TABLE V

AXIAL AND EQUATORIAL M–L BOND LENGTHS OF TRIGONAL-BIPYRAMIDAL COMPLEXES WITH FIVE IDENTICAL LIGANDS

Complex	d^x	Axial, Å	Equatorial, Å	Ref
$Fe(CO)_5$	d^8	1.81 (2)	1.79 (2)	*a, b, c, d*
$Co(CNCH_3)_5{}^+$	d^8	1.84 (2)	1.88 (2)	*e*
$Ni(CN)_5{}^{3-}$	d^8	1.838 (9)	1.94[f]	*g*
$Ni[P(OCH)_3(CH_2)_3]_5{}^{2+}$	d^8	2.14 (1)	2.19 (1)	*h*
$Pt(SnCl_3)_5{}^{3-}$	d^8	?	?	*i*
$CuCl_5{}^{3-}$	d^9	2.2964 (12)	2.3912 (13)	*j*

[a] A. W. Hanson, *Acta Cryst.*, **15,** 930 (1962). [b] J. Donohue and A. Caron, *ibid.*, **17,** 663 (1964). [c] M. I. Davis and H. P. Hanson, *J. Phys. Chem.*, **69,** 3405 (1965). [d] J. Donohue and A. Caron, *ibid.*, **70,** 603 (1966). [e] F. A. Cotton, T. G. Dunne, and J. S. Wood, *Inorg. Chem.*, **4,** 318 (1965). [f] This is an average of chemically nonequivalent bonds. [g] Reference 5. [h] Reference 6. [i] R. D. Cramer, R. V. Lindsey, Jr., C. T. Prewitt, and U. G. Stolberg, *J. Am. Chem. Soc.*, **87,** 658 (1965). [j] This work.

metal complex into ligand–ligand repulsions and d-electron–ligand repulsions one can examine the effects of various d-electron distributions on the geometry of the complex. From the ligand–ligand repulsions one always predicts the axial bond to be longer than the equatorial. However, the d-electron–ligand repulsions can favor either axial contraction or elongation, depending upon the d-electron configuration. For a low-spin d^8 or d^9 complex the metal 3d-electron density distribution is an *oblate* spheroid, since the d_{z^2} orbital is either empty or only half-filled. The metal–ligand electron repulsion along the trigonal (z) axis is therefore weakened and equilibrium is achieved at a shorter axial bond length than if the d-electron shell had spherical symmetry. The difference between axial and equatorial bond lengths is expected to be most pronounced for relatively ionic complexes with small ligands. The more covalent the metal–ligand bond and the larger the ligands, the more important the ligand–ligand repulsions become, with a concomitant lengthening of the axial bond.

A similar result can be formulated by using a molecular orbital model with either σ orbitals or both σ and π atomic orbitals. However, the additional sophistication of this model is not, to date, justified by greater predictive powers.

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Base Adducts of Bis(2,4-pentanedionato)cobalt(II). The Crystal and Molecular Structure of *trans*-Bis(2,4-pentanedionato)dipyridinecobalt(II), $Co(AA)_2(py)_2$

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A series of pyridine and water adducts to bis(2,4-pentanedionato)cobalt(II), $Co(AA)_2$, where the common name of acetylacetone is abbreviated AA, is reported. From crystallographic evidence these are *trans*-bis(2,4-pentanedionato)dipyridinecobalt(II), $Co(AA)_2(py)_2$ (orthorhombic, $a = 11.13$, $b = 16.18$, $c = 11.91$ Å, space group C_{mcm}, $z = 4$, measured density 1.28 g cm^{-3}, calculated density 1.29 g cm^{-3}), tetrakis(2,4-pentanedionato)pyridinedicobalt(II), $[Co(AA)_2py]_2$ (triclinic, $a = 9.70$, $b = 11.61$, $c = 15.03$ Å, $\alpha = 103° 35'$, $\beta = 103° 40'$, $\gamma = 92° 15'$, $z = 2$, measured density 1.40 g cm^{-3}, calculated density 1.40 g cm^{-3}), and tetrakis(2,4-pentanedionato)pyridineaquodicobalt(II), $[Co(AA)_2]_2pyH_2O$ (triclinic, $a = 8.84$, $b = 9.42$, $c = 17.37$ Å, $\alpha = 92° 30'$, $\beta = 96° 15'$, $\gamma = 95° 45'$, $z = 2$, measured density 1.38 g cm^{-3}, calculated density 1.41 g cm^{-3}). No crystals of the reported compound tetrakis(2,4-pentanedionato)pyridinedicobalt(II), $[Co(AA)_2]_2py$, were obtained. The structure of $Co(AA)_2(py)_2$ has been determined from three-dimensional, single-crystal X-ray data obtained on a Pailred diffractometer. The structure, refined by least-squares methods to a final conventional R factor for nonzero data of 0.047 and wR (all data) of 0.048, has molecular symmetry mm. All atoms including hydrogen were found and refined. The configuration of the molecule is that of the *trans*-dipyridine adduct with the planes of the two pyridine rings at 90° to each other. Both the molecular conformation and the cobalt–nitrogen atom bond lengths suggest the possibility of metal–nitrogen π bonding.

Introduction

Studies of the adducts of bis(2,4-pentanedionato)-cobalt(II), $Co(AA)_2$, where the common name of the acetylacetonate ligand $C_5H_7O_2{}^-$ has been abbreviated AA, with donors[1–4] such as water, pyridine, and cyclohexylamine have shown these compounds to be derived from the structure of the anhydrous tetramer,[5] $[Co(AA)_2]_4$. The tetramer (see Figure 1) is formed of four cobalt–oxygen octahedra, where the central bridge

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(1) F. A. Cotton and R. C. Elder, *Inorg. Chem.*, **5,** 423 (1966).

(2) F. A. Cotton and R. Eiss, *J. Am. Chem. Soc.*, **90,** 38 (1968).

(3) J. P. Fackler, Jr., *Inorg. Chem.*, **2,** 266 (1963).

(4) J. A. Bertrand, F. A. Cotton, and W. J. Hart, *ibid.*, **3,** 1007 (1964).

(5) F. A. Cotton and R. C. Elder, *ibid.*, **4,** 1145 (1965).

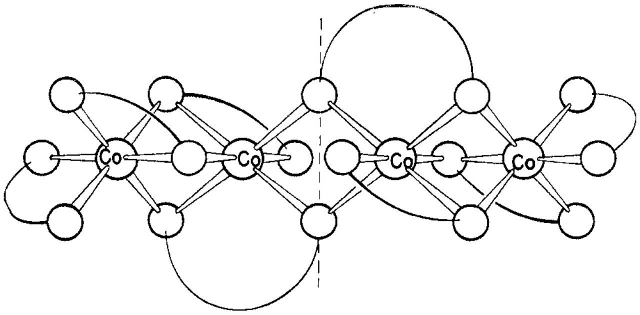

Figure 1.—A schematic illustration of the structure of the tetramer of bis(2,4-pentanedionato)cobalt(II). The unlabeled circles are oxygen atoms, the curved lines indicate the remainder of the acetylacetone ligand.

results from edge sharing and the terminal bridges are formed by face sharing. There are two types of adduct which may be derived from this tetramer. In the first type, the face-sharing, terminal bridges are broken. Removal of a terminal $Co(AA)_2$ group and addition of water to the vacant coordination position in the trimeric entity yields the structure found for $[Co(AA)_2]_3H_2O$.[2] Loss of the other terminal $Co(AA)_2$ group and addition of a second water molecule gives the structure of $[Co(AA)_2H_2O]_2$,[1] the second example of this first type of derivative. The second type of adduct results from breaking the central, edge-sharing bridge and the addition of one donor molecule to fill the vacancy in the octahedron, giving a formula $[Co(AA)_2]_2$(donor); such a structure has not been observed in X-ray studies but a compound of this type was reported by Fackler[3] with pyridine as the donor, $[Co(AA)_2]_2$py. This paper reports single-crystal studies of a series of adducts of pyridine to cobalt acetylacetonate, which were undertaken in an attempt to isolate and characterize a derivative of the type $[Co(AA)_2]_2$(donor).

