Contribution from the School of Chemistry, Georgia
Institute of Technology, Atlanta, Georgia 30332

Preparation, Properties, and Structure of Di-μ-acetato-tetrakis[μ_3-methoxo-2,4-pentanedionatocobalt(II,III)]

J. A. BERTRAND* and THOMAS C. HIGHTOWER

Received June 26, 1972

A cubane-type complex containing both cobalt(II) and cobalt(III) has been prepared by oxidation of a mixture of cobalt(II) acetate, 2,4-pentanedione, and potassium hydroxide in methanol with hydrogen peroxide. Di-μ-acetato-tetrakis[μ_3-methoxo-2,4-pentanedionatocobalt(II,III)], $Co_4(CH_3O)_4(CH_3CO_2)_2(C_5H_7O_2)_4$, crystallized in space group $P\bar{1}$ (a = 10.88 (1) Å, b = 22.51 (3) Å, c = 12.76 (1) Å, α = 110.22 (8)°, β = 123.34 (7)°, γ = 108.93 (7)°) with 2 molecules per unit cell (ρ_{calcd} = 1.57 g cm^{-3}; ρ_{obsd} = 1.56 (1) g cm^{-3}). The structure, which was refined to a conventional R value of 0.068, consists of a distorted cube with cobalt ions and methoxide oxygens at alternate corners; the octahedral coordination of each cobalt is completed by a chelated 2,4-pentanedionate group and by the oxygen of one of the acetate groups which bridge the top and bottom faces of the cube. The fact that cobalt–oxygen distances for one pair of cobalts are consistently shorter by 0.16–0.20 Å than those of the other pair indicates that the former are the cobalt(III) ions. The magnetic moment of 4.98 BM/g-atom of cobalt(II) at room temperature decreases to 4.62 BM at 77°K; superexchange through the acetate which bridges the divalent cobalt ions is suggested.

Introduction

Although cubane-type structures have been found for a number of different metal ions and different bridging groups,[1-21] there have been relatively few examples with first-row transition metal ions;[1,18-21] the recent observation[22] that two iron-sulfur cubane units are present in the structure of a ferredoxin protein makes the preparation and properties of this type of complex of considerable interest.

For many years, a cubane-type structure has been recognized[1] for compounds of the general formula $[Cu(R_3Y)X]_4$ (where X represents a halide ion, Y represents a group V element, and R represents an alkyl or aryl group); however, there have been relatively few studies of the properties of these compounds.

Several years ago, a series of compounds with the formula $[M(CH_3O)(AA)(ROH)]_x$ (in which M = Co, Ni, or Mg, AA represents the anion of a β-dicarbonyl compound, and R = CH_3) was reported;[23,24] structure studies indicate cubane-type structures for the compounds in which M = Co or Ni, AA = 2,4-pentanedionate, and R = CH_3;[20] a compound in which M = Ni, AA = salicylaldehydate, and R = C_2H_5 was also reported and shown to have a cubane-type structure.[19] In these structures, metal ions and methoxide oxygens occupy alternate corners of a distorted cube; the octahedral coordination of each metal ion is completed by a β-dicarbonyl chelate and a coordinated methanol. Although a number of isomeric complexes are possible depending upon the relative orientation of the chelate planes, both complexes studied have had S_4 symmetry either rigorously as the crystal site symmetry or accidentally. Magnetic studies of the nickel(II) complexes have indicated that the metal ions are ferromagnetically coupled.[20,25]

Although the copper(II) complexes of the formula $[Cu(CH_3O)(AA)]_x$ were found to[26] have x = 2 and, therefore, were not cubane-type complexes, a five-coordinate cubane-type structure was observed for the copper(II) complex of the Schiff base of 2,4-pentanedione and 2-aminoethanol.[21]

Several attempts to prepare cubane-type complexes of trivalent metal ions of the first transition series have resulted in poorly characterized products; however, attempts to oxidize cobalt(II) cubanes led to the isolation of a stable, paramagnetic compound. The preparation, properties, and structure of that compound are described in this paper.

Experimental Section

Preparation. Cobalt(II) acetate tetrahydrate (0.02 mol) was dissolved in 400 ml of methanol, heating only enough to dissolve the material. The cobalt(II) acetate was cooled to room temperature (25°), and a solution of 2,4-pentanedione (0.02 mol) in 25 ml of methanol was added with stirring. To this solution was added

---

(1) A. F. Wells, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, 94, 447 (1936).

(2) R. E. Rundle and J. H. Sturdivant, *J. Amer. Chem. Soc.*, 69, 1561 (1947).

(3) D. O. Cowan, N. G. Krieghoff, and G. Donnay, *Acta Crystallogr., Sect. B*, 24, 287 (1968); T. G. Spiro, D. H. Templeton, and A. Zalkin, *Inorg. Chem.*, 7, 2165 (1968).

(4) S. E. Binns, R. H. Cragg, R. D. Gillard, B. T. Heaton, and M. F. Pilbrow, *J. Chem. Soc. A*, 1227 (1969).

(5) L. F. Dahl, G. L. Davis, D. L. Wampler, and R. West, *J. Inorg. Nucl. Chem.*, 24, 1357 (1962).

