

bear a marked resemblance to certain molybdenum and tungsten compounds which we wish to discuss briefly at this time. Recently, complexes of general formula $M[\text{MoOX}_4]$, $M[\text{MoOX}_5]$, and $M[\text{WOX}_5]$ were prepared²⁸ and characterized, where M is a univalent cation and X is Cl or Br. From the chemical and physical properties reported for these compounds,²⁸ it is apparent that they are structurally very similar to the rhenium analogs described by us. In fact, X-ray studies by Rogers and Scane²⁹ have verified that in salts containing the (MoOBr_4) moiety, the basic structural unit is the square-pyramidal (MoOX_4) group, with perhaps a sixth ligand (H_2O) bonded weakly to the molybdenum atom at the base. Moreover, a comparison of the (orthorhombic) unit cell parameters and space groups of $[(\text{C}_2\text{H}_5)_4\text{N}][\text{ReBr}_4\text{O}(\text{H}_2\text{O})]_4$ and $[(\text{C}_2\text{H}_5)_4\text{N}][\text{MoOBr}_4(\text{H}_2\text{O})]_2$ ²⁹ shows that they are in fact isomorphous and, in all probability, isostructural.

Thus, the oxotetrahalo complexes and their deriva-

tives of Mo(V) and W(V) are quite similar to the series of Re(V) compounds reported by us, both in their chemical and structural properties. In view of the arguments presented^{3,5} for the existence of strong $\text{O} \rightarrow \text{M} \pi$ bonding in the rhenium compounds, it seems likely that this feature also occurs in the molybdenum and tungsten complexes. The degree of $\text{O} \rightarrow \text{M} \pi$ bonding (and, presumably, the *stability* of the complex) ostensibly depends upon two factors: first, incomplete occupancy of the $d\pi$ orbitals of the metal atom so that these orbitals are able to receive electrons from oxygen atoms, and, second, the high oxidation state of the metal atom, so that the resulting complex does not have too great a negative charge to stabilize, which it might perhaps do by delocalization back through the π orbitals onto the electronegative oxygen atom. In view of these two criteria, it seems possible that square-pyramidal tetrahalometallate complexes of Nb(V), Ta(V), Tc(V), Ru(VI), and Os(VI) might be prepared under the appropriate conditions.

Acknowledgment.—We wish to thank the MIT Computation Center for access to the IBM 7094 computer.

(28) E. A. Allen, B. J. Brisdon, D. A. Edwards, G. W. A. Fowles, and R. G. Williams, *J. Chem. Soc.*, 4649 (1963).

(29) D. Rogers, Department of Chemistry, Imperial College, London, private communication, Oct. 1965.

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The Crystal and Molecular Structure of Dimeric Bis(acetylacetonato)aquocobalt(II) and the Preparation of Some Other New Hydrates^{1a}

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Received July 30, 1965

The preparation of $[\text{Co}(\text{AA})_2\text{H}_2\text{O}]_2$ and other hydrated derivatives of $\text{Co}(\text{AA})_2$ is discussed (AA = the acetylacetonate anion). The structure of the former, determined by single-crystal X-ray techniques, is that of a centrosymmetric dimer, corresponding to the center of the $[\text{Co}(\text{AA})_2]_4$ structure with the missing bridge bonds replaced by bonds to water molecules. A second, triclinic, crystal form of the dihydrate, $\text{Co}(\text{AA})_2(\text{H}_2\text{O})_2$, has been isolated as well as a new compound which may be either $[\text{Co}(\text{AA})_2]_2\text{H}_2\text{O}$ or $[\text{Co}(\text{AA})_2]_2\text{H}_2\text{O}$.

Introduction

The solution chemistry of bis(acetylacetonato)cobalt(II), $\text{Co}(\text{AA})_2$, is rather complex. The tendency of the cobalt to achieve six-coordination is pronounced and appears to be the most important single structural principle governing the behavior of these systems. In donor solvents, the bis(acetylacetonate) reacts with two donor molecules, D, to form the octahedral complex, $\text{Co}(\text{AA})_2\text{D}_2$.^{2,3} In noncoordinating solvents, spectroscopic^{4a} studies have shown that $\text{Co}(\text{AA})_2$ exists as a tetrahedral monomer in very dilute solution; both spectroscopic^{4a} and cryoscopic^{4b} evidence indicate that

in more concentrated solutions octahedral coordination is achieved through polymerization. Polymerization has also been shown to occur in the solid $[\text{Co}(\text{AA})_2]_4$ formed by sublimation.⁵ If a small amount of some neutral donor ligand, D, is introduced into a solution of polymer in a noncoordinating solvent, complex equilibria are established and the following types of compounds can be obtained from such solutions: $[\text{Co}(\text{AA})_2]_4$, $[\text{Co}(\text{AA})_2]_2\text{D}$, $[\text{Co}(\text{AA})_2\text{D}]_2$, and $\text{Co}(\text{AA})_2\text{D}_2$, where D may be water, pyridine,⁶ or cyclohexylamine.⁷

While attempts to crystallize consistently an anhy-

(1) (a) Supported by a grant from the National Science Foundation; (b) National Institutes of Health Predoctoral Fellow, 1962–1964.

(2) G. J. Bullen, *Acta Cryst.*, **12**, 703 (1959).

(3) F. A. Cotton and R. H. Holm, *J. Am. Chem. Soc.*, **82**, 2979 (1960).

(4) (a) F. A. Cotton and R. H. Soderberg, *Inorg. Chem.*, **3**, 1 (1964); (b) D. P. Graddon, *Nature*, **195**, 891 (1962).