Experimental Section

Crystal Growth and Characterization.—Anhydrous cobalt acetylacetonate was dissolved in benzene to form a nearly saturated solution and to this was added pyridine to give varying pyridine:cobalt ratios from 3:1 to 1:10. These solutions were then allowed to mix slowly with isooctane. After 1 week had passed, several different crystalline compounds had formed in all instances except when the pyridine:cobalt ratio was 3:1; in that case only $Co(AA)_2(py)_2$ was obtained. After washing in isooctane, the crystals were separated by hand under a microscope. The compounds were then characterized by their infrared spectra, unit cells, and space groups, and, in the case of $Co(AA)_2(py)_2$, by three-dimensional, X-ray structure analysis.

trans-Bis(2,4-pentanedionato)dipyridinecobalt(II), $Co(AA)_2(py)_2$, crystallizes as orange columns. Its infrared spectrum shows no indications of the presence of water. Both the orange color and the infrared spectrum are reminiscent of the behavior of $Co(AA)_2(H_2O)_2$.[1,6] Although Fackler[7] reports that $Co(AA)_2(py)_2$ is isomorphous with the nickel analog (monoclinic, space group $P2_1/c$), these crystals are of the orthorhombic class. There are three possible choices for the space group based on systematic absences (hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$) observed from precession photographs: Cmcm (no. 63), Ama2 (no. 40), $Cmc2_1$ (no. 36).[8] The first of these three is the only centric choice, and it was judged to be correct on the basis of intensity statistics.[9] No piezoelectric measurements were performed. The correctness of this choice is substantiated by the final refinement of the structure. Since there are four molecules in the unit cell, the metal atoms are required to have either mm or 2/m symmetry, which requires that the molecule be a *trans* adduct but does not specify the conformation.

The unit cell constants found by a least-squares analysis[10] of ω values measured on a Pailred diffractometer using crystal-monochromatized molybdenum radiation (λ 0.7107 Å) are $a = 11.13 \pm 0.01$, $b = 16.18 \pm 0.02$, $c = 11.91 \pm 0.01$ Å, volume 2145 $Å^3$. The density measured by flotation is 1.28 ± 0.02 g cm^{-3}; that calculated for four molecules in the unit cell is 1.29 g cm^{-3}. The infrared spectrum of this compound run as a mull in Nujol has no bands in the region 4000–3100 cm^{-1}. In the region from 1300 to 650 cm^{-1} the following bands appear: 1258 s, 1218 w, 1199 m, 1151 m, 1076 m, 1055 w, 1036 s, 1009 s, 920 s, 768 s, 757 s, 700 s, 652 m cm^{-1}, where s, m, and w stand for strong, medium and weak, respectively. All spectra were recorded using a Beckman IR-5. All measurements described herein were taken at room temperature.

Since this compound was only suspected to be $Co(AA)_2(py)_2$ and since its behavior was different from that reported by Fackler, a full, three-dimensional X-ray structural analysis was carried out and is reported below.

Tetrakis(2,4-pentanedionato)dipyridinedicobalt(II), $[Co(AA)_2py]_2$, was obtained in the form of red triclinic crystals. The unit cell constants were derived from measurements of precession photographs using copper radiation with a nickel filter (λ 1.5418 Å), where the errors are estimated from the precision of the measurements; they are $a = 9.70 \pm 0.03$, $b = 11.61 \pm 0.02$, $c = 15.03 \pm 0.04$ Å, $\alpha = 103° 35' \pm 5'$, $\beta = 103° 40' \pm 5'$, $\gamma = 92° 15' \pm 10'$, volume 1597 $Å^3$. The density measured by flotation is 1.40 ± 0.02 g cm^{-3}. The density calculated for two dimeric molecules per unit cell is 1.40 g cm^{-3}. The infrared spectrum of a Nujol mull of this compound, which distinguishes these crystals from those of other compounds obtained by the same procedure, shows no indication of bands due to water in the region 4000–3100 cm^{-1}. In the region from 1300 to 650 cm^{-1} the following bands appear: 1252 s, 1214 w, 1063 w, 1040 w, 1012 s, 921 s, 772 m, 756 s, 719 w, 703 s, 651 m cm^{-1}.

A third crystalline compound, purple in color, which may be tetrakis(2,4-pentanedionato)pyridineaquodicobalt(II), $[Co(AA)_2]_2pyH_2O$, was also obtained. This compound is also triclinic. The unit cell constants obtained from precession photographs as above are: $a = 8.84 \pm 0.01$, $b = 9.42 \pm 0.02$, $c = 17.37 \pm 0.02$ Å, $\alpha = 92° 30' \pm 10'$, $\beta = 96° 15' \pm 5'$, $\gamma = 95° 45' \pm 5'$, volume 1426 $Å^3$. The density measured by flotation is 1.39 ± 0.02 g cm^{-3}. The calculated density for two molecules in the unit cell is 1.41 g cm^{-3}. The infrared spectrum of this compound shows broad bands at appoximately 3300 and 1600 cm^{-1} which may be attributable to water. Bands in the range 1300–650 cm^{-1} are 1256 s, 1217 m, 1198 w, 1063 w, 1043 m, 1020 s, 924 s, 780 m, 766 m, 722 w, 707 m, 667 w, 652 m cm^{-1}. No further attempts to characterize this complex are planned.

No other crystalline material was isolated in the many attempts to crystallize pyridine adducts of cobalt acetylacetonate. Since the material which Fackler reports[3] was obtained by pumping on a sample of $Co(AA)_2(py)_2$, it is possible that his analysis is merely an average set of values from $Co(AA)_2$ and $Co(AA)_2(py)_2$ in the sample and that $[Co(AA)_2]_2$py does not exist. At least this author has not been able to reproduce it.

Structure Determination of $Co(AA)_2(py)_2$.—A columnar crystal 0.5 mm long (c axis as rotation axis) by a mean diameter of 0.3 mm was mounted in a glass capillary tube to protect against the slow loss of pyridine and gradual uptake of water which is observed when these crystals are exposed to moist air for long

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

(7) J. T. Hashagen and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **87**, 2821 (1965).

(8) "International Tables for X-Ray Crystallography," Vol. 1, The Kynoch Press, Birmingham, England, 1952.

(9) For a discussion of this method see H. Lipson and W. Cochran, "The Determination of Crystal Structures," G. Bell and Sons, London, England, 1957, p 32 and following.

