contacts involving fluorine atoms of the anion with other atoms in the structure are listed in Table VII. No other contact below 3.6 Å is found.

The refinement of the structures of other Co(II) complexes of this series is in progress in this laboratory.

Structure and Magnetism of a Binuclear 1,3,5-Triketonate Complex of Cobalt(II), Bis(1,5-diphenyl-1,3-5-pentanetrionato)tetrapyridinedicobalt(II)–Tetrapyridine

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Structural and magnetic data are reported for the pyridine adduct of the binuclear cobalt(II) complex formed between 1,5-diphenyl-1,3,5-pentanetrione (H₂DBA) and CoCl₂·6H₂O. Two Co₂(DBA)₂(py)₄·4py, comprised of four coordinated and four uncoordinated molecules of pyridine per formula species, crystallize in a monoclinic unit cell with lattice parameters $a = 12.778$ (7), $b = 17.919$ (10), $c = 14.373$ (7) Å, and $\beta = 102.54$ (6)° and with symmetry $P2_1/n$. The structure was refined to a conventional discrepancy factor of 0.077 for 2298 independent diffractometric data for which $F^2 > 3.5\sigma(F^2)$. The molecular complex, possessing crystallographic site symmetry C_i-$\bar{1}$, consists of two cobalts coordinated to two 1,5-diphenyl-1,3,5-pentanetrionate ligands and to four pyridine ligands such that each Co(II) has an octahedral-like environment of four coplanar oxygens and two pyridine nitrogens located above and below the metal–oxygen plane. The central oxygen donor in each 1,5-diphenyl-1,3,5-pentanetrionate ligand is bonded to both cobalts thereby forming a four-membered ring containing two oxygens and two cobalts. The Co–Co distance is 3.272 (3) Å, while the intra-ring bond angles are O–Co–O = 77.28 (29)° and Co–O–Co = 102.71 (29)°. Temperature-dependent magnetic susceptibility measurements over the range 300–77°K indicate a strong antiferromagnetic interaction between the cobalts, presumably occurring *via* superexchange involving the bridging oxygens. The magnetic results are discussed in light of the structural data presented.

Introduction

The 1,3,5-triketonates represent a potentially useful class of ligands for the study of magnetic exchange between transition metals in that these ligands coordinate readily in a 1:1 molar ratio with various metals. One result of this coordination is the formation of four-membered rings containing two metal ions and two ketonic oxygens. Most work to date on chelates of 1,3,5-triketonates has dealt with the Cu(II) complexes.[1] However, complexes of Ni(II),[2] Fe(II), Mn(II), and Cr(III) have been studied in a preliminary manner,[3] and a Co(II) complex is reported herein. It is probable that the coordinating ability of the 1,3,5-triketonates will rival that of the parent 1,3-diketonates. Thus, these ligands offer an unusual opportunity to study magnetic exchange through bridging atoms in a large number of systems with similar metal environments. The work reported here was undertaken to obtain detailed stereochemical information relating to the magnetic properties of 1,3,5-triketonate metal chelates.

Experimental Section

The ligand 1,5-diphenyl-1,3,5-pentanetrione whose trivial name is dibenzoylacetone (H₂DBA) may be purchased from Eastman Organic Chemicals. It also may be conveniently prepared by the condensation of either 1-phenyl-1,3-propanedione or acetone with stoichiometric quantities of methyl benzoate in refluxing monoglyme with NaH used as the base. This procedure has been described by Miles, Harris, and Hauser.[4]

(1) (a) F. Sargara, H. Kobayaski, and K. Ueno, *Bull. Chem. Soc. Jap.*, **41**, 266 (1968); **45**, 794 (1972); (b) D. P. Murtha and R. L. Lintvedt, *Inorg. Chem.*, **9**, 1532 (1970); (c) D. Baker, C. W. Dudley, and C. Oldham, *J. Chem. Soc. A*, 2605 (1970).

(2) R. L. Lintvedt, L. L. Borer, and D. P. Murtha, submitted for publication.

(3) Unpublished results from our laboratory.

(4) M. L. Miles, T. M. Harris, and C. R. Hauser, *J. Org. Chem.*, **30**, 1007 (1965).