(6) T. R. R. McDonald and W. S. McDonald, *Proc. Chem. Soc., London*, 382 (1963).

(7) E. Weiss, E. A. C. Lucken, *J. Organometal. Chem.*, 2, 197 (1964); E. Weiss and G. Hencken, *ibid.*, 21, 265 (1970).

(8) E. Weiss, H. Alsdorf, H. Kuhr, and H. F. Grutzmacher, *Chem. Ber.*, 101, 3777 (1968).

(9) E. Weiss, K. Hoffman, and H. F. Grutzmacher, *Chem. Ber.*, 103, 1190 (1970).

(10) W. M. M. Shearer and C. B. Spencer, *Chem. Commun.*, 194 (1966).

(11) D. Mootz, A. Zinnius, and B. Bottcher, *Angew. Chem.*, 81, 398 (1969).

(12) F. Schindler, H. Schmidtbaur, and U. Kruger, *Angew. Chem., Int. Ed. Engl.*, 4, 876 (1965).

(13) G. Diltmar and E. Hellner, *Angew. Chem.*, 81, 707 (1969).

(14) V. Albano, P. Bellon, G. Ciani, and M. Manassero, *J. Chem. Soc. D*, 1242 (1969).

(15) D. Bright, *J. Chem. Soc. D*, 1169 (1970).

(16) R. A. M. McLean, E. W. Abel, W. Harrison, W. C. Marsh, and J. Trotter, *J. Chem. Soc. D*, 1531 (1970).

(17) B. Buss and B. Krebs, *Inorg. Chem.*, 10, 2795 (1971).

(18) L. F. Dahl and A. S. Foust, *J. Amer. Chem. Soc.*, 92, 7337 (1970).

(19) J. E. Andrew and A. B. Blake, *J. Chem. Soc. A*, 1456 (1969).

(20) J. A. Bertrand, A. P. Ginsberg, R. J. Kaplan, C. E. Kirkwood, R. L. Martin, and R. C. Sherwood, *Inorg. Chem.*, 10, 240 (1971).

(21) J. A. Bertrand and J. A. Kelley, *Inorg. Chim. Acta*, 4, 203 (1970).

(22) E. Adman, L. C. Sieker, and L. H. Jensen, Abstracts, American Crystallographic Association Meeting, Alberquerque, N. M., April 1972, No. L2.

(23) J. A. Bertrand and D. Caine, *J. Amer. Chem. Soc.*, 86, 2298 (1964).

(24) G. N. Schrauzer and J. Kohnle, *Chem. Ber.*, 97, 1727 (1964).

(25) J. E. Andrew and A. B. Blake, *Chem. Commun.*, 1174 (1967).

(26) J. A. Bertrand and R. I. Kaplan, *Inorg. Chem.*, 4, 1657 (1965).

dropwise a solution of potassium hydroxide (0.03 mol) in 25 ml of methanol. After the resulting solution had been stirred for about 15 min at room temperature, 25 drops of 30% hydrogen peroxide was added; the flask containing the solution was stoppered and allowed to stand overnight. The dark brown, platelike crystals were filtered, washed first with methanol and then with diethyl ether, and dried under vacuum at 100° for several hours. *Anal.* Calcd for $Co_4C_{28}H_{46}O_{16}$: Co, 26.97; C, 38.44; H, 5.31. Found: Co, 26.80; C, 38.42; H, 5.42. The compound can be recrystallized from anhydrous diethyl ether.

Magnetic Susceptibility. The magnetic susceptibility of the compound was determined by the Faraday method at 298, 193, and 77°K using $HgCo(NCS)_4$ as a calibrant. Diamagnetic corrections were made using published atomic values.[27] Assuming that the cobalt(III) is diamagnetic, the effective magnetic moments obtained per gram-atom of cobalt(II) are 4.98, 4.72, and 4.62 BM at 298, 193, and 77°K, respectively.

Collection and Reduction of the X-Ray Data. Crystals obtained from the initial preparation were of sufficient size for X-ray work without recrystallization; the crystal for the space group determination was a plate of approximate dimensions 0.1 × 0.2 × 0.5 mm; it was mounted along the long dimension (a^* axis). Precession photographs, using Zr-filtered Mo Kα radiation (λ 0.7107 Å), indicated a triclinic unit cell; $P\bar{1}$, No. 2,[28] was assumed to be the space group and the successful refinement of the structure has confirmed this assumption. The crystal was transferred to an automated Picker four-circle diffractometer; 20 reflections were used to refine cell parameters by a least-squares procedure. The cell parameters obtained are a = 10.88 (1) Å,[29] b = 22.51 (3) Å, c = 12.76 (1) Å, α = 110.22 (8)°, β = 123.34 (7)°, γ = 108.92 (7)°, and V = 1848.5 Å^3 (25°, Mo radiation). The calculated density of 1.57 g cm^{-3} for 2 molecules per unit cell agrees well with the observed density of 1.56 (1) g cm^{-3} measured by the flotation method using carbon tetrachloride and hexane.