(10) J. Ladell, *Norelco Reptr.*, **12**, 34 (1965).

periods. A Philips Pailred diffractometer was used with molybdenum radiation to measure the intensities. The take-off angle was set to 6°, a 0.1-cm beam tunnel was used, and a 3° collimator was placed in front of the detector. Alignment was checked by measuring the 006 reflection while ω was rotated through 360°. At no point did the observed intensity vary by more than 5% from the mean. This check was run after every second layer was measured. Also the $1\bar{7}0$ reflection was used as a monitor peak and was never found to deviate by more than 3% from the mean value observed. The value of the absorption coefficient for this compound is 9 cm^{-1}. Since the maximum error introduced by neglect of absorption for this crystal is 7% in the intensity measurement, no corrections were applied. Two octants of data (HKL, $\bar{H}KL$) were collected including the 1667 accessible reflections below $2\theta = 47°$. Reflections with a counting error greater than 0.8 were considered zero. The counting error was determined by the formula $E_{\text{cnt}} = (P + t^2B)^{1/2}/(P - tB)$, where P is the total counts recorded in the ω intensity scan, B is the sum of the background counts recorded with the crystal offset by ±1.3° in ω, and t normalizes B to the same counting time as that required to measure P. The two sets of data were averaged assuming orthorhombic symmetry after processing for backgrounds and Lp factors. The R_{sym} factor of agreement[11] for symmetry-related nonzero peaks was 2.5%. The reflections were arbitrarily assigned the following standard deviations: average of two reflections both with counting error less than 0.5, esd = 1.0; single reflection counting error less than 0.8, esd = 1.5; average of two reflections at least one of which had a counting error less than 0.8 and greater than 0.5 and both had a counting error less than 0.8, esd = 2.0; average of two reflections or a single reflection at least one of which was considered zero, esd = 3.0. All reflections which were calculated to have negative F's were set equal to 0.8, approximately half the value for the weakest nonzero reflections. After averaging, there were 589 nonzero reflections and 269 zeros. All data were given the same scale factor.

The nonzero reflections were used to solve the crystal structure with the aid of MAGIC, a direct-methods program.[12] The positions of the 13 nonhydrogen atoms in the asymmetric unit corresponded to the largest peaks on the first E map.[13] The structure was then refined by full-matrix least squares using a local variant of the ORFLS program[13] with the following modifications: anomalous dispersion corrections of the form $f = f_0 + \Delta f' + i\Delta f''$ were used for cobalt with values of $\Delta f' = 0.4$ and $\Delta f'' = 1.0$ taken from the "International Tables,"[8] and a one-parameter, least-squares-fitted extinction correction as suggested by Zachariasen[14] was applied to the calculated structure factors. The function $\Sigma w(|F_o| - |F_c|)^2$ was minimized.

Adjustment of the scale factor by least squares with the positions determined from the E map and with isotropic temperature factors set to 2.0 and 3.0 Å^2 for the metal atom and all other atoms, respectively, gave a conventional R factor[15] of 30%. Refinement of all positional parameters lowered this to R = 19%. Inclusion of isotropic temperature factors in the refinement gave R = 12% and a weighted R factor,[16] wR = 11%. Refinement of the extinction parameter as well as the parameters mentioned above gave R = 12.5%, wR = 9.0%. At this point anisotropic temperature factors were introduced, and they alone varied to yield R = 9.2%, wR = 6.5%. Refinement of all parameters introduced to this point dropped R to 8.76% and wR to 6.17% for all 858 reflections. A difference map yielded positions which were within 0.2 Å of those calculated for the ten hydrogen atoms in the asymmetric unit assuming normal angles and distances. The inclusion of the hydrogen atoms with isotropic temperature factors set at 4.0 Å^2 reduced wR to 6.06% and R to 8.70%. Further refinement of all atoms except hydrogen gave wR = 5.09% and R = 7.82%. In the final refinement all atom positions were allowed to vary, including hydrogen atoms, and the anisotropic temperature factors were varied on all nonhydrogen atoms. The final wR = 4.56% showed a significant improvement at the 0.005 level over the structure with fixed hydrogen atoms according to Hamilton's test.[17] The usual R factor for the 604 strongest reflections was 4.70%. The R factor for all reflections was 7.29% and the standard error of an observation of unit weight was 1.27. The scattering curves were for Co$^+$, O, N, C, and H as tabulated by Ibers in the "International Tables."[18] A final difference map showed no peaks greater than $^1/_3$ electron.

Results and Discussion

The final atomic positional parameters and their estimated standard deviations are listed in Table I. The anisotropic temperature factors are given in Table II and their effects are shown in Figure 2, which is a parallel projection of the molecule, composed with ORTEP.[19] The hydrogen atoms have been omitted from the drawing for clarity. The root-mean-square amplitudes of vibration for those atoms with anisotropic motion are listed in Table III; the directions of these motions are indicated in the drawing. Structure factor calculations after the last cycle of refinement are shown in Table IV. The last 269 reflections listed in the table are zeros. Table V contains the bond distances and Table VI the bond angles found in the molecule. As all contacts between molecules seem to be normal van der Waals distances, discussion will be restricted to intramolecular distances.

The structure is that of the *trans*-dipyridine adduct to cobalt acetylacetonate. The molecule is required to have mm symmetry. Both pyridine rings are required to be planar. One lies in the mirror plane perpendicular to a at $x = ^1/_2$; the other, in the plane perpendicular to c at $z = ^1/_4$. The acetylacetone ligand is not required to be planar; however, within 3σ all of these atoms, hydrogen atoms excepted, do lie in the same plane. The weighted least-squares best plane through the ligand carbon and oxygen atoms, calculated by SORFFE[13] using the variance–covariance matrix, has direction cosines: $L = -0.1008$, $M = 0.9949$, $N = 0.0000$ and is 2.06 Å from the origin. The distances of

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(11) The R_{sym} factor of symmetry agreement, a measure of the agreement of the two octants of data which were recorded, is computed: $R_{\text{sym}} = \Sigma|F_{\text{set1}} - F_{\text{set2}}|/\Sigma F_{\text{mean}}$.

(12) E. B. Fleischer, A. L. Stone, and R. B. K. Dewar, "MAGIC—Multiphase Automatic Generation from Intensities in Centric Crystals," University of Chicago, March 1966.

(13) The Fourier syntheses were calculated using "ERFR-2, a Fourier Summation Program," by W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende, Esso Research, CBRL-22M-52, June 1962. Structure factor calculations and least-squares refinements were performed with local versions of "ORFLS–Oak Ridge FORTRAN Least Squares," by W. R. Busing, K. O. Martin, and H. A. Levy, Oak Ridge National Laboratory, ORNL-TM-305, August 1962. Bond and contact distances were calculated using a local version of "ORFFE–Oak Ridge FORTRAN Function and Error Program," by W. R. Busing, K. O. Martin, and H. A. Levy, ORNL-TM-306, 1962. Dihedral angles were calculated with "MGEOM–Molecular Geometry Program," by J. S. Wood, Massachusetts Institute of Technology, April 1964.

(14) W. H. Zachariasen, *Acta Cryst.*, **23**, 558 (1967). The formulas used in the least-squares program SORFLS written by R. B. K. Dewar are $F_{\text{cor}} = KF_c/[1 + 2X]^{-1/4}$ and $X = [(1 + \cos^4 2\theta)/(1 + \cos^2 2\theta)]F_c{}^2Cr'/\sin 2\theta$; the quantity $200Cr'$ is varied as a least-square parameter. A value of zero corresponds to no correction. The final value obtained was 0.00036 ± 0.00002.

(15) $R = \Sigma||F_o| - |F_c||/\Sigma F_o$.

(16) $wR = \sqrt{\Sigma w(|F_o| - |F_c|)^2}/\sqrt{\Sigma wF_o{}^2}$.

(17) W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965).

(18) J. A. Ibers in "International Tables for X-ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1952, Table 3.3.1A.

(19) C. K. Johnson, "ORTEP–Oak Ridge Thermal Ellipsoid Plot Program for Crystal Structure Illustrations," Oak Ridge National Laboratory, ORNL-3794 UC-4-Chemistry, June 1965.