Preparation of a Powdered Sample of Bis(1,5-diphenyl-1,3-5-pentanetrionato)tetrapyridinedicobalt(II)–Dipyridine, Co₂(DBA)₂(py)₄·2py. The parent compound containing coordinated pyridine rather than coordinated water was prepared by the mixing of hot solutions of CoCl₂·6H₂O (1.79 g; 7.5 mmol) in 50 ml of water with H₂DBA (2.0 g; 7.5 mmol) in 150 ml of methanol. To this solution 0.3 g of NaOH in 10 ml of H₂O was added. The compound which analyzes for Co₂(DBA)₂(H₂O)₄·2H₂O precipitates immediately as a golden powder. This product was dried in a vacuum desiccator, dissolved in a minimum volume of pyridine, and filtered; the filtrate was then condensed to about half its original volume. Cooling of the solution yielded red crystals which crumble to a reddish brown powder in a vacuum desiccator. The analysis of this powder is as follows. *Anal.* Calcd for Co₂(C₁₇H₁₂O₃)₂·(C₅H₅N)₄·2C₅H₅N: C, 68.57; H, 4.86; N, 7.50. Found: C, 68.32; H, 5.06; N, 8.28.

Growth of Single Crystals. Single crystals were formed by dissolution of the powdered sample in hot pyridine followed by a slow cooling of the solution to room temperature over a 48-hr period. The resulting well-formed crystals decompose when exposed to X-rays in the absence of pyridine. Since the structural data reported herein establish four rather than two pyridines of crystallization per formula species, it is likely that the crystals lose pyridine and convert to the powder Co₂(DBA)₂(py)₄·2py.

Single-Crystal Characterization and X-Ray Data Collection. The decomposition of the single crystals required special techniques for mounting. The crystal used for precession photographs and data collection was oriented in a glass capillary with Silastic adhesive. In order to maintain a pyridine atmosphere, the sealed capillary also contained glass wool which had been soaked in pyridine. During the entire course of data collection, pyridine could be observed in the sealed capillary. The crystal used for the X-ray study had the dimensions of 0.69 mm × 0.42 mm × 0.46 mm. The instability of the single crystals in the absence of pyridine precluded either an experimental density determination or a chemical analysis.

Precession photographs taken with Cu Kα radiation showed Laue symmetry of C_{2h}-$2/m$ with systematic absences of $h + l = 2n + 1$ for {$h0l$} and $k = 2n + 1$ for {$0k0$} which uniquely defined the probable space group as $P2_1/n$. The lattice constants, initially obtained from precession photographs, were refined by least squares[5] from 23 reflections whose angles were accurately determined on a
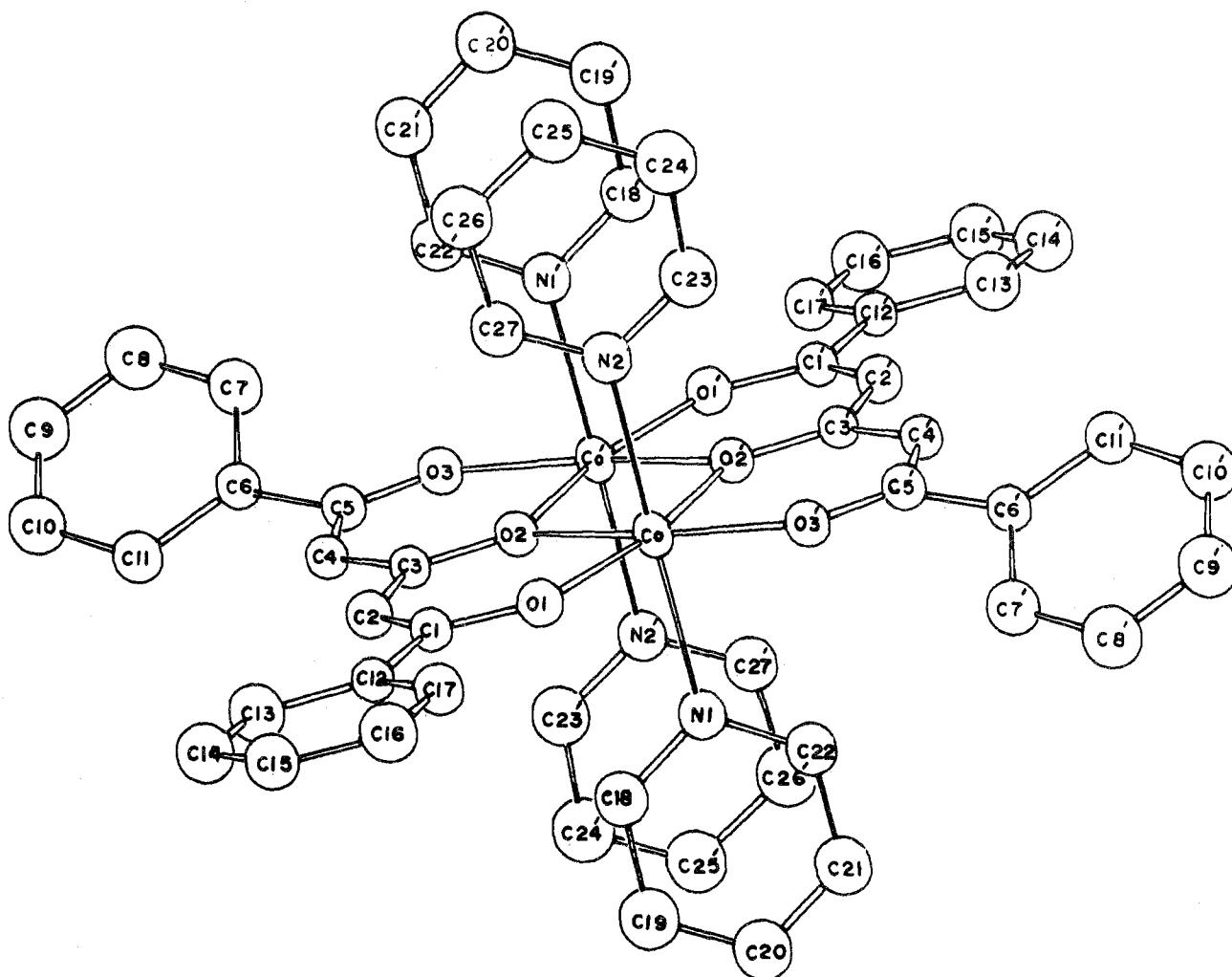
Figure 1. Molecular structure of bis(1,5-diphenyl-1,3,5-pentanetrionato)tetrapyridinedicobalt(II).

