] hydrogen atom scattering being included as a fixed contribution to $F_c$. Final convergence was reached ($R_1$ = 0.050, $R_2$ = 0.065),[16] refining positional parameters and anisotropic thermal parameters for nonhydrogen atoms. In the final cycle, the maximum shift was 0.05$\sigma$, the number of variables was 325 and the number of observations was 2664. A final difference map was essentially featureless, the highest peak occurring in the vicinity of a perchlorate group and representing 0.5 e Å$^{-3}$. Neutral-atom scattering factors[18] were used, with Co and

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(10) Ligand abbreviations: $Me_4[14]tetraeneN_4$ = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene; $Me_6[14]4,11\text{-dieneN}_4$ = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; $[14]aneN_4$ = 1,4,8,11-tetraazacyclotetradecane; dmgH$^-$ = dimethylglyoximate.

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(14) Computing programs were local modifications of ABSORB program of D. H. Templeton, Zalkin's FORDAP, Johnson's ORTEP, and the Busing–Martin–Levy ORFLS and ORFEE.

(15) The function minimized was $\sum w(|F_o| - |F_c|)^2$.

(16) $R_1 = \sum||F_o - |F_c||/\sum|F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2]^{1/2}/[\sum wF_c^2]^{1/2}$.

(17) $w = F^2/\sigma(F^2)$.

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Table II. Interatomic Distances (Å)

| | | | |
|---|---|---|---|
| | Cation | | |
| Co–N(1) | 1.920 (5) | C(2)–C(3) | 1.493 (9) |
| Co–N(8) | 1.987 (4) | C(2)–C(4) | 1.500 (9) |
| Co–N(11) | 1.924 (5) | C(4)–C(5) | 1.524 (9) |
| Co–N(18) | 1.979 (4) | C(5)–C(6) | 1.523 (8) |
| Co-C(1) | 1.971 (6) | C(5)–C(7) | 1.532 (9) |
| Co–O(1) | 2.115 (4) | C(9)–C(10) | 1.493 (8) |
| N(1)–C(2) | 1.274 (7) | C(12)–C(13) | 1.502 (9) |
| N(1)–C(20) | 1.490 (7) | C(12)–C(14) | 1.490 (9) |
| N(8)–C(5) | 1.511 (7) | C(14)–C(15) | 1.522 (9) |
| N(8)–C(9) | 1.480 (8) | C(15)–C(16) | 1.544 (8) |
| N(11)–C(10) | 1.476 (7) | C(15)–C(17) | 1.523 (8) |
| N(11)–C(12) | 1.288 (7) | C(19)–C(20) | 1.498 (8) |
| N(18)–C(15) | 1.508 (7) | | |
| N(18)–C(19) | 1.482 (7) | | |
| | Anion | | |
| Cl(1)–O(11) | 1.373 (6) | Cl(2)–O(21) | 1.370 (6) |
| Cl(1)–O(12) | 1.445 (8) | Cl(2)–O(22) | 1.328 (6) |
| Cl(1)–O(13) | 1.354 (7) | Cl(2)–O(23) | 1.355 (7) |
| Cl(1)–O(14) | 1.398 (6) | Cl(2)–O(24) | 1.434 (7) |

Table III. Interatomic Angles (Deg)