(5) F. A. Cotton and R. C. Elder, *Inorg. Chem.*, **4**, 1145 (1965). It is to be emphasized that tetramers were found in the solid, whereas the solutions were reported to contain either dimers^{4a} or trimers.^{4b} This point will be discussed in a later paper in this series.

(6) J. P. Fackler, Jr., *ibid.*, **2**, 286 (1963); *J. Am. Chem. Soc.*, **84**, 24 (1962).

(7) J. A. Bertrand, F. A. Cotton, and W. J. Hart, *Inorg. Chem.*, **3**, 1007 (1964).

drous polymeric compound have met with only limited success, crystals of $[\text{Co}(\text{AA})_2\text{H}_2\text{O}]_2$ have been isolated and their structure is reported here. This work was done principally to establish the over-all molecular structure and does not lead to precise molecular parameters. At present, it is the general patterns of structural changes among these molecules which we are seeking to establish.

Experimental Section

Preparation of $[\text{Co}(\text{AA})_2\text{H}_2\text{O}]_2$.—In the course of a series of attempts to prepare crystals of anhydrous cobalt(II) acetylacetonate from solution, it was observed that the solubility of the anhydrous material in noncoordinating solvents was much greater than the solubility of the hydrated material. Whenever an attempt was made to crystallize the anhydrous material, either no crystals were formed or those formed had the appearance and properties of the dihydrate. The solutions which did not yield any solid could be concentrated by distilling off the solvent at reduced pressure. However, some oxidation and/or decomposition may have taken place² as the solutions often yielded an oil on standing.

In one case, crystals were formed which did not resemble either the dihydrate or the anhydrous material. A concentrated, presumably saturated, solution was made by the addition of the anhydrous material to boiling toluene (previously distilled over sodium) until additional solid remained undissolved.⁸ The solution was filtered through a coarse glass frit in air, and the filtering flask was placed in a desiccator with paraffin shavings to absorb the toluene and with CaCl_2 to serve as a desiccant. After the solution had cooled, crystals formed in the filtering flask. The reproducibility of this method of preparation is poor.

A second and superior method allows crystals to be grown from solution by a slow-diffusion process. A concentrated solution (from 0.1 to 2.0 g/10 ml) of the anhydrous sublimed material in benzene which had been previously saturated with water was used to fill a 2-oz, wide-mouth jar. This jar was placed inside a 4-oz jar which was then filled slowly with isooctane, care being taken to avoid mixing the solutions. The outer jar was then capped and allowed to stand for several days. The jars were filled almost to the brim, but no further effort was made to exclude air; a small amount of oxidation occurred yielding a green product. After the solution had become almost homogeneous (essentially the same color throughout), the jar was opened, and the crystals which had precipitated were collected on a coarse glass frit. Several distinct crystal types and compounds were obtained and were mechanically separated under a microscope.

$\text{Co}(\text{AA})_2(\text{H}_2\text{O})_2$ was obtained in two orange crystalline forms. One form had the unit cell constants reported by Bullen,³ and the other was triclinic with $a = 5.55$, $b = 10.79$, $c = 11.99$, $\alpha = 90.4^\circ$, $\beta = 114.6^\circ$, $\gamma = 102.3^\circ$. The infrared mull spectra of both forms were the same, possibly because one form is converted into the other by grinding.

$[\text{Co}(\text{AA})_2]_4$ was obtained in an intensely purple dendritic growth. The unit cell constants and mull spectrum were the same as those obtained with the sublimed material.⁵

$[\text{Co}(\text{AA})_2]_{2-3}\text{H}_2\text{O}$ is a light purple, crystalline substance with a distinctive mull spectrum. The triclinic crystals have reduced cell constants $a = 9.04$, $b = 10.55$, $c = 19.52$, $\alpha = 94.4^\circ$, $\beta = 92.0^\circ$, $\gamma = 101.0^\circ$. As in all the hydrated forms, there is a broad band at approximately 3300 cm^{-1} which may be attributed to water. The analyses on this compound are such that it is not easy to distinguish between the two formulations. *Anal.* Calcd for $[\text{Co}(\text{AA})_2]_2\text{H}_2\text{O}$: C, 45.12; H, 5.68. $[\text{Co}(\text{AA})_2]_3\text{H}_2\text{O}$: C, 45.64; H, 5.62. Found: C, 45.57; H, 5.50. Further work is in progress on this substance.

$[\text{Co}(\text{AA})_2\text{H}_2\text{O}]_2$ crystallizes in the form of blood-red rectangular parallelepipeds. The crystals prepared by the first method

were the same in all respects as those prepared by the second method. The infrared spectra again showed a broad band near 3300 cm^{-1} . The agreement of the analysis with the expected values is relatively poor, which may perhaps be ascribed to difficulties in separation or to the instability of the compound. *Anal.* Calcd: C, 43.64; H, 5.86. Found: C, 46.3, 45.6, 45.0; H, 6.28, 5.69, 5.92. However, the subsequent X-ray analysis establishes that this formula is the correct one.

Preliminary Investigation: Unit Cell and Space Group.—The crystals, which were mounted in sealed capillaries, were examined on the precession camera. The monoclinic crystals have the following cell constants: $a = 20.00 \pm 0.02$, $b = 15.03 \pm 0.03$, $c = 19.26 \pm 0.03$, $\beta = 94.3 \pm 0.4^\circ$. Precession photographs established the following conditions for the systematic absences: hkl , $h + k \neq 2n$; $h0l$, $l \neq 2n$. These conditions are in agreement with those of the two space groups⁹ Cc (No. 9) and C2/c (No. 15), only the latter having a center of symmetry.