The X-ray intensity measurements were made on the same crystal as used for the unit cell determination and Mo radiation was again used. The intensities were measured with a scintillation counter mounted 21 cm from the crystal; the intensities were collected by the θ-2θ scan technique with a takeoff angle of 1.6° and a scan rate of 1°/min. A symmetrical scan of 2° was taken about the calculated position for each reflection; stationary background counts of 20 sec were taken at the beginning (bgd1) and at the end (bgd2) of the scan. Calibrated copper attenuators were used in the collection of data; the threshold point was set so that the counting rate would not exceed 10^4 counts/sec. The pulse height analyzer was set for approximately a 90% window, centered on the Mo Kα peak. A recorder monitored the scan of each peak and the scans were examined for erratic background and for the inclusion of Kβ peaks. A standard reflection (220) was intermittently scanned to check for instrument or crystal variation; no significant variation in the number of counts for this reflection was observed during the entire data collection period. Corrected intensities (I) were obtained by subtracting 3 times the total measured background from the total integrated peak count (CT)

$$I = \mathrm{CT} - 0.5(t_c/t_b)(\mathrm{bgd1} + \mathrm{bgd2})$$

where t_c is the scan time and t_b is the counting time of each background (either bgd1 or bgd2). The corrected intensities were assigned standard deviations according to the formula[30]

$$\sigma(I) = [\mathrm{CT} + 0.25(t_c/t_b)^2(\mathrm{bgd1} + \mathrm{bgd2}) + (pI)^2]^{1/2}$$

A total of 1166 reflections were accepted as statistically above background on the basis that $\sigma(I)/I$ was less than 0.33 with p = 0.03. The intensities were corrected for Lorentz and polarization effects. The linear absorption coefficient, μ, was 19 cm^{-1}. The value of $e^{-\mu t}$ ranged from a minimum of 0.68 to a maximum of 0.81. The actual range in integrated transmission factors is much smaller than this and so no absorption corrections were applied.

Table I. Final Positional and Thermal Parameters for $[Co_4(C_5H_7O_2)_4(CH_3O)_4(C_2H_3O_2)_2]$

Atom	x	y	z	B, Å^2
Co1	0.4132 (3)	0.3096 (2)	0.1967 (3)	2.69 (5)
Co2	0.0933 (3)	0.1523 (2)	−0.1336 (3)	2.54 (5)
Co3	0.0797 (3)	0.2952 (2)	−0.0735 (3)	3.16 (5)
Co4	0.0042 (3)	0.2180 (2)	0.0578 (3)	3.40 (6)
O1	0.1994 (16)	0.2013 (11)	0.0804 (15)	3.63 (27)
O2	0.2587 (16)	0.2668 (11)	−0.0276 (14)	2.81 (22)
O3	0.2445 (15)	0.3279 (11)	0.1641 (14)	3.29 (25)
O4	−0.0787 (15)	0.1712 (10)	−0.1669 (13)	3.30 (25)
O5	0.6037 (16)	0.4146 (10)	0.2897 (15)	3.91 (27)
O6	0.5298 (16)	0.3390 (10)	0.4003 (15)	4.07 (27)
O7	0.5523 (14)	0.2743 (10)	0.1926 (14)	2.77 (23)
O8	−0.0010 (16)	0.1163 (10)	−0.3366 (14)	3.50 (26)
O9	−0.0646 (16)	0.0463 (10)	−0.2160 (15)	4.23 (28)
O10	0.2932 (15)	0.1466 (10)	−0.0727 (13)	3.41 (25)
O11	−0.1035 (19)	0.3102 (12)	−0.0888 (17)	5.82 (34)
O12	−0.0658 (16)	0.2506 (12)	−0.3048 (15)	3.84 (26)
O13	0.2670 (16)	0.4108 (11)	0.0270 (16)	3.92 (28)
O14	−0.1612 (19)	0.2517 (12)	0.0060 (18)	4.96 (30)
O15	−0.1981 (17)	0.1041 (11)	−0.0462 (16)	4.79 (31)
O16	0.1165 (18)	0.2630 (11)	0.2817 (16)	4.68 (30)
M1C[a]	0.2319 (24)	0.1581 (18)	0.1396 (23)	3.26 (38)
M2C	0.3578 (27)	0.2949 (17)	−0.0713 (24)	4.68 (46)
M3C	0.3250 (29)	0.4122 (18)	0.3004 (26)	5.36 (49)
M4C	−0.2910 (25)	0.1035 (16)	−0.3303 (22)	4.12 (44)
R1C1[b]	0.8865 (34)	0.5552 (20)	0.4861 (29)	6.52 (56)
R1C2	0.7621 (26)	0.4802 (17)	0.4510 (24)	3.84 (42)
R1C3	0.8102 (28)	0.4778 (17)	0.5728 (24)	4.52 (45)
R1C4	0.6987 (28)	0.4135 (17)	0.5480 (24)	4.60 (44)
R1C5	0.7514 (28)	0.4156 (18)	0.6898 (26)	5.37 (49)
R2C1	−0.2882 (34)	−0.1023 (20)	0.3943 (29)	6.93 (59)
R2C2	−0.1849 (20)	−0.0248 (19)	−0.3737 (26)	5.07 (48)
R2C3	−0.2179 (29)	−0.0273 (18)	−0.4932 (25)	4.84 (47)
R2C4	−0.1316 (28)	0.0361 (18)	−0.4708 (24)	3.96 (41)
R2C5	−0.1777 (27)	0.0356 (18)	−0.6154 (25)	5.01 (48)
R3C1	−0.2038 (33)	0.2535 (20)	−0.5274 (29)	7.07 (62)
R3C2	−0.0448 (35)	0.3027 (23)	−0.3355 (30)	6.21 (54)
R3C3	0.0930 (39)	0.3863 (22)	−0.2308 (34)	7.35 (30)
R3C4	0.2388 (31)	0.4394 (20)	−0.0540 (29)	5.51 (51)
R3C5	0.3872 (40)	0.5342 (23)	0.0529 (35)	8.69 (72)
R4C1	0.2016 (36)	0.2705 (21)	0.5098 (32)	7.91 (65)
R4C2	0.0619 (32)	0.2158 (20)	0.3129 (27)	5.34 (49)
R4C3	−0.0806 (34)	0.1359 (20)	0.2041 (31)	6.41 (56)
R4C4	−0.2056 (32)	0.0848 (20)	0.0325 (30)	6.40 (56)
R4C5	−0.3640 (38)	−0.0169 (22)	−0.0791 (33)	7.90 (66)
A1C1[c]	0.4773 (22)	0.2099 (16)	0.0722 (21)	2.82 (36)
A1C2	0.6060 (26)	0.1897 (17)	0.0867 (23)	4.34 (43)
A2C1	−0.1857 (27)	0.2798 (20)	−0.0555 (26)	4.34 (44)
A2C2	−0.3198 (34)	0.3064 (20)	−0.0834 (30)	6.86 (60)