| | | | |
|---|---|---|---|
| N(1)–Co–N(11) | 177.9 (2) | N(11)–Co–O(1) | 89.0 (2) |
| N(1)–Co–C(1) | 91.2 (2) | C(1)–Co–N(18) | 89.3 (2) |
| N(1)–Co–N(18) | 85.6 (2) | C(1)–Co–N(8) | 89.7 (2) |
| N(1)–Co–N(8) | 94.9 (2) | C(1)–Co–O(1) | 179.2 (1.1) |
| N(1)–Co–O(1) | 88.9 (2) | N(18)–Co–N(8) | 179.0 (3) |
| N(11)–Co–C(1) | 90.8 (2) | N(18)–Co–O(1) | 89.9 (2) |
| N(11)–Co–N(18) | 95.0 (2) | N(8)–Co–O(1) | 91.1 (2) |
| N(11)–Co–N(8) | 84.6 (2) | | |
| C(2)–N(1)–C(20) | 119.1 (5) | N(8)–C(5)–C(4) | 106.7 (4) |
| C(2)–N(1)–Co | 128.8 (4) | C(6)–C(5)–C(7) | 109.7 (5) |
| C(20)–N(1)–Co | 112.0 (4) | C(6)–C(5)–C(4) | 108.5 (6) |
| C(9)–N(8)–C(5) | 114.9 (5) | C(7)–C(5)–C(4) | 109.7 (5) |
| C(9)–N(8)–Co | 105.6 (3) | N(8)–C(9)–C(10) | 108.0 (5) |
| C(5)–N(8)–Co | 121.4 (3) | N(11)–C(10)–C(9) | 109.8 (4) |
| C(12)–N(11)–C(10) | 119.1 (5) | N(11)–C(12)–C(14) | 121.2 (5) |
| C(12)–N(11)–Co | 127.9 (4) | N(11)–C(12)–C(13) | 122.4 (6) |
| C(10)–N(11)–Co | 112.8 (4) | C(14)–C(12)–C(13) | 116.3 (6) |
| C(19)–N(18)–C(15) | 116.6 (4) | C(12)–C(14)–C(15) | 117.8 (5) |
| C(19)–N(18)–Co | 105.7 (3) | N(18)–C(15)–C(14) | 108.2 (5) |
| C(15)–N(18)–Co | 120.9 (3) | N(18)–C(15)–C(17) | 110.0 (5) |
| N(1)–C(2)–C(3) | 123.7 (6) | N(18)–C(15)–C(16) | 111.6 (5) |
| N(1)–C(2)–C(4) | 120.7 (5) | C(14)–C(15)–C(17) | 108.7 (6) |
| C(3)–C(2)–C(4) | 115.5 (5) | C(14)–C(15)–C(16) | 110.5 (5) |
| C(2)–C(4)–C(5) | 117.5 (5) | C(17)–C(15)–C(16) | 107.8 (5) |
| N(8)–C(5)–C(6) | 109.8 (5) | N(18)–C(19)–C(20) | 108.2 (5) |
| N(8)–C(5)–C(7) | 112.3 (5) | N(1)–C(20)–C(19) | 109.9 (5) |
| O(13)–Cl(1)–O(11) | 112.7 (5) | O(22)–Cl(2)–O(23) | 109.5 (6) |
| O(13)–Cl(1)–O(14) | 111.5 (5) | O(22)–Cl(2)–O(21) | 109.8 (5) |
| O(13)–Cl(1)–O(12) | 109.2 (6) | O(22)–Cl(2)–O(24) | 107.9 (5) |
| O(11)–Cl(1)–O(14) | 108.4 (4) | O(23)–Cl(2)–O(21) | 112.2 (5) |
| O(11)–Cl(1)–O(12) | 105.8 (6) | O(23)–Cl(2)–O(24) | 108.8 (5) |
| O(14)–Cl(1)–O(12) | 109.0 (5) | O(21)–Cl(2)–O(24) | 108.6 (4) |

Cl corrected[19] for anomalous dispersion. An examination of the error of fit over intervals of increasing $F_o$ and $(\sin\theta)/\lambda$ showed only minor deviations; the overall value was 1.95. The value of $p$ in the calculation of $\sigma(I)$ was 0.05. Final atomic positional parameters are presented in Table I. Interatomic distances and angles are listed in Tables II and III, respectively. Tables containing anisotropic thermal parameters (Table SI), hydrogen positional parameters (Table SII), hydrogen bond lengths (Table SIII), and calculated and observed $F$'s (Table SIV) are available.[20]

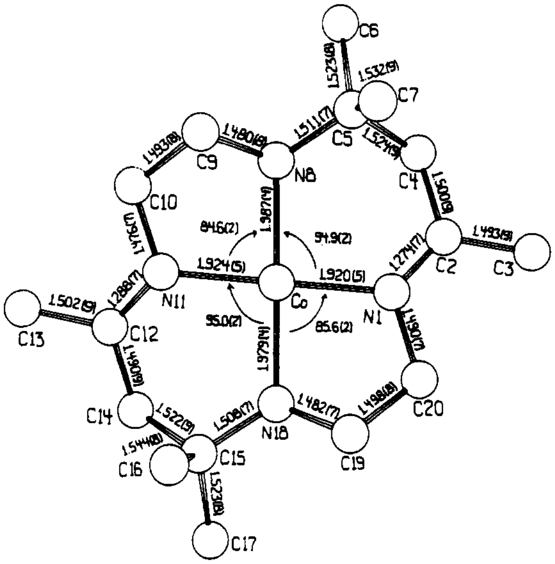

**Figure 1.** Atom numbering scheme and bond lengths of the equatorial ligand in $Co(d,l(N)\text{-}Me_6[14]4,11\text{-}dieneN_4)(OH_2)CH_3^{2+}$. The axial ligands have been omitted for clarity.