The volume of the cell is 5780 \AA^3 . The density was difficult to determine as only small quantities of the material were available and the compound was highly soluble in or reactive toward solvents ordinarily used for density determination by the flotation method. From the experimental work, a density of 1.4 ± 0.1 was estimated. If reasonable allowance is made for the introduction of H_2O , we may estimate from the density of 1.45 ± 0.05 for $[\text{Co}(\text{AA})_2]_4$ that the density of $\text{Co}(\text{AA})_2\text{H}_2\text{O}$ is $\sim 1.35 \pm 0.05$. Using this figure the number of $\text{Co}(\text{AA})_2\text{H}_2\text{O}$ groups in the unit cell is 16.5 ± 0.6 .

Data Measurement.—The crystal was removed from the Buerger camera and placed on the General Electric XRD-5 diffractometer. The stationary-crystal, stationary-counter technique¹⁰ was used to collect data. The mosaic spread was checked, and with a take-off angle of 7° all reflections below 50° in 2θ could be measured by this technique.

Since the number of positional parameters is only half as great in the centric as in the acentric space group, an attempt was made to distinguish between the two possibilities prior to the completion of data collection. The data for each of the principal zones was subjected to the statistical test of Howells, Phillips, and Rogers,¹¹ and in each case the presence of a center of inversion was indicated. Therefore, three-dimensional data were collected on the assumption that the space group was C2/c.

The data were collected using Mo $K\alpha$ radiation and the scintillation detector. Unfortunately, the noise level of the amplifier became excessive after the measurement of about 600 reflections. A pulse-height selector was obtained, and the remaining data were collected using the analyzer to remove the noise. The two portions of the data were scaled independently in later calculations. The absorption of molybdenum radiation is negligible when a relatively small crystal is used ($\mu = 15\text{ cm}^{-1}$). The crystal was $0.30 \times 0.18 \times 0.12\text{ mm}$ with the unique axis parallel to the long dimension of the crystal and coincident with the rotation axis of the goniometer.

Over 2200 reflections in the sphere bounded by $(\sin \theta)/\lambda = 0.45$ were measured. The settings necessary for these measurements were calculated using MIXG-2.¹² Two reflections were chosen as standards and checked frequently for any sign of decomposition. The values of the peak and the background for each reflection were punched onto the MIXG-2 cards and used as input to RAWRE-2.¹³ The values of $|F_o|^2$ obtained were used

(9) "International Tables of Crystallography," Vol. 1, Kynoch Press, Birmingham, England, 1952.

(10) T. C. Furnas, Jr., "Single Crystal Orienter Instruction Manual," X-Ray Department, General Electric, Co., Schenectady, N. Y., 1957.

(11) The statistical test was performed using "MICAST-Crystallographic Acentricity Statistical Test," a program for the IBM 709/7090 computer by R. C. Elder. IBM SHARE library distribution No. 3269, March 1965.

(12) D. P. Shoemaker, "MIXG-2-MIT X-Ray Goniometer Package," setting program for the IBM 709/7090 computer 1962.

(13) R. C. Elder, "RAWRE-2-Raw Data Reduction Program for the IBM 709/7090 Computer," 1964. This program computes for each reflection the product of the reciprocal Lorentz polarization factor times the value of the peak minus the background and times a weighting factor if desired.

(8) Roughly 5 g of $\text{Co}(\text{AA})_2$ in 5 ml of toluene.

to compute the Patterson function.¹⁴ Also, the full set of three-dimensional data was used with MICAST,¹¹ and again the centric space group was indicated.

Structure Determination.—The general position in C2/c gives rise to the Harker¹⁵ line $0, 2y, \frac{1}{2}$ and to the Harker plane $2x, 0, \frac{1}{2} + 2z$. Eighteen peaks were observed in the Patterson function; all peaks had x values in the range 0.000–0.100 or the range 0.433–0.500. From these, the peaks corresponding to the Harker line and plane for the general position were sought. For the two cobalt atoms the following coordinates were deduced: 0.216, 0.666, 0.533, and 0.250, 0.333, 0.450. A Fourier function was then calculated¹⁴ using signs for all reflections based upon the contribution of cobalt atoms at these positions. After a very careful examination of the Fourier map, it was possible to assign positions for all atoms in the structure except hydrogen atoms.

The positions for all atoms were now used to calculate signs for a Fourier synthesis on a fine grid (60th of the cell edges). The R value^{16,17} was about 0.38 using these initial positional parameters. The positional parameters were refined twice by Fourier methods, and then all atom positions were refined with equal weights for three cycles of least squares yielding a residual of 0.25.

The weighting scheme of Burnham¹⁸ for counter-diffractometer data was used for one cycle of refinement and gave $wR = 0.14$ and $R = 0.40$, thus showing that counting statistics were not the major cause of error in most of the data.

A second weighting scheme, that of Cruickshank¹⁹ in which $w = f(|F_o|)$ such that the condition $w\Delta = \text{constant}$ is fulfilled, was used for five cycles of refinement of all parameters and gave $wR = 0.20$ and $R = 0.23$. At this point a difference Fourier synthesis was computed. It gave clear evidence of anisotropic thermal vibrations. Six cycles of refinement with anisotropic thermal parameters for cobalt and oxygen atoms yielded $wR = 0.16$ and $R = 0.18$.

The weighting scheme was changed to a hybrid²⁰ of the Burnham and Cruickshank schemes. An attempt to refine the anisotropic thermal parameters of the carbon atoms was unsuccessful as almost half of the parameters did not test as positive-definite. Since it seemed that the data were not adequate to warrant such refinement, no further attempt was made. The cobalt and oxygen atoms which had shown anisotropic motion in the difference Fourier map were refined without difficulty.²¹ In the final two cycles, all parameters except the scale factors and the carbon thermal parameters were refined. The final weighted residual was 0.138. The parameters obtained and their standard deviations as estimated in the last cycle in which they were varied are listed in Tables I and II. The orthogonal coordinates of all the atoms are listed in Table III. The final values of F_o and those of $|F_c|$ are given in Table IV.