Picker four-circle card-controlled diffractometer with Mo Kα radiation (λ 0.70926 Å). The refined lattice constants are $a = 12.778 \pm 0.007$ Å, $b = 17.919 \pm 0.010$ Å, $c = 14.373 \pm 0.007$ Å, and $\beta = 102.54 \pm 0.06°$. The unit cell volume is 3212.60 Å³.

Intensity data were collected with Mo Kα radiation by means of the moving-crystal, moving-counter θ–2θ scan technique with a take-off angle of 2.7°. A symmetric scan of 2.5° (minimum) was used with an allowance for spectral dispersion and a scan rate of 2°/min. Stationary-background counts of 15 sec were taken at both ends of the scan. A zirconium filter of 1-mil thickness was used for all data with $2\theta \geqslant 10°$, while a filter of 2-mil thickness was used for data with $2\theta < 10°$. Copper attenuators were inserted for reflections in which the counting rate exceeded 9000 cps. The pulse height analyzer was set to accept approximately 90% of the pulse generated, and the counter aperture was 29.9 cm from the crystal for all data.

Independent data totaling 9754 reflections were collected in the quadrant ($\pm hkl$) to a limiting 2θ of 60° (($\sin \theta$)/λ < 0.705). During the course of data collection, the intensities of four standard reflections were measured after every 150 reflections as a check on crystal and electronic stability. These standards exhibited variations less than 5% during the entire data collection.

The intensity data were corrected for background and Lorentz–polarization effects, and standard deviations of F^2 were assigned in

(5) Local versions of the following programs were used in the solution and refinement of this structure: PICK 2, J. A. Ibers' least-squares program for lattice constants and orientation angles based on W. C. Hamilton's MODE 1; DACOR, D. L. Smith's program for the correction of diffractometric data and estimation of standard deviations; FORDAP, A. Zalkin's Fourier program; ORFLS and ORFEE, W. Busing, K. Martin, and H. Levy's full-matrix least-squares program and function and error program; ORTEP, C. K. Johnson's program for drawing thermal ellipsoids of crystal structures; GONO 9, W. C. Hamilton's general absorption–extinction program.

accord with previous work[6] with a factor for instrument instability of 0.05. The linear absorption coefficient, μ, for Mo Kα radiation was 6.01 cm⁻¹. Since calculation showed the corrections for absorption on F were within a small range of only 1.13–1.19, no corrections for absorption were deemed necessary.