Table IV. Least-Squares Planes[a]

| atom | dev, Å | atom | dev, Å |
|---|---|---|---|
| Co | 0.009 | C(10) | −0.257 |
| N(1)[b] | −0.025 | C(12) | 0.228 |
| N(8)[b] | 0.025 | C(13) | 0.280 |
| N(11)[b] | −0.025 | C(14) | 0.554 |
| N(18)[b] | 0.025 | C(15) | −0.257 |
| C(2) | 0.172 | C(16) | −1.76 |
| C(3) | 0.128 | C(17) | 0.175 |
| C(4) | 0.525 | C(19) | −0.726 |
| C(5) | −0.288 | C(20) | −0.242 |
| C(6) | 0.173 | H1N8 | 0.844 |
| C(7) | −1.78 | H1N18 | 0.845 |
| C(9) | −0.738 | | |

[a] Equation of the plane: $-0.3147x + -0.6055y + -0.7309z = -3.8191$, where $x$, $y$, and $z$ are coordinates in Å of the orthonormal cell defined by $a^*$, $b$, and $c$. [b] Atoms defining the plane.

Table V. Possible Hydrogen Bonds

| H···X | dist, Å | A–H···X | angle, deg |
|---|---|---|---|
| H1N8···O(21)[a] | 2.55 | N(8)–H1N8···O(21)[a] | 144 |
| H1N8···O(24)[a] | 2.84 | N(8)–H1N8···O(24)[a] | 164 |
| H1N18···O(23)[b] | 2.53 | N(18)–H1N18···O(23)[b] | 166 |
| H1O1···O(91) | 1.96 | O(1)–H1O1···O(91) | 157 |
| H1O91···O(93) | 2.24 | O(91)–H1O91···O(93) | 131 |
| H2O91···O(92)[c] | 2.18 | O(91)–H2O91···O(92)[c] | 138 |
| H2O92···O(14) | 2.45 | O(92)–H2O92···O(14) | 141 |

[a] Transformed by $\bar{x}$, $1-y$, $\bar{z}$. [b] Transformed by $^1/_2+x$, $^1/_2-y$, $^1/_2+z$. [c] Transformed by $x-{}^1/_2$, $^1/_2-y$, $z-{}^1/_2$.

## Description of the Structure

The crystal structure of the title complex consists of six-coordinate cobalt cations, in which the cobalt center is surrounded by four N donors from the equatorial macrocyclic ligand, $Me_6[14]4,11\text{-}dieneN_4$, and an aquo and methyl group in the axial positions, and uncoordinated perchlorate ions. A weak network of hydrogen bonds is present (see Table V and the supplementary Figure). Figure 1 illustrates the numbering of the cobalt–macrocycle portion of the complex and contains selected bond length and angle information. Figure 2 is a stereoscopic view of the entire cation. Table IV contains least-squares planes calculations and shows the cobalt atom to be in the plane defined by the four nitrogen atoms. The backbone geometry of the macrocycle is normal for these types of $CoN_4$ systems.[21,22]

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(19) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; p 149.

(20) See paragraph at end of paper regarding supplementary material.

(21) Curtis, N. F. In "Coordination Chemistry of Macrocyclic Compounds"; Melson, G. A., Ed.; Plenum Press: New York, 1979; Chapter 4.