The scattering curve used for cobalt was that for the dipositive

(14) W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende, "A Two- and Three-Dimensional Crystallographic Fourier Summation Program for IBM 709/7090 Computer-ERFR-2," 1962.

(15) M. J. Buerger, "Vector Space and Its Application in Crystal Structure Investigation," John Wiley and Sons, Inc., New York, N. Y., 1959, p 132 ff.

(16) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic, Full-Matrix Least-Squares Program," 1962.

(17) The usual discrepancy factor $R = \sum |F_o - F_c| / \sum |F_o|$ and the weighted value $wR = \sqrt{\sum w(F_o - F_c)^2} / \sqrt{\sum wF_o^2}$.

(18) C. W. Burnham, Ph.D. Thesis, Massachusetts Institute of Technology, 1961. This scheme is based on considerations of counting statistics alone.

(19) D. W. J. Cruickshank, *et al.*, in "Computing Methods and the Phase Problem in X-Ray Crystal Analysis," R. Pepinsky, J. M. Roberts, and J. C. Speakman, Ed., Pergamon Press Inc., New York, N. Y., 1961.

(20) Since the agreement for reflections of low observed intensity was very poor, it seemed that for these reflections the counting statistics might be the principal source of error, and thus they were weighted by the Burnham scheme. For more intense reflections, where counting errors were insignificant, the Cruickshank scheme was used. This seemed a more reasonable process than merely indiscriminately downweighting all values below a certain level.

(21) The thermal parameters of one oxygen atom, R_3O_2 , did not test positive-definite and so were reset. There are thus no standard deviations available for these values.

TABLE I
POSITIONAL AND TEMPERATURE PARAMETERS^a

Atom	x	y	z	B^b
Co ₁	0.2141 (2)	0.3387 (3)	0.0344 (2)	b
Co ₂	0.2471 (2)	0.3404 (4)	0.4553 (2)	b
R ₁ O ₁	0.130 (1)	0.411 (1)	0.043 (1)	b
R ₁ O ₂	0.175 (1)	0.259 (2)	0.113 (1)	b
R ₁ C ₁	0.040 (2)	0.485 (3)	0.094 (2)	10 (1)
R ₁ C ₂	0.087 (2)	0.397 (3)	0.103 (2)	6 (1)
R ₁ C ₃	0.078 (2)	0.330 (3)	0.160 (2)	8 (1)
R ₁ C ₄	0.126 (2)	0.269 (3)	0.155 (2)	4 (1)
R ₁ C ₅	0.100 (2)	0.210 (3)	0.210 (2)	7 (1)
R ₂ O ₁	0.248 (1)	0.436 (2)	0.091 (2)	b
R ₂ O ₂	0.302 (1)	0.269 (2)	0.036 (1)	b
R ₂ C ₁	0.330 (2)	0.512 (3)	0.159 (2)	4 (1)
R ₂ C ₂	0.307 (2)	0.430 (3)	0.115 (2)	4 (1)
R ₂ C ₃	0.362 (2)	0.366 (2)	0.108 (2)	5 (1)
R ₂ C ₄	0.354 (2)	0.286 (3)	0.072 (2)	4 (1)
R ₂ C ₅	0.410 (2)	0.222 (3)	0.070 (2)	6 (1)
O ₁	0.249 (1)	0.395 (2)	0.939 (1)	b
R ₃ O ₁	0.310 (1)	0.444 (1)	0.443 (2)	b
R ₃ O ₂	0.311 (1)	0.272 (1)	0.507 (1)	b
R ₃ C ₁	0.417 (2)	0.529 (3)	0.445 (2)	6 (1)
R ₃ C ₂	0.368 (2)	0.445 (3)	0.456 (2)	5 (1)
R ₃ C ₃	0.411 (2)	0.376 (3)	0.497 (2)	7 (1)
R ₃ C ₄	0.372 (2)	0.288 (3)	0.520 (2)	5 (1)
R ₃ C ₅	0.426 (2)	0.228 (2)	0.569 (2)	6 (1)
R ₄ O ₁	0.189 (1)	0.416 (2)	0.395 (1)	b
R ₄ O ₂	0.274 (1)	0.266 (2)	0.370 (1)	b
R ₄ C ₁	0.145 (2)	0.486 (2)	0.293 (2)	5 (1)
R ₄ C ₂	0.193 (2)	0.411 (2)	0.334 (2)	4 (1)
R ₄ C ₃	0.224 (2)	0.352 (3)	0.287 (2)	5 (1)
R ₄ C ₄	0.267 (2)	0.276 (3)	0.306 (2)	4 (1)
R ₄ C ₅	0.299 (2)	0.213 (2)	0.253 (2)	5 (1)
O ₂	0.203 (1)	0.395 (2)	0.548 (1)	b

^a Numbers in parentheses are standard deviations occurring in the last digit of the parameter. ^b An anisotropic temperature factor, found in Table II, was used.