Table I

Fractional Atomic Positional Parameters[a]

Atom	x	y	z
Co	0.5 (–)	0.15476 (7)	0.25 (–)
O	0.3706 (3)	0.1539 (2)	0.1294 (2)
N_1	0.5 (–)	0.2893 (4)	0.25 (–)
N_2	0.5 (–)	0.0190 (4)	0.25 (–)
C_1	0.3987 (6)	0.3318 (3)	0.25 (–)
C_2	0.3959 (8)	0.4168 (4)	0.25 (–)
C_3	0.5 (–)	0.4586 (6)	0.25 (–)
C_4	0.2612 (5)	0.1455 (3)	0.1459 (5)
C_5	0.2045 (7)	0.1418 (5)	0.25 (–)
C_6	0.1850 (9)	0.1419 (4)	0.0385 (8)
C_7	0.5 (–)	−0.0237 (4)	0.1563 (6)
C_8	0.5 (–)	−0.1082 (5)	0.1533 (7)
C_9	0.5 (–)	−0.1511 (7)	0.25 (–)
H_1	0.332 (5)	0.300 (4)	0.25 (–)
H_2	0.324 (5)	0.440 (4)	0.25 (–)
H_3	0.5 (–)	0.522 (5)	0.25 (–)
H_4	0.128 (6)	0.138 (4)	0.25 (–)
H_5	0.162 (4)	0.202 (2)	0.026 (3)
H_6	0.210 (5)	0.098 (3)	0.013 (4)
H_7	0.138 (4)	0.104 (3)	0.053 (4)
H_8	0.5 (–)	0.013 (3)	0.092 (4)
H_9	0.5 (–)	−0.123 (4)	0.101 (5)
H_{10}	0.5 (–)	−0.206 (5)	0.25 (–)

[a] The estimated errors in the last digit reported are given in parentheses. (–) means that this coordinate was symmetry fixed and there is no error.

Table II

Anisotropic[a] Thermal Parameters (×10^4)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	106 (2)	40 (1)	69 (1)	0 (–)	0 (–)	0 (–)
O	118 (4)	55 (1)	93 (3)	7 (2)	21 (2)	2 (2)
N_1	108 (9)	40 (3)	69 (5)	0 (–)	0 (–)	0 (–)
N_2	153 (10)	43 (4)	68 (6)	0 (–)	0 (–)	0 (–)
C_1	128 (8)	35 (3)	103 (6)	1 (4)	0 (–)	0 (–)
C_2	139 (10)	47 (4)	131 (7)	15 (5)	0 (–)	0 (–)
C_3	196 (17)	31 (4)	137 (10)	0 (–)	0 (–)	0 (–)
C_4	135 (6)	43 (2)	129 (5)	22 (3)	42 (5)	3 (3)
C_5	88 (7)	64 (4)	160 (10)	3 (4)	0 (–)	0 (–)
C_6	232 (12)	75 (4)	227 (10)	−38 (6)	−111 (9)	5 (6)
C_7	258 (13)	44 (4)	91 (6)	0 (–)	0 (–)	2 (4)
C_8	322 (18)	55 (4)	113 (9)	0 (–)	0 (–)	24 (5)
C_9	251 (20)	43 (5)	167 (15)	0 (–)	0 (–)	0 (–)

[a] The thermal parameters are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Those nondiagonal terms reported as zero with no error estimates are required for atoms on symmetry positions.

Table III

Root-Mean-Square Amplitudes of Vibration (Ångströms ×10^3)

Atom	1	2	3	Atom	1	2	3
Co	223	229	259	C_4	209	265	348
O	236	264	296	C_5	196	320	340
N_1	222	230	260	C_6	252	333	485
N_2	221	238	310	C_7	242	257	402
C_1	216	272	283	C_8	231	317	449
C_2	238	305	307	C_9	239	346	397
C_3	204	315	351				

the ligand atoms from this plane are: O, 0.000 ± 0.003 Å; C_4, −0.012 ± 0.004 Å; C_5, −0.008 ± 0.008 Å; C_6, 0.015 ± 0.006 Å. The cobalt atom is 0.131 ± 0.001 Å out of this plane toward N_2. The dihedral angle between the two acetylacetone planes is 168.4°.

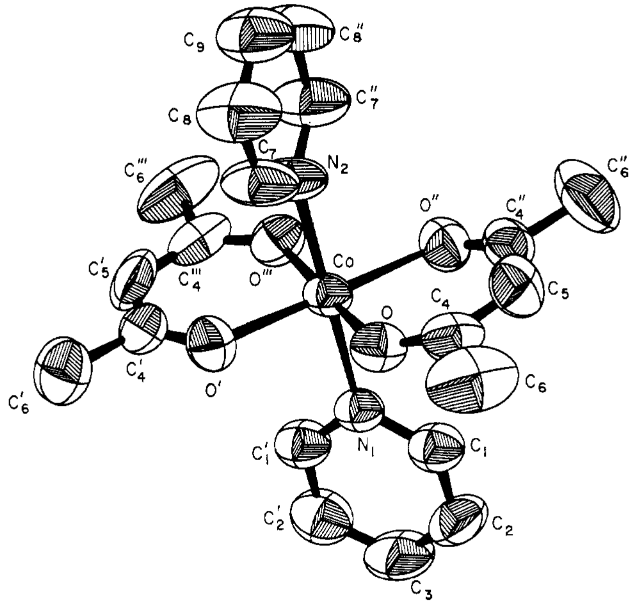

Figure 2.—A parallel projection of the $Co(AA)_2(py)_2$ molecule composed using ORTEP. The hydrogen atoms are not shown for clarity. The molecule has mm symmetry. One of the mirror planes contains N_1, C_2, C_3, C_2', C_1', Co, N_2, and C_9; the other contains N_2, C_7, C_8, C_9, C_8'', C_7'', Co, N_1, and C_3. The acetylacetone ligand is planar within experimental error.

Similar distortions have been noted[20] in other structures of this kind. Here, a possible explanation for the distortion may be the steric interaction of H_1 on C_1 of the pyridine ring with C_5 of the acetylacetone ligand from which it is 2.9 Å distant. Certainly any steric interaction of this type will tend to bend the acetylacetone ligand in the direction observed.

The bond angles about the cobalt atom are close to the values expected for a tetragonal complex. The metal–oxygen atom bond length is within the range of those[1,5,6,20] reported previously. The metal–nitrogen atom bond lengths seem to indicate some π bonding between the metal atom and the pyridine ligand (see below). The asymmetric unit contains two halves of pyridine rings; thus each of the chemically different distances in pyridine is determined twice. The differences listed in Table V show the close agreement between the two sets. All of these distances are somewhat shorter than those obtained spectroscopically,[21] *i.e.:* N_1–C_1, 1.340 (1); C_1–C_2, 1.395 (1); C_2–C_3, 1.394 (1) Å, where the estimated errors in the last digit are given in parentheses. The value for $C_{2,8}$–$C_{3,9}$, 1.343 (6) Å, from the present study is in especially poor agreement with the spectroscopic results. There are no other crystallographic reports of pyridine coordinated to a transition metal of sufficient accuracy to warrant a comparison. The thermal motions of the pyridine rings are large and the motion is greatest perpendicular to the plane of the rings. No correction for thermal motion has been applied to these distances. A more relevant comparison may be possible once the determination of the struc-

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(20) F. A. Cotton and J. S. Wood, *Inorg. Chem.*, **3**, 245 (1964). This article summarizes data for several acetylacetonate complexes.

(21) B. Bak, L. Hansen-Nygaard, and J. Rastrup-Andersen, *J. Mol. Spectry.*, **2**, 361 (1958).