Of the 9754 data examined, the 2298 reflectors with $F^2 > 3.5\sigma(F^2)$ were used for the solution and refinement of the structure.

Structure Determination. The calculated density indicated two binuclear cobalt(II) molecules in the unit cell. Three-dimensional Patterson techniques yielded the position of the independent cobalt ion, which gave an unweighted discrepancy factor of 0.562 (where $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$). Subsequent three-dimensional Fourier maps allowed the positioning of the remaining atoms. Full-matrix, isotropic least-squares refinement on F of all nonhydrogen atoms resulted in an unweighted R value of 0.178 and a weighted discrepancy factor of $R_w = 0.258$ (where $R_w = \{\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2\}^{1/2}$). On the basis of the microanalysis of the powder sample, the number of *uncoordinated* pyridines in the unit cell of the crystal was initially considered to be 4. Since the discrepancy indices were high at this stage of refinement and since a Fourier difference synthesis (in which the $Co_2(DBA)_2(py)_4 \cdot 2py$ species were excluded) showed a number of positions with high residual electron density, it was assumed that the initial formulation of two *free* pyridines per molecule was incorrect. In fact, the regions of high electron density were subsequently identified as the third and fourth free pyridine of the asymmetric unit corresponding to *four* uncoordinated pyridines per molecule. Full-matrix isotropic least-squares refinement (with the new pyridines incorporated) resulted in an R of 0.113 and an R_w of 0.117. Unambiguous assignment of nitrogen positions in the *free* pyridine molecules was found impossible due to high thermal motion; it is likely that each pyridine molecule is sixfold disordered.

A Fourier difference map revealed the positions of all hydrogen

(6) L. J. Radonovich and M. D. Glick, *Inorg. Chem.*, **10**, 1463 (1971).

atoms except those on the solvent pyridine molecules. Two cycles of isotropic refinement, with fixed contributions from the hydrogens yielded an R value of 0.091 and an R_w value of 0.117. Two cycles of least-squares refinement, with anisotropic thermal parameters for the independent cobalt and each atom of the free pyridine rings and with anomalous scattering effects included for the cobalt, produced a final R value[7] of 0.077 and an R_w of 0.103. The error of fit was 2.6891. The highest residual electron density from the final difference Fourier map of 0.38 e/A^3 substantiated the correctness of the structure at this point.

The large thermal parameters for the *free* pyridine rings suggested either that these sites might be only partially occupied or that each solvent molecule may be distributed in more than one orientation in the crystal. Variation of occupancy factors in the least-squares refinement indicated 100% occupancy. The somewhat high discrepancy factors may be attributed to the necessary pyridine atmosphere during data collection and to the possible crystal disorder of the *free* pyridine molecules in the crystalline arrangement.

Magnetic Susceptibility Measurements. Magnetic susceptibility was measured by both the Gouy and Faraday methods with Hg-[Co(SCN)₄] used as the calibrant. The agreement between the two methods was within experimental error. The magnetic susceptibility was measured as a function of temperature (between 77 and 300°K) and as a function of the field strength (between about 1700 and 9700 G). No field dependence was observed. The temperatures were achieved with liquid nitrogen and standard baths. The temperature was monitored with a copper–constantan thermocouple connected to a Leeds and Northrup temperature potentiometer. The accuracy is estimated to be ±0.5°K. A Varian Associates Model V-4004 (4-in.) electromagnet was used to provide the magnetic field. Correction for diamagnetic effects were made by use of Pascal's constants. In addition, the diamagnetism for H_2DBA was determined experimentally to be -130×10^{-6} cgsu. The calculated value is -137×10^{-6} cgsu.

Results

The molecular structure consists of two cobalt(II) atoms chelated to two ligands of the triketonate 1,5-diphenyl-1,3-5-pentanetrionate and linked to four pyridines such that each cobalt is octahedrally coordinated to four coplanar carbonyl oxygen atoms and two pyridine nitrogen atoms situated above and below the metal–oxygen plane. The four oxygens coordinated to each cobalt are of two distinct types—*viz.*, two terminal ketonate oxygens and two central bridging ketonate oxygens. The latter are arranged in such a way that the two cobalt octahedra share these atoms on a common edge. In addition to the *coordinated* pyridines, there are eight *uncoordinated* solvent pyridine molecules in the unit cell occupying the "empty space" between adjacent phenyl rings of the triketones, and it may be this fact that permits crystallization of this species. The molecular configuration of bis(1,5-diphenyl-1,3,5-pentanetrionato)tetra-pyridinedicobalt(II) is shown in Figure 1, and a diagram of the unit cell is given in Figure 2. Positional coordinates and thermal parameters are listed in Table I. The bond distances and bond angles are presented in Tables II–IV.