TABLE II
ANISOTROPIC THERMAL PARAMETERS^a $\times 10^3$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co ₁	31 (2)	29 (3)	45 (3)	-5 (2)	-5 (3)	-4 (3)
Co ₂	37 (2)	23 (2)	39 (2)	-3 (2)	-18 (2)	1 (3)
R ₁ O ₁	32 (11)	41 (13)	50 (12)	-8 (9)	-9 (7)	26 (11)
R ₁ O ₂	20 (8)	77 (18)	26 (9)	-16 (10)	-3 (7)	4 (11)
R ₂ O ₁	52 (13)	25 (15)	82 (16)	24 (11)	-18 (12)	-30 (12)
R ₂ O ₂	44 (11)	28 (13)	43 (11)	18 (10)	-9 (8)	1 (11)
O ₁	52 (11)	33 (14)	38 (11)	-4 (11)	-26 (9)	-10 (10)
R ₃ O ₁	60 (12)	11 (12)	80 (15)	15 (11)	-34 (11)	25 (11)
R ₃ O ₂	47 (11)	55 (15)	12 (9)	-11 (10)	5 (8)	11 (11)
R ₄ O ₁	38 (12)	38 (14)	42 (12)	4 (9)	1 (9)	5 (11)
O ₂	30 (10)	61 (16)	24 (10)	1 (9)	-1 (8)	-3 (11)

^a Figures in parentheses represent standard deviations occurring in the last digit of the parameter.

valence state as calculated by Watson and Freeman.²² Those for neutral carbon and oxygen were by Hoerni and Ibers.²³

Results

The values of bond distances were calculated from the positional parameters of Table III using MGEOM.²⁴ They are listed in Table V. The bond angles are found in Table VI. Figure 1 illustrates the asymmetric unit projected on the (010) plane. The asymmetric unit consists of two parts, each of which is half a centrosymmetric dimer. There are thus two crystallographi-

(22) R. E. Watson and A. J. Freeman, *Acta Cryst.*, **14**, 27 (1961).

(23) J. A. Hoerni and J. A. Ibers, *ibid.*, **7**, 744 (1954).

(24) J. S. Wood, "MGEOM—Molecular Geometry Program for the IBM 709/7090/7094 Computer," 1964.

TABLE III
 ORTHOGONAL COORDINATES^a OF ALL ATOMS [Co(AA)₂H₂O]₂

Atom	X coord	Y coord	Z coord
Co ₁	4.23	5.07	0.65
Co ₂	4.28	5.11	8.69
R ₁ O ₁	2.52	6.16	0.82
R ₁ O ₂	3.31	3.88	2.18
R ₁ C ₁	0.57	7.32	1.83
R ₁ C ₂	1.55	6.04	1.88
R ₁ C ₃	1.32	5.06	2.95
R ₁ C ₄	2.22	4.06	2.95
R ₁ C ₅	1.70	3.14	3.96
R ₂ O ₁	4.93	6.57	1.75
R ₂ O ₂	6.00	4.08	0.68
R ₂ C ₁	6.34	7.76	3.08
R ₂ C ₂	6.04	6.52	2.24
R ₂ C ₃	7.04	5.51	2.07
R ₂ C ₄	6.97	4.34	1.37
R ₂ C ₅	8.07	3.37	1.30
O ₁	5.04	5.93	-1.19
R ₃ O ₁	5.63	6.64	8.45
R ₃ O ₂	5.48	4.08	9.72
R ₃ C ₁	7.65	7.93	8.48
R ₃ C ₂	6.72	6.64	8.72
R ₃ C ₃	7.40	5.59	9.52
R ₃ C ₄	6.66	4.34	9.90
R ₃ C ₅	7.59	3.42	10.82
R ₄ O ₁	3.20	6.23	7.53
R ₄ O ₂	4.96	3.98	7.08
R ₄ C ₁	2.48	7.28	5.60
R ₄ C ₂	3.37	6.16	6.34
R ₄ C ₃	4.06	5.29	5.48
R ₄ C ₄	4.83	4.19	5.89
R ₄ C ₅	5.53	3.24	4.88
O ₂	3.26	5.89	10.48

^a The axes of the orthogonal coordinate system are chosen so that the Y axis is coincident with the y axis and the Z axis normal to the xy plane. The coordinates are in angstroms.

cally independent dimers. Each of them has the type of structure shown in an idealized ball and stick form in Figure 2. Each dimer is a *meso* molecule since the two halves are enantiomorphs.

Several of the dimensions of the dimer differ from one to the other of the crystallographically independent entities by amounts which are significant in a statistical sense (*i.e.*, the difference is $\geq 3\Sigma$, where Σ represents the sum of the standard deviations). The most conspicuous of such differences is that between the two Co-Co distances, which are 3.22 ± 0.01 and 3.33 ± 0.01 . However, it does not appear that any of the *statistically* significant differences have any chemical significance.

The chelate rings are all planar (see Table VII) within the significance of the data although there are deviations of the methyl carbon atoms, especially in rings 1 and 3, which are certainly significant statistically. These appear to be attributable to intermolecular contacts. Once again the tendency of the metal atoms to be outside the plane of the β -ketoenolate ion^{5,25} is evident, the distances ranging here from 0.14 to 0.26 Å, with a mean of 0.20 Å.

The intermolecular contacts were calculated using DISTAN, a FORTRAN program by D. P. Shoemaker.²⁶ All contacts were larger than 4.0 Å, the

(25) Cf. F. A. Cotton and J. S. Wood, *Inorg. Chem.*, **3**, 245 (1964).

(26) D. P. Shoemaker, "DISTAN—Crystallographic Bond Distance, Bond Angle, and Dihedral Angle Computer Program," 1963.