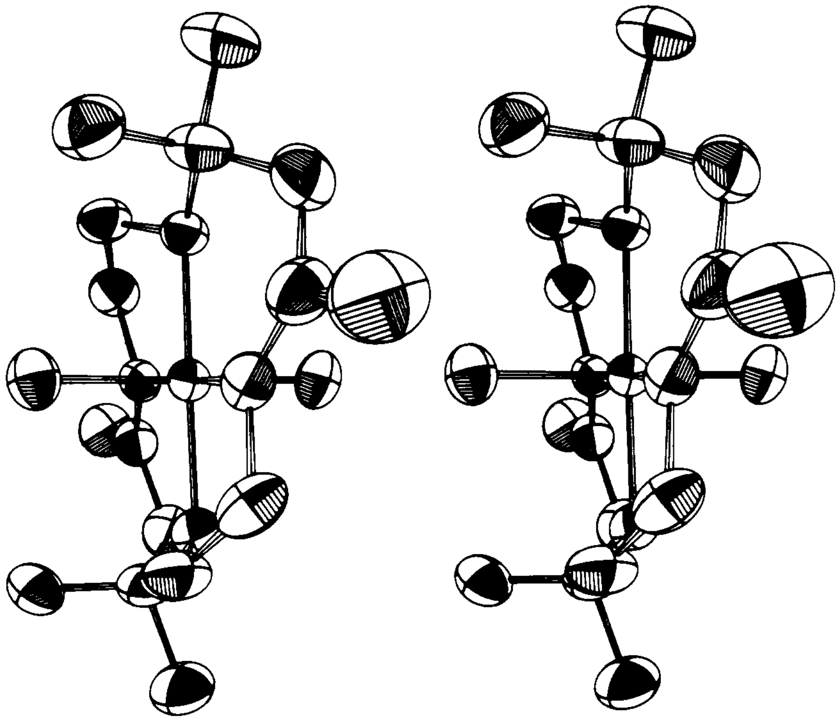

**Figure 2.** Stereoscopic view of Co(*d,l*(*N*)Me$_6$[14]4,11-dieneN$_4$)(OH$_2$)CH$_3^{2+}$.

The *d,l*(*N*) isomer is characterized by having hydrogen atoms of both amino groups pointing to the same side of the donor atom plane, i.e., toward the coordinated methyl group. These hydrogen atoms are involved in weak hydrogen bonds to perchlorate oxygen atoms. It is expected that these amine hydrogen atoms would assume the axial positions, allowing the larger methylene group (C(9), C(19)), also bound to the amine, to occupy the more stable equatorial position.[23] Further, the *d,l*(*N*) isomer requires that the terminal methyl groups which also occupy axial positions in the ring (C(16), C(7)) be oriented toward the same side of the donor atom plane, in this case toward the coordinated water molecule. This results in close contacts (less than the sum of the van der Waals radii) between the terminal methyl groups (C(7), C(16)) and the coordinated oxygen atom (O(1)). Besides this contact, there is a substantial hydrogen bond between one of the waters of hydration (O(91)) and a hydrogen atom on the coordinated water (O(1)). Figure 3 is a perspective view of the molecule illustrating these close contacts. Our qualitative observation that the *d,l*(*N*) crystalline complex is more difficult to dehydrate than the *meos*(*N*) isomer[9] may be the result of caging in the coordinated water with these close contacts.

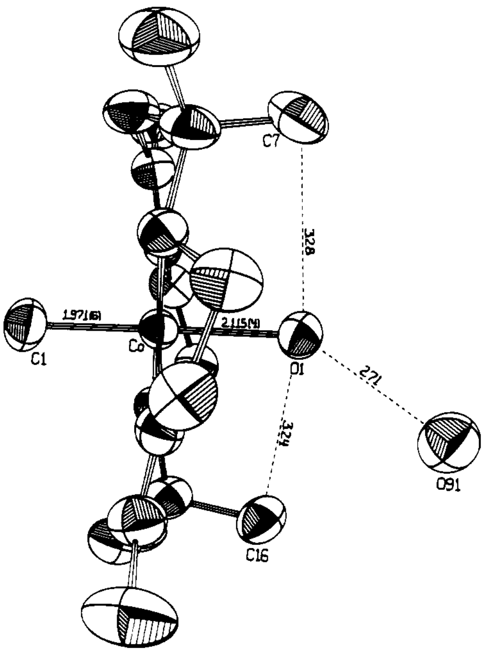

**Figure 3.** Structural view illustrating axial interactions in Co(*d,l*-(*N*)-Me$_6$[14]4,11-dieneN$_4$)(OH$_2$)CH$_3^{2+}$. Ellipsoids represent 50% probability.