[a] M1, M2, M3, and M4 denote the methoxides. [b] R1, R2, R3, and R4 denote the 2,4-pentanedionato chelate rings. [c] A1 and A2 denote the acetates.

Solution of the Structure. Computations were carried out on a Burroughs B-5500 computer and on a Univac 1108 computer; programs employed included modified versions of F. L. Carter's program for calculating diffractometer settings, Zalkin's FORDAP Fourier summation program, the Busing-Martin-Levy XFLS and ORFFE least-squares and function and error programs, Johnson's ORTEP thermal ellipsoid plotting program, and various locally written programs. In structure factor calculations, the scattering factors tabulated by Ibers[31] were employed for all atoms.

The four cobalts and sixteen oxygen atoms were located from a three-dimensional Patterson synthesis. Four cycles of full-matrix least-squares refinement using the four cobalts and the four bridging oxygen atoms resulted in a conventional R_1 value ($\Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 0.389; the remaining oxygen atoms were introduced and four cycles of least-squares refinement produced an R_1 value of 0.321. From an electron density map phased on the four cobalt and sixteen oxygen atoms, thirteen carbon atoms were located; from the two succeeding electron density maps, the remaining fifteen carbon atoms were located. A weighting scheme based on counting statistics ($w = 4I/\sigma^2(I)$) was introduced and least-squares refinement of a scale factor, coordinates of each atom,

---

(27) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Wiley-Interscience, New York, N. Y., 1960, p 403.

(28) N. F. M. Henry and K. Lonsdale, Ed., "International Tables for X-Ray Crystallography," Vol. 1, Kynoch Press, Birmingham, England, 1965.

(29) Numbers in parentheses here and elsewhere in this paper indicate estimated standard deviations in the least significant digits.

(30) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 6, 197 (1967).

(31) J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962.

Table II. Interatomic Distances (Å) and Angles (Deg) in $[Co_4(C_5H_7O_2)_4(CH_3O)_4(C_2H_3O_2)_2]$