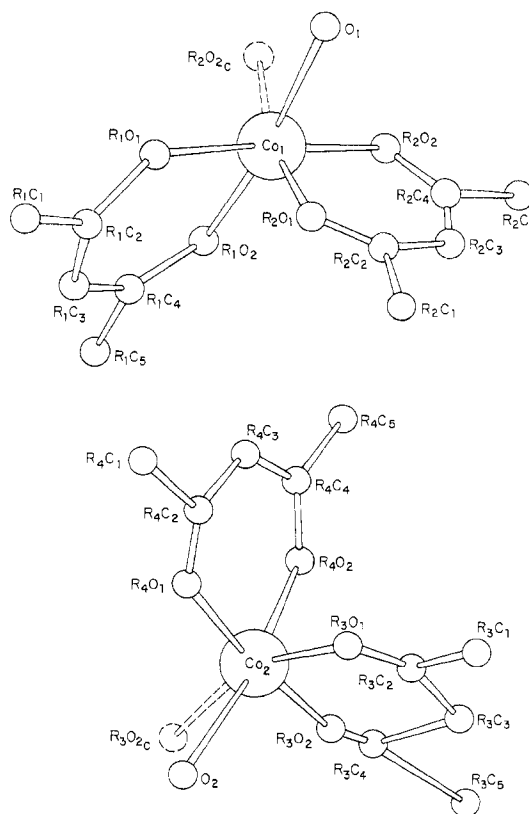


Figure 1.—The asymmetric unit projected on the (010) plane. Each separate Co(AA)₂H₂O unit is half a centrosymmetric dimer.

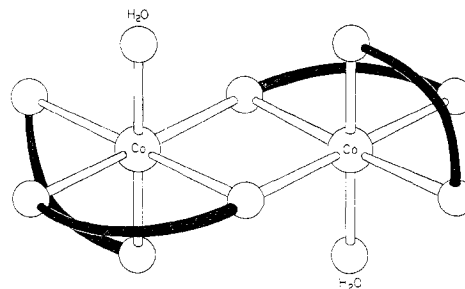


Figure 2.—An idealized (ball and stick) view of the [Co(AA)₂H₂O]₂ dimer. Heavy black lines represent the chelate rings. The ideal octahedral geometry indicated here is distorted *appreciably* in the actual molecules, but this sketch helps to show the relationship of this structure to the center part of the [Co(AA)₂]₄ structure.

methyl-methyl van der Waal's contact distance, and so all further discussion will be about the dimer itself.

Discussion

The centrosymmetric dimer, [Co(AA)₂H₂O]₂, corresponds to the central two cobalt atom units of the tetrameric [Co(AA)₂]₄, with two positions which were filled by bridges from the terminal Co(AA)₂ units now filled by the oxygen atoms of water molecules. The structural parameters found here are similar to those determined for [Co(AA)₂]₄. The bridge bonds in this structure are all approximately coplanar with the chelate rings, and thus π bonding should be possible for the bridges. The average value, 2.16 Å, is in good agree-

TABLE IV: OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (IN ELECTRONS X 20.9) FOR [Co(AA)₂H₂O]₂

Table with multiple columns of numerical data representing observed and calculated structure amplitudes. The columns are organized into groups labeled with 'H', 'K', 'F', 'OBS', 'CAL', and 'F' for different reflections. The data is presented in a dense grid format.

TABLE V
 [Co(AA)₂(H₂O)]₂ BOND LENGTHS^{a,b}

Primary cobalt keto-oxygen Co-O _K (1)				
Co ₁	R ₁ O ₁	2.04 ± 0.03		
Co ₁	R ₁ O ₂	2.14 ± 0.03		
Co ₁	R ₂ O ₁	1.98 ± 0.03		
Co ₁	R ₂ O ₂ ^c	2.03 ± 0.03		
Co ₂	R ₃ O ₁	2.06 ± 0.03		
Co ₂	R ₃ O ₂ ^c	1.89 ± 0.03		
Co ₂	R ₄ O ₁	1.94 ± 0.03		
Co ₂	R ₄ O ₂	2.08 ± 0.03		
Av. 2.02				
Secondary or bridging cobalt keto-oxygen bonds Co-O _K (2) _p				
Co ₂	R ₃ O _{2C}	2.20 ± 0.03		
Co ₁	R ₂ O _{2C}	2.12 ± 0.03		
Av 2.16				
Cobalt water-oxygen Co-O _{H₂O}				
Co ₁	O ₁	2.19 ± 0.03		
Co ₂	O ₂	2.20 ± 0.03		
Av 2.20				
Oxygen-carbon bonds				
R ₁ O ₁	R ₁ C ₂	1.43 ± 0.05	R ₁ O ₂	R ₁ C ₄ 1.34 ± 0.05
R ₂ O ₁	R ₂ C ₂	1.21 ± 0.05	R ₂ O ₂	R ₂ C ₄ 1.22 ± 0.04
R ₃ O ₁	R ₃ C ₂	1.12 ± 0.05	R ₃ O ₂	R ₃ C ₄ 1.23 ± 0.05
R ₄ O ₁	R ₄ C ₂	1.20 ± 0.04	R ₄ O ₂	R ₄ C ₄ 1.21 ± 0.05
Av 1.25				
Ring carbon-carbon bonds				
R ₁ C ₂	R ₁ C ₃	1.46 ± 0.05	R ₁ C ₃	R ₁ C ₄ 1.33 ± 0.06
R ₂ C ₂	R ₂ C ₃	1.43 ± 0.05	R ₂ C ₃	R ₂ C ₄ 1.37 ± 0.05
R ₃ C ₂	R ₃ C ₃	1.48 ± 0.06	R ₃ C ₃	R ₃ C ₄ 1.50 ± 0.06
R ₄ C ₂	R ₄ C ₃	1.40 ± 0.05	R ₄ C ₃	R ₄ C ₄ 1.40 ± 0.05
Av 1.42				
Terminal carbon β-carbon bonds				
R ₁ C ₁	R ₁ C ₂	1.62 ± 0.08	R ₁ C ₄	R ₁ C ₅ 1.47 ± 0.07
R ₂ C ₁	R ₂ C ₂	1.53 ± 0.06	R ₂ C ₄	R ₂ C ₅ 1.47 ± 0.06
R ₃ C ₁	R ₃ C ₂	1.61 ± 0.07	R ₃ C ₄	R ₃ C ₅ 1.60 ± 0.07
R ₄ C ₁	R ₄ C ₂	1.61 ± 0.05	R ₄ C ₄	R ₄ C ₅ 1.56 ± 0.06
Av 1.56				
Cobalt-cobalt distances				
Co ₁	Co _{1C}	3.33 ± 0.04		
Co ₂	Co _{2C}	3.22 ± 0.04		