## Discussion

The structure of Co(*d,l*(*N*)-Me$_6$[14]4,11-dieneN$_4$)(OH$_2$)-CH$_3^{2+}$ does show evidence of significant stereochemical repulsions between the axial ligands and the equatorial N$_4$ macrocycle. However, these interactions are not clearly manifested in simple variations in the coordination sphere bond lengths.

Among cobalt complexes with equatorially coordinated 14-membered tetraaza macrocycles there is a remarkable similarity of equatorial Co–N bond lengths, independent of the formal oxidation state of the metal, the axial ligands, or the exact nature of the macrocycle.[22a] However, the Co–N bond length does depend on the hybridization of the donor atom: 1.92 Å for Co–imine; 1.98 Å for Co–amine.[22a,d] The present structure extends this pattern to yet another class of cobalt complexes.

Axial bond lengths among *trans*-Co$^{III}$(N$_4$)X$_2$ complexes are also dependent on the donor atom but nearly independent of the equatorial macrocyclic ligand.[22a] A sampling of the available data is contained in Table VI. In contrast there is great variability in the axial bond lengths of low-spin *trans*-Co$^{II}$(N$_4$)X$_2$ complexes.[22d] It is of particular interest that in the *trans*-diaquo complexes with N$_4$ = *meso*(*N*)-Me$_6$[14]-

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(22) (a) Endicott, J. F.; Durham, B.; Glick, M. D.; Anderson, T. J.; Kuszaj, J. M.; Schmonsees, W. G.; Balakrishnan, K. P. *J. Am. Chem. Soc.*, in press. (b) Glick, M. D.; Kuszaj, J. M.; Endicott, J. F. *Ibid.* **1973**, *95*, 5097. (c) Durham, B.; Anderson, T. J.; Switzer, J. A.; Endicott, J. F.; Glick, M. D. *Inorg. Chem.* **1977**, *16*, 271. (d) Endicott, J. F.; Lilie, J.; Kuszaj, J. M.; Ramaswamy, B. S.; Schmonsees, W. G.; Simic, M. G.; Glick, M. D.; Rilleman, D. P. *J. Am. Chem. Soc.* **1977**, *99*, 429.

(23) Eliel, E. L. "Stereochemistry of Carbon Compounds"; McGraw-Hill: New York, 1962; p 239.

Table VI. Comparison of Axial Bond Lengths in Macrocyclic Complexes of Cobalt

| | | axial bond lengths, Å[b] | | | |
|---|---|---|---|---|---|
| | approx Co–$CH_3$ bond dissocn energy[a] | for $Co(N_4)(OH_2)CH_3$ | | for $Co(N_4)X_2$ | |
| equatorial ligand | | Co–$CH_3$ | Co–$OH_2$ | $Co^{III}$–X | $Co^{II}$–$OH_2$ |
| *d,l*(*N*)-$Me_6$[14]4,11-diene$N_4$ | 33 | 1.971 (6)[c] | 2.115 (4)[c] | | |
| *meso*(*N*)-$Me_6$[14]4,11-diene$N_4$ | ~36 | | | 1.954 (6)[d] | 2.482 (5) |
| dmgH⁻ | 47 | 1.990 (5)[e] | 2.058 (3)[e] | 1.960[d,f] | |
| $Me_4$[14]tetraene$N_4$ | 46 | 2.01[g] | 2.11[g] | 1.97 (1)[d] | 2.289 (15) |
| [14]ane$N_4$ | 39 | 1.99[g] | 2.16[g] | 1.913 (4)[h] | |

[a] In kcal $mol^{-1}$; from ref 11. [b] Reference 22a except as indicated. [c] This work. [d] X = $NH_3$. [e] McFadden, D. L.; McPhail, A.T. *J. Chem. Soc., Dalton Trans.* 1974, 363. [f] Heeg, M. J.; Elder, R. C. *Inorg. Chem.* 1980, *19*, 932. [g] Butler, W.; Endicott, J. F.; Glick, M. D., unpublished work. [h] X = $H_2O$.