Atoms	Distances, Å	Atoms	Angles, deg	Atoms	Angles, deg
Co1-Co2	2.825 (10)	O1-Co1-O2	81.7 (7)	Co3-O3-Co4	90.9 (5)
Co1-Co3	3.142 (7)	O2-Co2-O4	82.6 (7)	Co2-O4-Co3	101.1 (5)
Co1-Co4	3.170 (6)	O4-Co2-O8	95.1 (6)	Co2-O4-Co4	103.4 (6)
Co1-O1	1.89 (2)	O4-Co2-O9	94.0 (7)	Co3-O4-Co4	90.0 (5)
Co1-O2	1.92 (1)	O1-Co2-O4	82.1 (6)	Co1-O1-M1C	120.0 (11)
Co1-O3	1.87 (2)	O2-Co2-O10	92.0 (7)	Co2-O1-M1C	117.1 (16)
Co1-O5	1.86 (2)	O8-Co2-O10	89.6 (6)	Co4-O1-M1C	114.8 (11)
Co1-O6	1.85 (1)	O9-Co2-O10	90.9 (7)	Co1-O2-M2C	120.1 (10)
Co1-O7	1.94 (2)	O1-Co2-O10	92.7 (6)	Co3-O12-R3C2	120.7 (17)
Co2-Co3	3.114 (7)	O2-Co2-O8	91.5 (7)	Co2-O2-M2C	120.9 (14)
Co2-Co4	3.183 (4)	O8-Co2-O9	94.9 (7)	Co3-O2-M2C	111.9 (15)
Co2-O1	1.91 (1)	O1-Co2-O9	91.4 (7)	Co1-O3-M3C	120.2 (11)
Co2-O2	1.90 (2)	O1-Co2-O2	82.1 (7)	Co3-O3-M3C	113.8 (16)
Co2-O4	1.91 (2)	O2-Co3-O3	71.7 (5)	Co4-O3-M3C	117.8 (11)
Co2-O8	1.87 (1)	O2-Co3-O13	96.1 (7)	Co2-O4-M4C	118.4 (14)
Co2-O9	1.83 (2)	O2-Co3-O12	98.8 (6)	Co3-O4-M4C	121.4 (16)
Co2-O10	1.93 (1)	O2-Co3-O4	73.4 (6)	Co4-O4-M4C	117.7 (10)
Co3-Co4	3.017 (6)	O3-Co3-O11	95.6 (6)	Co1-O5-R1C2	125.8 (16)
Co3-O2	2.09 (2)	O11-Co3-O13	94.6 (8)	Co1-O6-R1C4	124.2 (16)
Co3-O3	2.14 (1)	O11-Co3-O12	92.9 (6)	Co2-O8-R2C4	121.7 (17)
Co3-O4	2.12 (2)	O4-Co3-O11	95.7 (7)	Co2-O9-R2C2	123.7 (16)
Co3-O11	2.04 (2)	O3-Co3-O13	93.5 (7)	O2-Co1-O3	81.5 (6)
Co3-O12	2.00 (2)	O12-Co3-O13	91.5 (8)	O3-Co1-O5	95.8 (8)
Co3-O13	1.99 (2)	O3-Co3-O4	83.0 (7)	O3-Co1-O6	94.6 (6)
Co4-O1	2.16 (2)	O4-Co3-O12	90.5 (7)	O1-Co1-O3	80.6 (7)
Co4-O3	2.09 (2)	O1-Co4-O3	69.8 (7)	O2-Co1-O7	90.9 (6)
Co4-O4	2.14 (1)	O1-Co4-O4	71.2 (6)	O5-Co1-O7	89.8 (7)
Co4-O14	2.04 (2)	O1-Co4-O15	98.2 (8)	O6-Co1-O7	92.2 (6)
Co4-O15	1.99 (2)	O1-Co4-O16	100.2 (6)	O1-Co1-O7	93.0 (7)
Co4-O16	2.01 (2)	O3-Co4-O14	95.7 (8)	O2-Co1-O5	92.1 (7)
O1-M1C	1.44 (3)	O4-Co4-O14	94.3 (6)	O5-Co1-O6	95.3 (7)
O2-M2C	1.53 (2)	O14-Co4-O15	95.8 (8)	O1-Co1-O6	90.5 (7)
O3-M3C	1.54 (3)	O14-Co4-O16	93.9 (7)	Co3-O13-R3C4	126.1 (14)
O4-M4C	1.49 (2)	O3-Co4-O16	92.7 (6)	Co4-O16-R4C2	124.6 (15)
A1C1-O7	1.20 (2)	O15-Co4-O16	89.9 (7)	Co4-O15-R4C4	125.0 (16)
A1C1-O10	1.31 (2)	O3-Co4-O4	83.6 (5)	Co1-O7-A1C1	124.0 (12)
A1C1-A1C2	1.54 (3)	O4-Co4-O15	92.2 (6)	Co2-O10-A1C1	121.5 (16)
A2C1-O11	1.29 (3)	Co1-O1-Co2	96.1 (8)	O7-A1C1-O10	130.3 (20)
A2C1-O14	1.14 (4)	Co1-O1-Co4	102.8 (10)	O7-A1C1-A1C2	118.5 (16)
A2C1-A2C2	1.66 (4)	Co2-O1-Co4	103.0 (8)	O10-A1C1-A1C2	110.9 (20)
		Co1-O2-Co2	95.2 (8)	Co3-O11-A2C1	122.0 (22)
		Co1-O2-Co3	103.1 (6)	Co4-O14-A2C1	126.5 (17)
		Co2-O2-Co3	102.5 (5)	O11-A2C1-O14	132.8 (27)
		Co1-O3-Co3	103.2 (6)	O11-A2C1-A2C2	105.9 (29)
		Co1-O3-Co4	106.2 (10)	O14-A2C1-A2C2	120.3 (22)

and individual isotropic temperature factors (192 variable parameters) was continued until no parameter varied by as much as 20% of its estimated standard deviation; R_1 and R_2 ($R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{1/2}$) converged to values of 0.068 and 0.061, respectively. Final structure parameters are listed in Table I.[32]

Discussion

The preparation, with the exception of the hydrogen peroxide, is essentially the same as was used for the preparation of the cobalt(II) cubane $[Co(CH_3O)(acac)(CH_3OH)]_4$. A large excess of hydrogen peroxide was added in order to oxidize all of the cobalt to the trivalent state; however, the crystalline product isolated, which analyzed as $Co_4(CH_3O)_4(ac)_2(acac)_4$, was found to be paramagnetic with a moment of 3.6 BM/g-atom of cobalt at room temperature. The stoichiometry and charge balance indicate two trivalent and two divalent cobalt ions per molecule; assuming that the cobalt(III) ions are diamagnetic, the room temperature magnetic moment per gram atom of cobalt(II), 4.98 BM, is in the normal range for octahedral coordination. The moment is, however, temperature dependent, decreasing to a value of 4.62 BM/g-atom of cobalt(II) at 77°K; the cobalt(II) ions, thus, show antiferromagnetic[20,25] coupling in contrast to the ferromagnetic coupling exhibited by the nickel(II) cubanes.