^a Including contribution from uncertainties in unit cell dimensions. ^b Subscript C indicates an atom related by the center of symmetry to the one designated. ^c These oxygens form secondary bonds also.

ment with the 2.13 Å found in [Co(AA)₂]₄ for a Co-O_K(2)_p type and is significantly shorter than the value of 2.24 Å found for the bridge bonds in which multiple bonding is not possible. The average Co-Co distance in the present case is 3.27 Å, to be compared with 3.57 Å for the distance between the comparable pair of Co atoms in the tetramer. While this is a rather large difference, it seems to be of little importance in itself, being due chiefly to the fact that the O-Co-O angles in the four-membered rings are ~69° in the tetramer and ~76° in the dimer. Within the relatively large standard deviations, nearly all "chemically equivalent" internuclear distances differ by less than twice the sum of their standard deviations, there being three cases in which the differences are just slightly larger than this.

The structure of the [Co(AA)₂(H₂O)]₂ molecule is of considerable interest in respect to understanding the structural aspect of the degradation of the tetrameric

 TABLE VI
 BOND ANGLES IN [Co(AA)₂(H₂O)]₂ (DEG)^a

Atom A	Atom B	Atom C	Angle ABC	Std dev ABC
R ₁ O ₁	Co ₁	R ₁ O ₂	82.7	0.7
R ₁ O ₁	Co ₁	R ₂ O ₁	81.3	0.8
R ₁ O ₁	Co ₁	R ₂ O _{2C}	111.8	0.7
R ₁ O ₁	Co ₁	O ₁	100.0	0.7
R ₁ O ₂	Co ₁	R ₂ O ₁	100.3	0.8
R ₁ O ₂	Co ₁	R ₂ O ₂	95.5	0.7
R ₁ O ₂	Co ₁	R ₂ O _{2C}	88.5	0.7
R ₂ O ₁	Co ₁	R ₂ O ₂	93.0	0.7
R ₂ O ₁	Co ₁	O ₁	92.1	0.7
R ₂ O ₂	Co ₁	O ₁	82.8	0.7
R ₂ O ₂	Co ₁	R ₂ O _{2C}	74.0	0.9
R ₂ O _{2C}	Co ₁	O ₁	79.0	0.7
Co ₁ C	Co ₁	O ₁	78.8	0.5
R ₃ O ₁	Co ₂	R ₃ O ₂	92.8	0.7
R ₃ O ₁	Co ₂	R ₄ O ₁	82.2	0.7
R ₃ O ₁	Co ₂	R ₄ O ₂	95.6	0.7
R ₃ O ₁	Co ₂	O ₂	97.8	0.7
R ₃ O ₂	Co ₂	R ₄ O ₂	85.5	0.7
R ₃ O ₂	Co ₂	O ₂	92.6	0.7
R ₃ O ₂	Co ₂	R ₃ O _{2C}	76.5	1.0
R ₄ O ₁	Co ₂	R ₄ O ₂	91.6	0.7
R ₄ O ₁	Co ₂	O ₂	91.2	0.7
R ₄ O ₁	Co ₂	R ₃ O _{2C}	108.6	0.7
R ₄ O ₂	Co ₂	R ₃ O _{2C}	90.4	0.6
O ₂	Co ₂	R ₃ O _{2C}	76.1	0.6
Co ₂ C	Co ₂	O ₂	76.1	0.6
R ₁ C ₁	R ₁ C ₂	R ₁ O ₁	108.2	2.6
R ₁ O ₁	R ₁ C ₂	R ₁ C ₃	133.7	3.0
R ₁ C ₃	R ₁ C ₄	R ₁ O ₂	129.4	2.8
R ₁ O ₂	R ₁ C ₄	R ₁ C ₅	126.6	2.7
R ₂ C ₁	R ₂ C ₂	R ₂ O ₁	111.4	2.5
R ₂ O ₁	R ₂ C ₂	R ₂ C ₃	128.8	2.7
R ₂ C ₃	R ₂ C ₄	R ₂ O ₂	120.6	2.5
R ₂ O ₂	R ₂ C ₄	R ₂ C ₅	115.4	2.5
R ₃ C ₁	R ₃ C ₂	R ₃ O ₁	121.5	2.9
R ₃ O ₁	R ₃ C ₂	R ₃ C ₃	125.2	3.0
R ₃ C ₃	R ₃ C ₄	R ₃ O ₂	128.1	2.9
R ₃ O ₂	R ₃ C ₄	R ₃ C ₅	121.6	2.7
R ₄ C ₁	R ₄ C ₂	R ₄ O ₁	109.4	2.3
R ₄ O ₁	R ₄ C ₂	R ₄ C ₃	135.2	2.6
R ₄ C ₃	R ₄ C ₄	R ₄ O ₂	118.9	2.6
R ₄ O ₂	R ₄ C ₄	R ₄ C ₅	118.9	2.4

^a Subscript C indicates an atom related by the symmetry center to the atom designated.