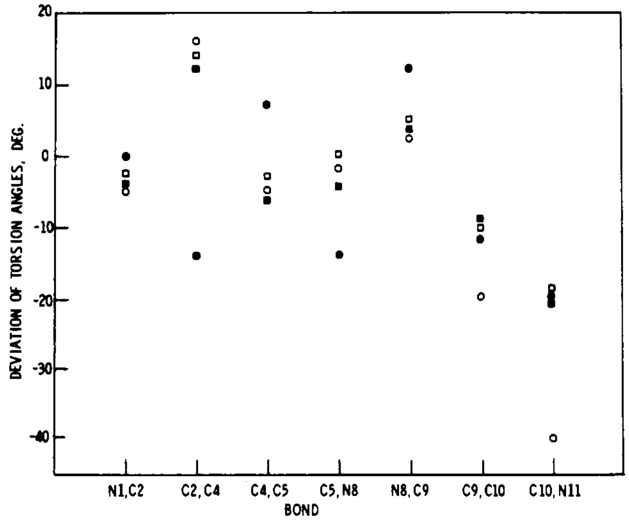

**Figure 4.** Torsion angles for several M($Me_6$[14]4,11-diene$N_4$) complexes: Co(*d,l*(*N*)-$Me_6$[14]4,11-diene$N_4$)($OH_2$)$CH_3^{2+}$, open circles; Ni(*d,l*(*N*)-$Me_6$[14]4,11-diene$N_4$)$^{2+}$,[28] closed circles; Co(*meso*(*N*)-$Me_6$[14]4,11-diene$N_4$)$(NH_3)_2^{3+}$,[22a] open squares; Co(*meso*(*N*)-$Me_6$[14]4,11-diene$N_4$)$(OH_2)_2^{2+}$,[22d] closed squares. All points relative to strain-free torsion angles according to ref 25. Torsion angles between atoms indicated.

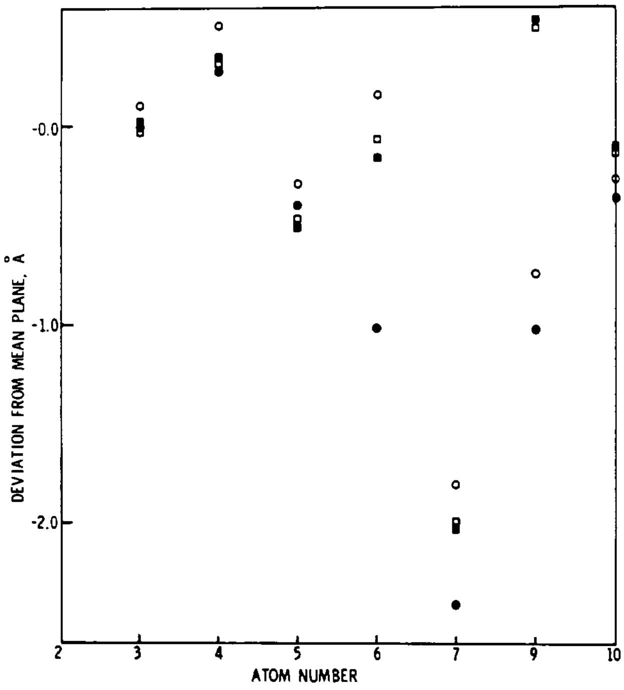

**Figure 5.** Displacements of equatorial ligand atoms from the mean $N_4$ plane. Complexes and conventions are the same as in Figure 4.

4,11-diene$N_4$, the $Co^{II}$–$OH_2$ bond length is 2.48 Å while the regularity of the $Co^{III}$ axial bond lengths indicates that the $Co^{III}$–$OH_2$ bond would be ~1.91 Å. The significant (0.2–0.3 Å) lengthening of the Co–$OH_2$ bond in the aquo–methyl complexes is an expected manifestation of the "ground-state trans influence" of the coordinated methyl group. An overly simple but instructive interpretation of these structural variations is that the axial bonding interaction puts more electron density on the metal in aquo–methyl complexes than is found in $Co^{III}(N_4)(OH_2)_2$ complexes but less than is found in $Co^{II}(N_4)(OH_2)_2$ complexes. This is as expected for a "covalent" Co–$CH_3$ bond in view of the small electron affinity of the methyl radical[24] and various proposed bonding models (e.g., see ref 12).