The complex, Figures 1 and 2, consists of octahedrally coordinated metal ions and methoxide oxygens at alternate corners of a distorted cube; in addition to three μ_3-methoxide oxygens, each metal ion is coordinated to a chelate 2,4-pentanedionate group and to an acetate oxygen. The acetate groups form μ_2 bridges across the top and bottom faces of the cubane unit. Although the complex occupies a crystallographic site which requires no symmetry, it approaches C_{2v} symmetry; in fact, except for differences which result from differences in cobalt-oxygen distances, the complex would approach D_{2d} symmetry. However, as indicated in Table II, all of the cobalt-oxygen distances for the upper two cobalts (1.83-1.94 Å) are shorter than those of the lower two cobalts (1.99-2.16 Å); since stoichiometry and charge balance require two divalent and two trivalent cobalts per molecule, it would appear that the upper two metal ions are trivalent and the lower two divalent. The difference in bond lengths for these cobalt-oxygen bonds (0.16-0.22 Å) is comparable to the 0.15-Å difference found for the cobalt(II)- and cobalt(III)-nitro-

---

(32) A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-206.

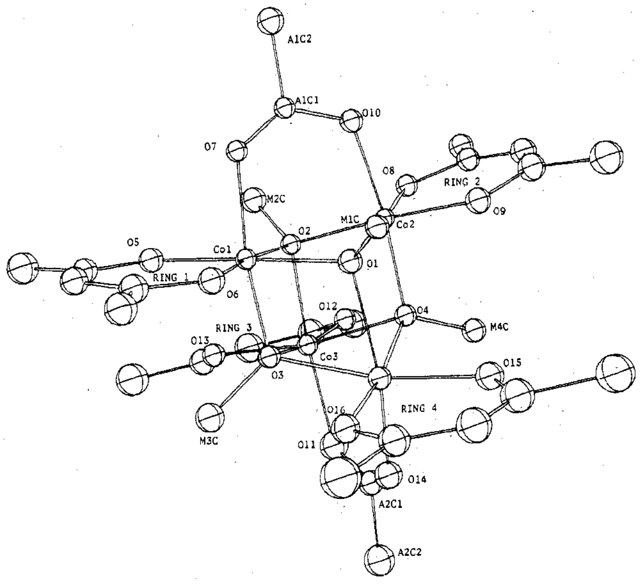

Figure 1. A perspective drawing of the molecular structure of $[Co_4(CH_3O)_4(C_5H_7O_2)_4(C_2H_3O_2)_2]$.

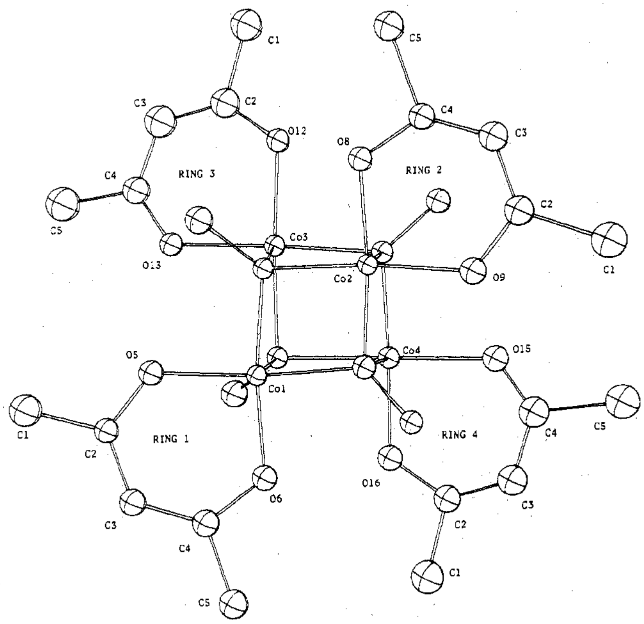

Figure 2. The structure of $[Co_4(CH_3O)_4(C_5H_7O_2)_4(C_2H_3O_2)_2]$ viewed down the pseudo-twofold axis. The acetate groups have been omitted for clarity.

gen distances in the hexaammine complexes.[33]

The distortion of the cubane unit is most apparent in the four-membered cobalt-oxygen rings which form the top and bottom of the cube. The four-membered rings are considerably bent; the bending can be thought of as a folding along the cobalt-cobalt axis so that all of the oxygens move toward the center of the cube. The dihedral angles between the O-Co-O planes of those rings are 21.9° for the upper or cobalt(III) ring and 36.3° for the lower cobalt(II) ring.