[Co(AA)₂]₄ to monomeric Co(AA)₂ and Co(AA)₂D₂, where D may be H₂O or an amine. It is to be noted that the structure determined here is a different isomer from that proposed⁷ for the dimeric cyclohexylamine (CHA) complex, [Co(AA)₂(CHA)]₂. The structure suggested for the latter was preferred because it appeared to account for the dissociation of this compound into presumed square pyramidal monomers with a minimum of rearrangement. However, this is not a very compelling line of argument, and it is entirely possible that [Co(AA)₂(CHA)]₂ may have a structure similar to that reported here for [Co(AA)₂(H₂O)]₂. However, a discussion of the structural changes which might occur in the stepwise degradation of [Co(AA)₂]₄ to Co(AA)₂(H₂O)₂ is best deferred until the identity and structure of [Co(AA)₂]_{2,3}(H₂O) are established since the course of events would have to be quite different for each of the possible formulas and corresponding structures. It might, however, be suspected from the

TABLE VII
 "BEST PLANES" OF LIGANDS

Direction cosines		Distances to origin	
$L = 0.567$	$M = 0.552$	$N = 0.611$	$D = 5.34$
Distances of atoms from plane			
R_1O_1	-0.011		
R_1O_2	0.011	Co_1	0.258
R_1C_2	0.022	R_1C_1	0.139
R_1C_3	0.013	R_1C_5	-0.221
R_1C_4	-0.036		
$L = -0.383$	$M = 0.493$	$N = 0.781$	$D = -3.76$
R_2O_1	0.006		
R_2O_2	-0.011	Co_1	0.162
R_2C_2	-0.006	R_2C_1	-0.076
R_2C_3	-0.026	R_2C_6	0.030
R_2C_4	0.038		
$L = -0.242$	$M = 0.445$	$N = 0.862$	$D = 8.87$
R_3O_1	0.003		
R_3O_2	0.001	Co_2	-0.141
R_3C_2	-0.019	R_3C_1	0.119
R_3C_3	0.025	R_3C_5	0.138
R_3C_4	-0.012		
$L = 0.796$	$M = 0.602$	$N = 0.052$	$D = 6.71$
R_4O_1	-0.009		
R_4C_2	0.009	Co_2	0.235
R_4C_3	0.022	R_4C_1	-0.058
R_4C_4	0.005	R_4C_5	-0.096
R_4C_4	-0.028		

present structure that this compound will turn out to be $[Co(AA)_2]_3H_2O$, derived from $[Co(AA)_2]_4$ by removal of one of the terminal $Co(AA)_2$ groups and insertion of the water molecule into the position thus opened on one of the cobalt atoms.

The persistence of the central part of the $[Co(AA)_2]_4$ molecule in which two octahedra share only an edge, while the shared faces are lost, is not necessarily surprising. Although in a kinetic sense a species with three bridging groups might be in general more stable than one with only two, in a thermodynamic sense, the effects of ring distortions and repulsions may tend to cancel the advantage of additional bonding. Moreover, the coplanar arrangement of the metal atoms and the two chelate rings to which the bridging oxygen atoms belong may permit a significant degree of π bonding to occur, thus increasing the stability of this portion of the $[Co(AA)_2]_4$ molecule.

Acknowledgment.—We wish to thank Mrs. S. M. Morehouse, who measured a large portion of the data on the XRD-5, and Professors D. P. Shoemaker and A. Davison for some helpful discussions. Computation necessary to determine the crystal structure was performed on the MIT Computation Center IBM 7090 and 7094 machines.

CONTRIBUTION FROM CYANAMID EUROPEAN RESEARCH INSTITUTE,
COLOGNY, GENEVA, SWITZERLAND

The Reaction of Hexacarbonylvandium with Aromatic Compounds.

III. Reduction of the $[V(CO)_6\text{arene}]^+$ Cations to Tetracarbonyl- π -cyclohexadienylvanadium Derivatives¹

BY FAUSTO CALDERAZZO

Received October 11, 1965

The hexacarbonylvandate of the $[V(CO)_6C_6H_6]^+$ cation reacts with sodium tetrahydridoborate to give the red crystalline volatile $V(CO)_4C_6H_7$ in about 60% yield. On the basis of infrared and nmr data this is shown to be tetracarbonyl- π -cyclohexadienylvanadium. Methyl-substituted cyclohexadienyl compounds $V(CO)_4C_6H_{7-n}(CH_3)_n$ are also described, being obtained by reduction of the methyl-substituted arene vanadium compounds $[V(CO)_6C_6H_{6-n}(CH_3)_n]^+$. Similar reactions with $NaBD_4$ yielded the corresponding deuterated compounds. The nmr spectra suggest that the addition of hydrogen occurs preferentially at unsubstituted positions of the aromatic ring in $[V(CO)_6C_6H_{6-n}(CH_3)_n]^+$. The type of bonding between the metal and the cyclohexadienyl system and the conformation of the cyclohexadienyl ligand are briefly discussed.

Introduction

The reactions of hexacarbonylvandium with aromatic compounds to give the tetracarbonylarenevanadium(I) hexacarbonylvandate(-I), $[V(CO)_6\text{arene}]^+$, have been described previously.^{2,3}

It was conceivable that the still unknown $V(CO)_3\text{-arene}$ compounds could be obtained by reduction of the $[V(CO)_6\text{arene}]^+$ cations. However, some attempts to

synthesize them by sodium metal or lithium tetrahydridoaluminate reductions were unsuccessful. In the course of similar experiments with $NaBH_4$ it was found instead that the vanadium cations were reduced to a new class of complexes, namely the tetracarbonyl- π -cyclohexadienylvanadium derivatives. The properties of these new compounds are described in the present paper.

Experimental Section

All the operations were carried out in an atmosphere of purified nitrogen.

(1) Presented at the Second International Symposium on Organometallic Chemistry, Madison, Wis., Aug. 30-Sept. 3, 1965.

(2) Part II: F. Calderazzo, *Inorg. Chem.*, **4**, 233 (1965).

(3) F. Calderazzo, *ibid.*, **3**, 1207 (1964).