TABLE IV

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (ELECTRONS × 31.0) FOR $Co(AA)_2(py)_2$

H	K	FOBS	FCAL
****L = 0******			
2	0	3282	3140
4	0	3184	3250
6	0	2671	2933
8	0	2518	2726
10	0	933	1094
12	0	400	248
1	1	3342	3248
3	1	4590	4597
5	1	1364	1488
7	1	1875	1864
9	1	604	662
0	2	2018	1991
2	2	1906	1993
4	2	848	858
8	2	541	483
10	2	213	90
1	3	2271	2201
3	3	2438	2502
7	3	2056	1994
9	3	858	931
0	4	7774	7999
2	4	2472	2431
6	4	316	374
8	4	1039	1131
10	4	282	414
1	5	685	704
3	5	586	516
0	6	6778	6783
2	6	1135	1178
4	6	1384	1409
6	6	1444	1540
8	6	1372	1437
10	6	427	412
1	7	4405	4447
3	7	2450	2424
5	7	758	804
7	7	1853	1867
9	7	1036	1074
0	8	2000	1966
2	8	555	636
4	8	1287	1279
1	9	995	1116
3	9	361	342
5	9	597	621
7	9	890	972
9	9	423	484
0	10	3663	3675
4	10	738	749
6	10	583	602
8	10	867	836
1	11	569	569
5	11	510	578
0	12	1066	1093
2	12	571	614
4	12	453	528
8	12	533	455
1	13	1125	1122
3	13	729	729
5	13	604	606
7	13	795	763
0	14	1190	1246
2	14	355	364
4	14	394	392
1	15	386	451
5	15	458	448
0	16	1456	1525
2	16	739	727
4	16	444	436
1	17	394	460
****L = 1******			
1	1	4370	4147
3	1	841	908
7	1	1748	1747
9	1	1139	1145
0	2	4425	4151
2	2	2958	2997
4	2	1569	1631
6	2	1196	1273
8	2	1213	1206
1	3	425	396
3	3	654	647
5	3	925	849
7	3	322	215
0	4	4612	4662
2	4	482	492
4	4	811	861
6	4	872	933
8	4	947	922
12	4	361	89
1	5	2530	2587
3	5	816	882
7	5	1472	1444
9	5	803	865
0	6	4263	4241
4	6	1127	1102
6	6	633	573
8	6	670	696
1	7	2443	2525
3	7	919	936
5	7	647	649
7	7	776	822
9	7	498	502
0	8	4531	4526
2	8	724	798
4	8	1237	1285
6	8	1108	1156
8	8	1193	1227
10	8	413	395
1	9	706	743
3	9	834	827
5	9	469	500
7	9	790	711
2	10	1039	1012
4	10	735	763
6	10	825	826
1	11	1919	1945
3	11	578	598
7	11	742	686
9	11	587	527
0	12	2135	2132
4	12	727	700
6	12	464	370
8	12	598	554
0	14	880	839
2	14	639	598
4	14	617	683
6	14	710	672
1	15	916	892
3	15	394	441
0	16	431	590
1	17	512	509
****L = 2******			
2	0	6047	5940
4	0	3600	3580
6	0	1679	1637
8	0	1934	1879
10	0	966	1063
1	1	1823	1769
3	1	2084	1951
5	1	2310	2282
7	1	1071	1062
0	2	408	302
2	2	292	280
4	2	548	623
6	2	251	246
8	2	303	373
1	3	2234	2247
3	3	1713	1713
5	3	2200	2266
7	3	1308	1356
9	3	327	334
0	4	1993	1875
2	4	1334	1350
4	4	721	793
8	4	818	740
10	4	422	384
1	5	273	250
3	5	326	265
0	6	3155	3245
2	6	2300	2322
4	6	2246	2243
6	6	1177	1152
8	6	966	935
10	6	535	515
1	7	3276	3250
3	7	2062	2121
5	7	1799	1719
7	7	1251	1267
9	7	632	575
11	7	450	405
0	8	479	406
4	8	670	632
1	9	815	808
3	9	1231	1301
5	9	1045	1066
7	9	855	811
9	9	337	284
0	10	1666	1759
2	10	1055	1076
4	10	1279	1252
6	10	634	630
8	10	482	550
10	10	378	314
1	11	516	533
0	12	964	980
2	12	478	462
1	13	864	897
3	13	1076	1050
5	13	935	918
7	13	734	644
0	14	538	487
4	14	510	476
5	15	384	362
0	16	965	952
2	16	731	753
4	16	623	577
****L = 3******			
1	1	3378	3285
3	1	2836	2771
5	1	1590	1574
7	1	1091	1192
9	1	448	454
11	1	680	691
0	2	2896	2845
2	2	2317	2371
4	2	3931	3872
6	2	1420	1458
10	2	499	509
1	3	1474	1469
3	3	597	603
0	4	618	634
2	4	995	1100
4	4	1568	1535
6	4	647	637
10	4	382	397
1	5	498	489
3	5	2095	2115
5	5	1078	1139
7	5	689	785
11	5	521	534
0	6	565	568
2	6	1511	1516
4	6	1427	1442
6	6	668	670
8	6	297	233
1	7	1207	1210
3	7	1418	1466
5	7	866	891
9	7	452	351
0	8	709	784
2	8	1972	1968
4	8	2086	2075
6	8	1173	1203
10	8	578	594
3	9	1517	1523
5	9	1016	1011
7	9	595	611
0	10	408	357
4	10	792	764
6	10	479	525
1	11	521	524
3	11	847	827
2	12	491	544
4	12	564	574
6	12	387	365
1	13	436	386
0	14	370	317
2	14	782	756
4	14	1049	1031
6	14	720	691
1	15	482	552
3	15	752	689
5	15	399	398
1	17	328	375
****L = 4******			
2	0	3302	3234
4	0	2875	2808
6	0	1849	1885
10	0	1220	1264
1	1	2151	2101
3	1	2952	2862
5	1	917	868
7	1	623	598
0	2	573	675
2	2	1474	1475
4	2	1301	1301
6	2	751	804
1	3	416	363
3	3	4840	4759
5	3	1743	1768
7	3	876	909
11	3	619	538
0	4	386	279
2	4	1160	1128
4	4	1213	1328
6	4	825	763
10	4	610	662
1	5	309	360
5	5	304	373
9	5	291	270
0	6	594	600
2	6	2498	2507
4	6	2351	2318
6	6	1429	1405
10	6	760	691
1	7	1070	1132
3	7	3221	3127
5	7	1247	1167
7	7	990	984
0	8	867	841
1	9	604	651
3	9	1989	1966
5	9	1485	1443
7	9	446	394
0	10	353	410
2	10	1693	1685
4	10	1423	1466
6	10	1019	997
3	11	587	520
5	11	380	332
0	12	504	450
2	12	696	669
1	13	598	601
3	13	1541	1540
5	13	1024	1002
7	13	476	443
2	14	688	664
4	14	444	475
6	14	573	510
3	15	415	163
5	15	498	438
0	16	330	396
2	16	603	697
****L = 5******			
1	1	1730	1820
3	1	3985	3932
5	1	1005	951
7	1	861	812
9	1	601	570
11	1	448	596
2	2	2229	2162
4	2	2510	2529
6	2	2124	2081
10	2	669	620
1	3	1049	1077
3	3	1645	1563
7	3	330	372
0	4	799	678
2	4	658	641
4	4	698	750
6	4	735	760
10	4	331	388
1	5	444	333
3	5	2649	2670
5	5	401	430
7	5	519	463
0	6	693	796
2	6	934	971
4	6	700	741
6	6	915	895
1	7	1065	1070
3	7	1223	1195
5	7	918	879
9	7	479	419
0	8	673	699
2	8	1932	1942
4	8	1527	1572
6	8	1404	1397
10	8	771	642
3	9	1898	1897
5	9	678	638
7	9	558	590
0	10	774	821
4	10	496	482
3	11	576	561
0	12	327	382
6	12	520	464
1	13	493	575
2	14	816	846
4	14	895	868
6	14	640	639
3	15	760	757
****L = 6******			
2	0	3154	3160
4	0	856	900
6	0	1393	1440
8	0	674	742
10	0	806	932
1	1	263	230
3	1	1132	1182
5	1	826	839
7	1	383	396
0	2	882	844
2	2	1115	1125
4	2	632	657
6	2	578	503
1	3	1109	1149
3	3	2205	2182
5	3	1380	1355
7	3	788	707
9	3	433	394
0	4	921	885
2	4	1318	1351
6	4	693	683
10	4	536	453
1	5	301	327
0	6	1475	1422
2	6	1896	1900
4	6	1122	1109
6	6	1002	1015
8	6	414	395
10	6	541	521
1	7	2524	1494
3	7	1710	1725
5	7	937	914
7	7	726	714
9	7	553	474
0	8	480	530
2	8	301	79
1	9	861	864
3	9	1249	1189
5	9	985	933
7	9	519	465
0	10	901	924
2	10	1270	1269
4	10	734	669
6	10	773	746
0	12	712	662
2	12	621	538
1	13	804	777
3	13	1065	984
5	13	813	753
0	14	412	372
2	14	598	578
****L = 7******			
1	1	2718	2737
3	1	702	710
5	1	725	702
7	1	886	922
9	1	656	649
0	2	1254	1185
2	2	1402	1444