The distortion of the octahedral coordination of the metal ions is reflected in the oxygen-cobalt-oxygen angles. The angles at cobalt(III) vary from 80.6 to 95.8° while the angles at cobalt(II) vary from 71.2 to 100.2°; the greater

Table III. Interatomic Distances (Å) in Six-Membered Chelate Rings in $[Co_4(C_5H_7O_2)_4(CH_3O)_4(C_2H_3O_2)_2]$

	Ring 1	Ring 2	Ring 3	Ring 4
C2–C3	1.37 (3)	1.34 (3)	1.34 (4)	1.29 (4)
C3–C4	1.34 (3)	1.25 (4)	1.42 (3)	1.39 (3)
C1–C2	1.49 (4)	1.57 (4)	1.56 (3)	1.61 (3)
C4–C5	1.54 (3)	1.62 (3)	1.53 (4)	1.65 (4)
C2–O	1.32 (2)	1.36 (2)	1.35 (4)	1.34 (3)
C4–O	1.32 (2)	1.32 (3)	1.35 (3)	1.25 (3)
C_2–C_3–C_4	126 (2)	124 (3)	124 (3)	125 (3)
C_1–C_2–C_3	124 (2)	126 (2)	117 (4)	122 (3)
C_3–C_4–C_5	124 (4)	125 (2)	119 (3)	116 (3)
O–C_2–C_3	123 (3)	125 (3)	131 (3)	126 (2)
O–C_4–C_3	126 (2)	130 (2)	124 (3)	129 (3)
O–C_2–C1	113 (2)	109 (2)	112 (3)	112 (2)
O–C_4–C_5	110 (2)	104 (2)	117 (2)	115 (2)

Table IV. Equations of Least-Squares Atomic Planes[a] and Distances of Atoms from These Planes for $[Co_4(C_5H_7O_2)_4(CH_3O)_4(C_2H_3O_2)_2]$

Atom	Distance from plane, Å	Atom	Distance from plane, Å
(a) Equation of the Plane Including Co2, O1, and O2 $0.899X - 0.266Y + 0.347Z + 0.676 = 0$			
Co1	0.528	O2	0.000
Co2	0.000	O3	−1.281
O1	0.000		
(b) Equation of the Plane Including Co4, O3, and O4 $0.70X - 0.583Y + 0.404Z + 3.749 = 0$			
Co3	−0.885		
Co4	0.000		
O3	0.000		
O4	0.000		
O6	2.190		
(c) Equation of the Best Least-Squares Plane of Ring 1 (O5, O6, R1C2, R1C3, R1C4) $0.907X - 0.398Y + 0.138Z + 1.415 = 0$			
Co1	0.071	R1C1	−0.066
O1	0.038	R1C2	−0.026
O2	0.045	R1C3	0.024
O5	0.012	R1C4	−0.013
O6	0.004	R1C5	−0.064
O7	1.994		
(d) Equation of the Best Least-Squares Plane of Ring 2 (O8, O9, R2C2, R2C3, R2C4) $0.901X - 0.271Y + 0.339Z + 0.739 = 0$			
Co2	0.054	R2C1	0.010
O1	0.036	R2C2	0.023
O2	0.036	R2C3	−0.015
O8	0.006	R2C4	−0.001
O9	−0.011	R2C5	−0.140
O10	1.953		
(e) Equation of the Best Least-Squares Plane of Ring 3 (O12, O13, R3C2, R3C3, R3C4) $0.996X - 0.084Y + 0.023Z + 1.017 = 0$			
Co3	−0.316	R3C1	−0.055
O3	−0.373	R3C2	−0.029
O4	−0.301	R3C3	0.026
O11	−2.338	R3C4	−0.024
O12	0.018	R3C5	0.032
O13	0.012		
(f) Equation of the Best Least-Squares Plane of Ring 4 (O15, O16, R4C2, R4C3, R4C4) $0.910X - 0.333Y + 0.246Z + 3.273 = 0$			
Co4	0.151	R4C1	0.059
O3	0.709	R4C2	0.006
O4	0.632	R4C3	0.017
O14	1.796	R4C4	−0.027
O15	0.018	R4C5	0.134
O16	−0.010		

[a] The orthogonal X axis is coincident to a and the orthogonal Z axis is coincident to c^*.

---

(33) M. T. Barnet, B. M. Craven, H. C. Freeman, N. E. Kime, and J. A. Ibers, *Chem. Commun.*, 307 (1966).

distortion at the cobalt(II) ions is consistent with the smaller crystal field stabilization of the divalent d^7 ions relative to the trivalent d^6 ions.

The bond distances and bond angles for the 2,4-pentanedionate groups are listed in Table III and the least-squares planes of the rings and deviations of the individual atoms from these planes are given in Table IV; these groups do not show any unusual features when compared to 2,4-pentanedionate groups from other structures.

Within each acetate, there is a significant difference in the two carbon-oxygen distances; the long carbon-oxygen distances within the two acetates differ by less than the sum of their standard deviations and the short carbon-oxygen distances differ by the sum of their standard deviations. However, the shortest carbon-oxygen distance has an abnormally high standard deviation; the carbon-carbon distance of that acetate is extremely long and also has a high standard deviation. Attempts to find better positions for the atoms in this region resulted in refinement to the same final positions.

The difference in magnetic properties between the present compound and the nickel(II) cubanes needs further investigation; however, the difference is not surprising when one considers (1) the change in electronic structure in going from d^8 nickel(II) to d^7 cobalt(II) and (2) the additional bridging by the acetate in the present structure. The change from d^8 to d^7 provides a vacancy in the t_{2g} orbitals and the acetate provides a π pathway for superexchange; since the half-filled t_{2g} orbital can be oriented in such a way as to overlap with the acetate π system, an antiferromagnetic coupling is possible.