Axial bond lengths of several $Co(N_4)(OH_2)CH_3$ complexes are compared in Table VI. While there is more variability in axial bond lengths among aquo–methyl complexes than is found among the axial bond lengths of $Co^{III}(N_4)X_2$ complexes, there is no strong correlation of bond length with equatorial ligand stereochemistry or with the apparent Co–$CH_3$ bond dissociation energy.

The torsion angles of several $Me_6$[14]4,11-diene$N_4$ complexes are compared in Figure 4. Strain angles for Co(*meso*(*N*)-$Me_6$[14]4,11-diene$N_4$)$(NH_3)_2^{3+}$ and Co(*meso*-(*N*)$Me_6$[14]4,11-diene$N_4$)$(OH_2)_2^{2+}$ are essentially identical despite the very great difference in axial bond lengths. This may be indicative of a relatively strain-free conformation, in reasonable accord with the estimates of Maxwell and Bailey[25] (see Figure 4). However, there is some difference in the geminal methyl–axial ligand distance in these two complexes: 3.19 and 3.27 Å, respectively, for the cobalt(III) and the cobalt(II) complexes.

Both Ni(*d,l*(*N*)-$Me_6$[14]4,11-diene$N_4$)$^{2+}$ and Co(*d,l*(*N*)-$Me_6$[14]4,11-diene$N_4$)($OH_2$)$CH_3^{2+}$ exhibit considerable strain. Maxwell and Bailey[25] attributed strain in the nickel complex in part to the relatively long Ni–N bonds. Since the Co–N bonds are not quite so long, some of the differences in equatorial ligand stereochemistry may result from the differences in M–N bond lengths. However, the shorter M–N bond length does not remove the manifestations of ring strain. The principal loci of strain appear to be around the central carbon (C(4)) of the six-membered chelate ring and (surprisingly) in the five-membered chelate ring. One very striking structural feature of the Ni(*d,l*(*N*)-$Me_6$[14]4,11-diene$N_4$)$^{2+}$ complex is that the geminal methyl groups (i.e., C(7) and C(7)′) effectively block one of the axial coordination sites (the geminal methyl–geminal methyl distance, across the axial site, is 4.32

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(24) Ellison, G. B.; Engelking, D. C.; Lineberger, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 2556.

(25) Maxwell, I. E.; Bailey, M. F. *J. Chem. Soc., Dalton Trans.* **1972**, 935.

*Inorg. Chem.* **1981**, *20*, 1201-1206 **1201**

Å). Insertion of a water molecule at this site in Co(*d,l*-(*N*)-$Me_6$[14]4,11-diene$N_4$)($OH_2$)$CH_3^{2+}$ forces these geminal methyl groups back toward the mean $N_4$ plane (see Figure 5; the water–geminal methyl distance is 3.26 Å; the geminal methyl–geminal methyl distance is 6.14 Å). In this regard it is interesting that we have found no evidence for the Co($N_4$)($OH_2$)$CH_3^{2+}$ isomer with the methyl group in this coordination site. Apparently the title compound is at least 2 kcal $mol^{-1}$ more stable than the isomer with Co–$CH_3$ on the same side of the molecule as the geminal methyl groups.

While it is not possible to determine the magnitude of the strain energies involved, relaxation of the strained equatorial ligand in the five-coordinate intermediates would contribute to a diminished Co–$CH_3$ bond energy and could also effect a diminished activation barrier for water loss in the Co($Me_6$[14]4,11-diene$N_4$)($OH_2$)$CH_3^{2+}$ complexes.

**Registry No.** [Co(*d,l*(*N*)-$Me_6$[14]4,11-diene$N_4$)($OH_2$)$CH_3$]($ClO_4$)$_2$·3$H_2O$, 76581-80-1.

**Supplementary Material Available**: Tables of anisotropic thermal parameters, hydrogen atom positional parameters, bond lengths to hydrogen, and structural factors and a figure showing the crystal structure of the title compound (18 pages). Ordering information is given on any current masthead page.