4	2	1073	1022
6	2	908	915
8	2	664	657
1	3	975	939
0	4	880	862
2	4	572	623
6	4	425	377
8	4	342	403
1	5	1433	1464
3	5	322	328
5	5	447	419
7	5	636	636
9	5	521	469
0	6	894	961
2	6	721	711
1	7	1174	1179
3	7	688	628
5	7	420	435
7	7	490	455
0	8	1758	1764
2	8	1298	1327
4	8	788	728
6	8	827	342
8	8	634	664
1	9	929	839
3	9	569	626
5	9	581	598
7	9	488	408
6	10	370	262
1	11	640	642
0	12	444	430
2	12	398	273
0	14	573	518
2	14	530	516
4	14	566	495
1	15	569	583
****L = 8******			
2	0	1738	1706
4	0	906	931
6	0	893	866
8	0	1169	1136
1	1	1082	1030
3	1	516	540
5	1	603	575
7	1	692	639
0	2	838	878
2	2	288	290
8	2	385	300
1	3	1547	1573
3	3	434	461
5	3	633	590
7	3	915	926
9	3	382	405
0	4	1825	1861
2	4	361	351
8	4	544	536
0	6	2017	2039
2	6	874	927
4	6	603	514
6	6	649	618
8	6	626	666
1	7	1689	1692
3	7	547	565
5	7	494	588
7	7	797	789
1	9	787	775
3	9	423	410
5	9	478	459
7	9	494	521
0	10	1274	1268
2	10	432	472
4	10	346	330
0	12	591	654
1	13	700	704
3	13	507	406
0	14	475	466
****L = 9******			
1	1	1538	1561
3	1	529	567
5	1	305	282
7	1	797	738
9	1	460	516
0	2	1600	1662
4	2	716	710
6	2	647	630
8	2	416	515
1	3	183	260
0	4	1266	1317
2	4	382	342
4	4	412	344
6	4	434	440
8	4	332	359
1	5	1190	1196
3	5	369	428
7	5	660	644
0	6	1118	1174
4	6	432	459
6	6	343	249
1	7	831	816
3	7	397	348
5	7	368	260
7	7	389	331
0	8	1624	1617
2	8	549	557
4	8	630	626
6	8	655	573
1	9	504	494
3	9	325	318
5	9	333	277
2	10	362	293
4	10	310	211
1	11	810	739
0	12	866	821
****L = 10******			
2	0	1169	1245
4	0	1102	1064
6	0	946	795
8	0	733	694
1	1	707	698
3	1	825	822
5	1	665	643
7	1	361	382
0	2	289	291
1	3	507	543
3	3	620	623
5	3	541	542
0	4	988	1038
4	4	297	290
0	6	1193	1210
2	6	606	551
4	6	643	661
6	6	563	464
1	7	923	923
3	7	778	745
5	7	611	551
3	9	423	340
5	9	445	360
0	10	716	688
4	10	478	394
****L = 11******			
1	1	584	643
3	1	636	633
5	1	528	482
7	1	387	308
0	2	173	228
2	2	336	285
4	2	768	764
6	2	415	375
0	4	370	361
2	4	379	347
4	4	538	516
6	4	340	242
1	5	435	444
3	5	648	623
5	5	530	451
0	6	333	418
4	6	321	375
1	7	435	384
3	7	456	333
0	8	564	554
2	8	487	444
4	8	700	651
3	9	322	325
****L = 12******			
2	0	593	950
4	0	679	945
1	1	286	295
3	1	387	613
5	1	375	448
4	2	279	178
3	3	445	613
5	3	308	455
2	4	272	248
4	4	267	361
0	6	294	389
2	6	404	539
1	7	369	459
****L = 13******			
1	1	335	394
0	2	152	66
2	2	402	383
****L = 0******			
11	1	32	21
6	2	111	312
12	2	80	83
5	3	63	154
11	3	32	103
4	4	128	152
5	5	32	99
7	5	105	117
9	5	228	221
11	5	32	31
11	7	133	122
6	8	305	249
8	8	179	140
10	8	82	64
2	10	90	82
10	10	32	249
3	11	32	22
7	11	165	173
9	11	244	328
6	12	32	52
6	14	131	135
3	15	323	334
3	17	259	320
****L = 1******			
5	1	126	124
11	1	209	282
10	2	54	201
12	2	281	75
9	3	268	278
11	3	87	47
10	4	40	215
5	5	202	93
11	5	294	96
2	6	215	227
10	6	308	311
11	7	130	156
9	9	326	336
0	10	146	44
8	10	57	224
10	10	32	75
5	11	199	175
2	12	32	266
1	13	171	113
3	13	359	317
5	13	261	292
7	13	91	34
5	15	84	238
2	16	32	105
4	16	143	222
3	17	261	264
****L = 2******			
12	0	275	372
9	1	242	218
11	1	145	171
10	2	57	233
12	2	266	100
11	3	302	299
6	4	32	175
5	5	67	100
7	5	75	185
9	5	32	73
11	5	145	11
2	8	74	128
6	8	227	147
8	8	175	106
10	8	32	79
3	11	256	63
5	11	71	153
7	11	32	119
9	11	100	102
4	12	32	81
6	12	200	72
8	12	318	224
2	14	276	256
6	14	192	176
1	15	260	225
3	15	387	382
1	17	255	359
3	17	47	279
****L = 3******			
8	2	126	144
12	2	160	235
5	3	118	95
7	3	266	352
9	3	71	62
11	3	272	208
8	4	32	87
9	5	99	132
10	6	353	359
7	7	356	352
11	7	167	244
8	8	335	371
1	9	299	325
9	9	212	76
2	10	162	131
8	10	143	29
5	11	242	317
7	11	185	208
9	11	171	235
0	12	70	71
8	12	142	79
3	13	110	37
5	13	32	127
7	13	32	128
0	16	32	53
2	16	236	188
4	16	136	76
****L = 4******			
8	0	247	132
9	1	112	185
11	1	202	326
8	2	184	31
10	2	221	339
9	3	32	50
8	4	223	266
3	5	33	165
7	5	197	250
11	5	32	40
8	6	117	63
9	7	312	172
2	8	123	339
4	8	152	257
6	8	310	197
8	8	161	199
10	8	125	14
9	9	132	300
8	10	107	120
1	11	166	205
7	11	158	290
4	12	255	240
6	12	281	80
8	12	218	81
0	14	292	222
1	15	130	21
****L = 5******			
0	2	160	241
8	2	216	284
5	3	15	47
9	3	95	72
11	3	267	193
8	4	116	222
9	5	329	253
8	6	275	123
10	6	383	420
7	7	271	188
8	8	192	90
1	9	70	324
9	9	303	40
2	10	118	38
6	10	86	170
8	10	32	52
1	11	227	86
5	11	123	154
7	11	61	41
2	12	271	319
4	12	274	131
3	13	257	55
5	13	214	184
7	13	98	136
0	14	307	273
1	15	368	442
0	16	32	51
2	16	223	197
****L = 6******			
9	1	224	195
8	2	222	219
10	2	32	256
4	4	32	104
8	4	99	193
3	5	128	67
5	5	142	101
7	5	194	55
9	5	32	82
4	8	161	45
6	8	186	259
8	8	237	108
9	9	218	303
8	10	91	174
1	11	130	272
3	11	83	196
5	11	216	209
7	11	275	111
4	12	32	106
6	12	122	59
4	14	264	286
1	15	111	33
3	15	134	115
****L = 7******			
10	2	32	322
3	3	168	136
5	3	50	76
7	3	253	183
9	3	131	185
4	4	32	220
10	4	200	221
4	6	249	293
6	6	290	390
8	6	192	316
9	7	310	323
0	10	63	190
2	10	79	27
4	10	125	271
3	11	206	107
5	11	32	45
7	11	254	251
4	12	32	49
6	12	94	198
1	13	106	235
3	13	121	58
5	13	168	101
****L = 8******			
9	1	109	248
4	2	194	105
6	2	192	259
4	4	196	206
6	4	157	163
1	5	158	131
3	5	32	51
5	5	38	15
7	5	152	50
9	5	74	82
0	8	75	37
2	8	208	122
4	8	100	264
6	8	142	5
8	8	32	53
6	10	277	325
1	11	184	296
3	11	183	136
5	11	125	105
2	12	223	344
4	12	34	82
****L = 9******			
2	2	75	82
3	3	166	77
5	3	136	123
7	3	32	131
5	5	258	251
2	6	98	169
8	6	233	294
0	10	159	14
3	11	222	217
2	12	186	171
****L = 10******			
2	2	175	23
4	2	32	118
6	2	103	125
8	2	189	141
7	3	331	418
2	4	78	131
6	4	124	208
1	5	53	120
3	5	32	26
5	5	32	35
7	5	40	81
0	8	204	187
2	8	44	29
4	8	174	238
6	8	170	82
1	9	171	311
2	10	221	169
1	11	275	119
3	11	32	21
****L = 11******			
1	3	32	12
3	3	97	40
5	3	96	9
2	6	231	235
5	7	318	248
1	9	69	99
0	10	120	81
****L = 12******			
0	2	80	23
2	2	88	112
1	3	41	143
0	4	43	144
1	5	32	62
3	5	121	85
****L = 13******			
1	3	77	82
0	4	149	59