Registry No. $Co_4(CH_3O)_4(CH_3CO_2)_2(C_5H_7O_2)_4$, 36731-69-8.

Acknowledgment. This work was supported by NSF Grant GP-20885. Funds from the Quality Improvement Program of the State of Georgia for the purchase of X-ray diffraction equipment are gratefully acknowledged; the help of the Rich Electronic Computer Center of Georgia Institute of Technology with computations is appreciated.

Contribution from Ames Laboratory–U. S. Atomic Energy Commission and
Department of Chemistry, Iowa State University, Ames, Iowa 50010

Crystal Structure of Hexaamminecobalt Hexachloroantimonate(III)

DONALD R. SCHROEDER and ROBERT A. JACOBSON*

Received August 15, 1972

Hexaamminecobalt hexachloroantimonate(III), $Co(NH_3)_6SbCl_6$, crystallizes in the orthorhombic space group *Pbca* (D_{2h}^{15}) with unit cell parameters $a = 11.50 \pm 0.03$ Å, $b = 11.53 \pm 0.03$ Å, and $c = 11.51 \pm 0.02$ Å. The observed and calculated densities were both found to be 2.19 g/cm^3 with $Z = 4$. Data were collected on an automated four-circle diffractometer equipped with scintillation counter using the θ–2θ step-scan technique and Mo Kα radiation (λ 0.71069 Å). The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares techniques to a final discrepancy index $R = 0.061$ for the 416 independent reflections significantly above background. The structure consists of $SbCl_6^{3-}$ anions and $Co(NH_3)_6^{3+}$ cations both of which have exact $\bar{1}$ crystallographic symmetry. Both also have approximately octahedral symmetry with all Sb–Cl bond lengths in $Sb^{III}Cl_6$ of 2.643 (6) Å (2.652 (6) Å when corrected for thermal motion); the mean Co–N bond distance is 1.982 (10) Å.

Introduction

The crystal structure investigation of hexaamminecobalt hexachloroantimonate(III) was undertaken as part of a series of investigations of halo-coordinated antimony compounds being performed in this laboratory.[1-7] Through these studies an attempt is being made to evaluate the effects of cation size and type on the stereochemistry of different antimony halides and to determine what effect, if any, the lone pair plays in the coordination geometry. The structures of a number of bromide complexes have previously been reported including $[(CH_3)_4N]_3Sb_2Br_9\cdot Br_2$[2] and $(C_5H_5NH)_5Sb_2Br_9\cdot Br_2$,[3] both of which contain $Sb_2Br_9^{3-}$ species, and $(NH_4)_4Sb^{III}Sb^{V}Br_{12}$,[4] $Rb_4Sb^{III}Sb^{V}Br_{12}$,[5] $(C_5H_5NH)_6Sb^{III}Sb^{V}_3Br_{24}$,[6] and $(C_7H_{13}NH)_4Sb^{III}Sb^{V}Br_{12}\cdot 2Br_2$,[7] all of which contain octahedral $SbBr_6^{3-}$ units. Of the chloride complexes, accurate crystal structure determinations of only $(NH_4)_2SbCl_5$[8] and $(C_5H_5NH)SbCl_4$[9] have been reported. In addition the stoichiometric formula found for the present complex indicated the presence of an $SbCl_6^{3-}$ anion; a structural study of such an anion has not been reported previously.

Experimental Section

Preparation. The salt was prepared by the reaction of hexaamminecobalt(III) chloride and antimony trioxide in a solution of 2 *M* hydrochloric acid. Hexaamminecobalt(III) chloride was first prepared by adding 24.0 g (0.1 mol) of cobalt(II) chloride hexahydrate and 16.0 g (0.3 mol) of ammonium chloride to 20.0 ml of H_2O. To this was added 0.4 g of activated decolorizing charcoal and 50.0 ml of concentrated NH_3. Air was then bubbled vigorously through the mixture for approximately 4 hr to enhance oxidation of Co(II). The crystals were filtered and then added to a solution of 3.0 ml of con-

---

(1) S. L. Lawton and R. A. Jacobson, *Inorg. Chem.*, 7, 2124 (1968).

(2) C. R. Hubbard and R. A. Jacobson, *Inorg. Chem.*, 11, 2247 (1972).

(3) S. K. Porter and R. A. Jacobson, *J. Chem. Soc. A*, 1356 (1970).

(4) S. L. Lawton and R. A. Jacobson, *Inorg. Chem.*, 5, 743 (1966).

(5) C. R. Hubbard and R. A. Jacobson, *Proc. Iowa Acad. Sci.*, 75, 85 (1968).

(6) S. L. Lawton, R. A. Jacobson, and R. S. Frye, *Inorg. Chem.*, 9, 701 (1970).

(7) S. L. Lawton and R. A. Jacobson, *Inorg. Chem.*, 10, 709 (1971).

(8) M. Edstrand, M. Inge, and N. Inqri, *Acta Chem. Scand.*, 9, 122 (1955).

(9) S. K. Porter and R. A. Jacobson, *J. Chem. Soc. A*, 1359 (1970).