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# Tetracarbon Metallacarboranes. 10.[1] On the Thermodynamically Favored Geometry of Large Nido Cages. Structure of the Thermal Rearrangement Product (Isomer III) of ($\eta^5$-$C_5H_5$)Co($CH_3$)$_4C_4B_7H_7$

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The preferred structure of 12-vertex, 28-electron (nido) polyhedral cages, which contain two skeletal electrons beyond the 26 required for a regular closo icosahedral system and which have thus far been found in at least seven different structural classes, was the focus of this investigation. The crystal and molecular structure of the title compound, which was formed by thermal rearrangement of isomer I at 140 °C, were determined by single-crystal X-ray diffraction. Isomer III has an open-cage geometry in which all four carbon atoms and two borons reside on a 6-membered open face, with one of the carbons isolated from the other three. The cage is isostructural with the previously characterized metallacarboranes ($\eta^5$-$C_5H_5$)Fe($CH_3$)$_4C_4B_7H_8$ and ($\eta^5$-$C_5H_5$)$_2Co_2C_4B_6H_{10}$ (isomer VII); however, the structures of the three isomers of ($\eta^5$-$C_5H_5$)Co($CH_3$)$_4C_4B_7H_7$ are grossly different from each other. The observed geometry of isomer III implies a thermodynamic preference of skeletal carbon atoms for low-coordinate vertices on the open rim, even though this requires three of the four carbons to remain adjacent. The adoption of a high-coordinate vertex by cobalt is also significant. The seven established classes of 12-vertex, 28-electron cage systems are discussed in light of the present study. Crystal data are as follows: mol wt 314.9, space group *C*2/*c*, *Z* = 8; *a* = 25.944 (8), *b* = 8.686 (3), *c* = 15.410 (5) Å; *β* = 108.47 (3)°; *V* = 3294 Å$^3$; *R* = 0.052 for 1542 independent reflections having $F_o^2 > 3\sigma(F_o^2)$.

## Introduction

The four-carbon carboranes ($CH_3$)$_4C_4B_8H_8$, ($CH_3$)$_4C_4B_8H_8^{2-}$, and ($CH_3$)$_4C_4B_7H_9$ and the metallacarboranes derived from them form a structurally diverse family of cages having 11–14 vertices. As revealed by X-ray investigations,[2] the framework geometries of many of these systems are highly irregular, in that they deviate markedly from ideal closo polyhedra or fragments thereof. In most of the metal-containing species it is apparent that the cage structures are dictated primarily by the mode of metal attack on the carborane framework[3] and are kinetically rather than thermodynamically stabilized. This has been conclusively established[4] for the 14-vertex ($\eta^5$-$C_5H_5$)$_2Fe_2$($CH_3$)$_4C_4B_8H_8$ isomers I–IV, which form by metal insertion into ($CH_3$)$_4C_4B_8H_8^{2-}$ under mild conditions and feature asymmetric, open-cage structures; at 300 °C these isomers ultimately rearrange to the thermodynamically favored $D_{2d}$ closo polyhedron. For most other $C_4$ metallacarborane systems, however, the most stable geometry has not been determined.

An intrinsically important class of cage structures consists of species having 12 framework atoms and 28 skeletal electrons (Figure 1).[5] These molecules are (2*n* + 4)-electron (nido) systems[6] whose special significance lies in the presence of two "extra" electrons beyond the normal allotment of 26 for a regular 12-vertex icosahedron. Known 26-electron species such as $B_{12}H_{12}^{2-}$ and $C_2B_{10}H_{12}$ are closed-shell electronic systems in which the 13 available bonding molecular orbitals in the cage skeleton are precisely filled;[7] introduction of more electrons must therefore induce distortion from icosahedral symmetry. However, the nature of such distortions depends cru-

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[1] Part 9: Grimes, R. N.; Sinn, E.; Pipal, J. R. *Inorg. Chem.* **1980**, *19*, 2087.

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[6] For descriptions of skeletal electron-counting procedures and structural classifications see: (a) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1. (b) Mingos, D. M. P. *Nature* (*London*), *Phys. Sci.* **1972**, *236*, 99. (c) Rudolph, R. W. *Acc. Chem. Res.* **1976**, *9*, 446. (d) Williams, R. E. *Inorg. Chem.* **1971**, *10*, 210.

[7] (a) Lipscomb, W. N. "Boron Hydrides"; Benjamin: New York, 1963. (b) Longuet-Higgins, H. C.; Roberts, M. deV. *Proc. R. Soc. London, Ser. A* **1954**, *224*, 336; **1955**, *230*, 110. (c) Moore, E. B., Jr; Lohr, L. L., Jr.; Lipscomb, W. N. *J. Chem. Phys.* **1961**, *35*, 1329.

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