TABLE V

$Co(AA_2)(py)_2$ BOND LENGTHS (ÅNGSTRÖMS)

Co–O	2.034 (3)	O–C_4	1.241 (6)
Co–N_1	2.176 (7)	C_4–C_5	1.393 (6)
Co–N_2	2.197 (7)	C_4–C_6	1.535 (8)
N_1–C_1	1.321 (7)	N_2–C_7	1.312 (7)
C_1–C_2	1.375 (9)	C_7–C_8	1.369 (10)
C_2–C_3	1.342 (9)	C_8–C_9	1.345 (10)

Mean distances		Differences
Co–$N_{1,2}$	2.187 (5)	0.021 (10)
$N_{1,2}$–$C_{1,7}$	1.317 (5)	0.009 (10)
$C_{1,7}$–$C_{2,8}$	1.372 (7)	0.006 (13)
$C_{2,8}$–$C_{3,9}$	1.343 (6)	0.003 (13)

Carbon–hydrogen distances			
C_1–H_1	0.88 (6)	C_7–H_8	0.96 (6)
C_2–H_2	0.87 (6)	C_8–C_9	0.76 (6)
C_3–H_3	1.03 (8)	C_9–H_{10}	0.86 (9)
C_5–H_4	0.84 (7)	C_6–H_5	1.00 (4)
C_6–H_6	0.84 (4)	C_6–H_7	0.80 (4)

Av carbon–hydrogen distance 0.88

TABLE VI

BOND ANGLES[a] IN $Co(AA)_2(py)_2$ (DEGREES) WHERE THE CENTRAL ATOM IS AT THE VERTEX

Metal Coordination Angles			
N_1–Co–O	90.4 (1)	N_2–Co–O	89.6 (1)
O–Co–O″	89.8 (2)	O–Co–O‴	179.2 (2)
Pyridine Ring Angles			
Co–N_1–C_1	121.4 (4)	Co–N_2–C_7	121.7 (4)
N_2–C_1–C_2	122.7 (7)	N_2–C_7–C_8	123.2 (7)
C_1–C_2–C_3	118.9 (8)	C_7–C_8–C_9	119.6 (8)
C_2–C_3–C_2'	119.5 (10)	C_8–C_9–C_8''	117.9 (11)
C_1–N_1–C_1'	117.2 (8)	C_7–N_2–C_7''	116.6 (8)
Acetylacetone Angles			
Co–O–C_4	125.8 (3)	O–C_4–C_5	126.1 (5)
O–C_4–C_6	114.5 (6)	C_4–C_5–C_4''	125.9 (7)
Hydrogen Atom Angles			
H_1–C_1–N_1	113 (4)	H_8–C_7–N_2	110 (4)
H_1–C_1–C_2	124 (4)	H_8–C_7–C_8	126 (3)
H_2–C_2–C_1	117 (4)	H_9–C_8–C_7	113 (7)
H_2–C_2–C_3	124 (4)	H_9–C_8–C_9	127 (4)
H_3–C_3–C_2	120 (1)	H_{10}–C_9–C_8	121 (1)
H_5–C_6–C_4	103 (2)	H_6–C_6–C_4	99 (4)
H_7–C_6–C_4	102 (4)	H_4–C_5–C_4	117 (1)
H_5–C_6–H_6	149 (5)	H_5–C_6–H_7	125 (5)
H_6–C_6–H_7	70 (4)		

[a] To generate the atoms of an entire molecule, the following transformations have been made from the unprimed atomic coordinates: single prime, $1 - x, y, z$; double prime, $x, y, {}^1/_2 - z$; triple prime, $1 - x, y, {}^1/_2 - z$. These transformations are those used in Figure 2.

ture of $Ni(AA)_2(py)_2$, now in progress, has been completed.

The bond distances in the acetylacetone ligand may be compared with several reports[20] including the recent refinement of the structure of $Fe(AA)_3$ by Iball and Morgan.[22] All distances reported here are within 2σ of these reports. The thermal motion of this ligand (Figure 2) seems consistent with that observed previously.[22]

Although the positions obtained from refinement of the hydrogen atoms result in a significant improvement in the wR factor, the placement of these atoms is probably not very accurate. Thus, H_6, one of the three hydrogen atoms of the methyl group, is almost certainly misplaced as can be seen from the H_5–C_6–H_6 angle of 149° and the H_6–C_6–H_7 angle of 70°. When this atom was placed 1.0 Å from C_6 and at the tetrahedral angles and refined a second time, it moved again to the position reported. It may be that the methyl group is rotationally disordered, as its hydrogen atoms were by far the weakest ones found in the difference map used to locate the hydrogen atoms. The average of 0.88 Å found for the hydrogen–carbon atom bond lengths is shortened relative to that found in neutron diffraction and spectroscopic studies (1.08 Å). This is presumably due to the bonding concentration of electron density between the nuclei.[23]

Multiple Bonding between Metal and Ligands.—The possibility of forming an additional bond of the $d\pi$–$p\pi$ type by donation from filled metal d orbitals into empty π^* orbitals on both of these types of ligand has been previously suggested. Nmr experiments[24] on paramagnetic, first-row, transition metal acetylacetonates have been interpreted on this basis. Thermochemical experiments[25] have been postulated to show π bonding between cobalt and pyridine in $CoCl_2(py)_4$; although infrared[26] and nmr[27] studies (the latter on $Co(AA)_2(py)_2$) have been claimed to refute this interpretation. The nmr studies must be considered to be only partially useful owing to a large pseudo-contact shift which may mask a π-delocalization effect.

Two lines of evidence, obtained in this study, support the possibility of multiple bonding between the cobalt atom and the pyridine rings. First, the configurations adopted by the two pyridine rings are such that the maximum amount of π bonding from metal to ligand is possible. The arrangement of the two pyridine rings so that one is rotated 90° with respect to the other about the axis (C_3, N_1, Co, N_2, C_9) is certainly not the stereochemically favored one (see above). One of the rings (N_1, C_1, C_2, C_3, C_2', C_1') seems to interact strongly enough with the acetylacetone ligand to deform it. A rotation of this pyridine ring by 90° would remove the steric interaction. Indeed this is the case in the structure of $Ni(AA)_2(py)_2$ for which Fackler[7] reports and this author's studies have confirmed that there are two molecules in a monoclinic cell of space group $P2_1/c$. This requires that the nickel atoms lie on centers of symmetry and therefore that the two pyridine rings must be *trans* and that the rings cannot be rotated with respect to each other. However, this conformation requires that both of the pyridine rings compete for electron density from the same metal orbital. Calculations of packing energies, now in progress, for these two

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(22) J. Iball and C. H. Morgan, *Acta Cryst.*, **23**, 239 (1967).

(23) B. Dawson, *Australian J. Chem.*, **18**, 595 (1965).

(24) D. R. Eaton, *J. Am. Chem. Soc.*, **87**, 3097 (1965).

(25) J. de O. Cabral, H. C. A. King, S. M. Nelson, T. M. Shepherd, and E. Koros, *J. Chem. Soc.*, 859 (1966), and references therein.

(26) D. P. Graddon and E. C. Watton, *Australian J. Chem.*, **18**, 507 (1965).

(27) W. D. Horrocks, Jr., R. C. Taylor, and G. N. La Mar, *J. Am. Chem. Soc.*, **86**, 3031 (1964).

conformations should allow estimates of these π-bond energies and will be reported in a later paper.

The second form of evidence suggesting multiple bonding between the metal atom and the pyridine groups comes from the metal–nitrogen atom bond lengths. The values determined here are nearly equal and average 2.187 Å. Values of 2.12 and 2.14 Å have been reported for this distance in $Co(NCS)_2(py)_2$[28] and $CoCl_2(py)_2$,[29] where the cobalt atom in both cases is octahedrally coordinated through bridging by the nonpyridine ligands; however, both of these structures were done only with projections and no reliable estimate of the errors involved is available. Further, these distances might also be shortened from the ideal single-bond distance. The value for hypothetical single-bond distances for the fifth and sixth coordination positions of a cobalt acetylacetonate is needed, and the structure[6] of $Co(AA)_2(H_2O)_2$ provides that information. There is little reason to believe that there is any double bonding between the cobalt atom and the water molecule; thus the $Co–O_{H_2O}$ distance of 2.23 ± 0.01 Å may be taken to represent the single bond distance between cobalt and oxygen atoms of neutral molecules in cobalt acetylacetonate adducts. In going from oxygen to nitrogen a correction[30] of 0.04 Å must be added to give the expected cobalt–nitrogen atom distance of 2.27 Å. Thus the distance, 2.187 Å, determined in this study seems to indicate some shortening due to π bonding.

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(28) M. A. Porai-Koshits and G. N. Tischenko, *Kristallografiya*, **4**, 239 (1959).

(29) J. D. Dunitz, *Acta Cryst.*, **10**, 307 (1957).

(30) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 224 f. Table 7.2 lists the covalent radius for the nitrogen atom as 0.70 Å and that for the oxygen atom as 0.66 Å, whereas Table 7.5 gives the Schomaker–Stevenson radii of both atoms as 0.74 Å; however, the second distances must be corrected for electronegativity differences between cobalt and nitrogen or oxygen by -0.09 Å $|\chi_{Co} - \chi_{N,O}|$, which gives nitrogen as 0.045 Å larger than oxygen.

CONTRIBUTION FROM THE MALLINCKRODT LABORATORY, DEPARTMENT OF CHEMISTRY,
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The Crystal and Molecular Structure of π-Cyclopentadienyl(1,2-dicyanoethene-1,2-dithiolato)cobalt[1,2]

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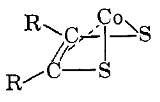
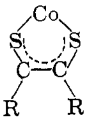
π-Cyclopentadienyl(1,2-dicyanoethene-1,2-dithiolato)cobalt, π-$C_5H_5CoS_2C_2(CN)_2$, crystallizes in the monoclinic space group C2/c (C_{2h}^6; no. 15) with $a = 17.05 \pm 0.02$ Å, $b = 8.50 \pm 0.01$ Å, $c = 14.82 \pm 0.02$ Å, $\beta = 109.48 \pm 0.05°$, $Z = 8$. Observed and calculated densities are, respectively, 1.72 ± 0.02 and 1.732 g cm^{-3}. A single-crystal X-ray diffraction study, based on data to $\sin \theta = 0.40$, has led to the location of all atoms (including hydrogens). The final discrepancy index is $R_F = 7.1\%$ for 1337 independent nonzero reflections. The crystal is composed of distinct molecular units of π-$C_5H_5CoS_2C_2(CN)_2$ separated by normal van der Waals forces. The cobalt atom may be considered pentacoordinate since it is linked to a bidentate dithiolate ligand and a formally tridentate π-cyclopentadienyl ligand. The molecule possesses approximate C_s symmetry. Cobalt–sulfur distances average 2.117 ± 0.003 Å; other distances within the dithiolate system include: C–S = 1.702 ± 0.007 Å and C–C = 1.364 ± 0.010 Å.

Introduction

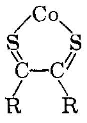
Infrared spectral studies on the 1,2-disubstituted ethene-1,2-dithiolate complexes, π-$C_5H_5CoS_2C_2R_2$ (R = CF_3,[3] CN[4]), led to the suggestion that the dithiolate ligand might bond to the metal *via* both cobalt–sulfur and cobalt–olefin bonding (I), rather than by cobalt–sulfur bonding alone (II). A crystallographic examination of π-$C_5H_5CoS_2C_2(CN)_2$ was originally[5] undertaken to resolve this ambiguity. However, while our investigation of the complex was still incomplete, a study[6] of the closely related molecule π-$C_5H_5CoS_2C_2(CF_3)_2$ showed structure II to be appropriate. The bond distances within the $S_2C_2(CF_3)_2$ ligand (particularly the carbon–carbon bond length of 1.48 ± 0.05 Å within the "ethene") led to the proposal[6] that the molecule should be described as an ethane-1,2-dithione complex (III) rather than as an ethylene-1,2-dithiolate de-



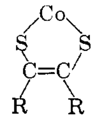
I



II



III



IV

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(1) We have followed Ibers[2] in using the term "ethene-1,2-dithiolate" to describe the ligand in such a way as not to predispose the reader toward any one valence bond description of the complex. The structural formula II is in keeping with this policy.

(2) R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **5**, 411 (1966), particularly footnote 20.

(3) R. B. King, *J. Am. Chem. Soc.*, **85**, 1587 (1963).

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(5) See footnote 17 of ref 4.

(6) H. W. Baird and B. M. White, *J. Am. Chem. Soc.*, **88**, 4744 (1966).