The presence of strong magnetic interactions between the two cobalt(II) atoms in the molecule is evidenced by the low magnetic moment measured at room temperature. The sharp decrease in the magnetic moment at lower temperatures is a further indication of a strong antiferromagnetic coupling. The measured magnetic moments on a per Co(II) basis are as follows: at 300°K, μ_{eff} = 4.28 BM; at 195°K, μ_{eff} = 4.07 BM; at 77°K, μ_{eff} = 3.36 BM. There is no appreciable field dependence at any of these temperatures.
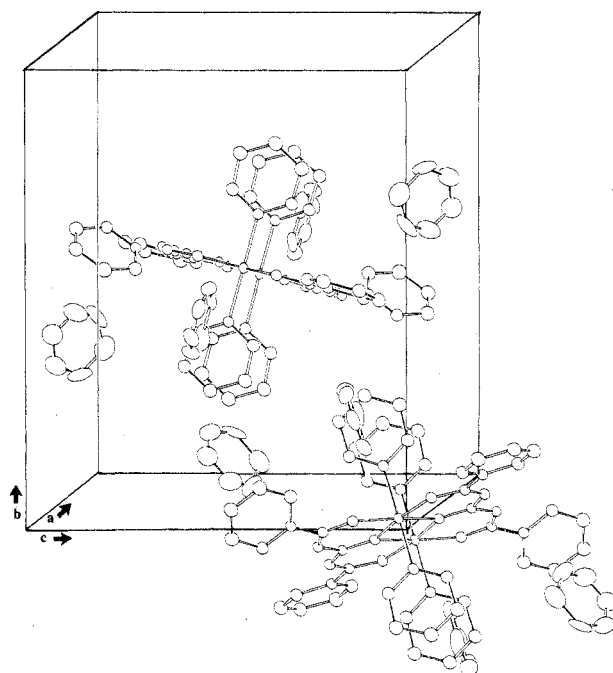
Figure 2. The packing of $Co_2(DBA)_2(py)_4 \cdot 4py$ showing the anisotropy of the uncoordinated pyridine molecules.
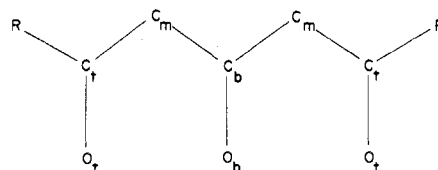

Figure 3. Labeling scheme for the 1,3,5-triketonate ligand.

The antiferromagnetic exchange observed is considered to be entirely due to intramolecular interactions, since the closest intermolecular Co–Co distance is 9.886 (6) Å.

Discussion

The results of this investigation may be conveniently discussed in two parts. First, a comparison of structural features of $Co_2(DBA)_2(py)_4$ with related complexes will be made. Second, we shall discuss the features of this complex which make it structurally and magnetically interesting. In order to facilitate this discussion, we shall use the labeling scheme shown in Figure 3 in which the subscripts t, b, and m stand for terminal, bridging, and methine.

Since the work reported herein represents the first structural determination of a 1,3,5-triketonate-chelated metal complex, no direct comparison to other complexes containing this ligand can be made. However, several comparisons between $Co_2(DBA)_2(py)_4$ and 1,3-diketonate chelates can be made. Lingafelter and Braun[8] have tabulated interatomic distances and angles for thirteen acetylacetonate transition metal complexes whose structures have been determined by three-dimensional X-ray methods. They concluded that the metal–oxygen and oxygen–oxygen distances and the oxygen–metal–oxygen and metal–oxygen–carbon bond angles are functions of the particular metal ion. Other structural features associated with the ligand are, within experimental error, essentially invariant. In addition to the structures discussed by Lingafelter and Braun,[8] Cotton and his coworkers have published a series

(8) E. C. Lingafelter and R. L. Braun, *J. Amer. Chem. Soc.*, **88**, 2951 (1966).

Table I. Positional and Thermal Parameters[a,b] with the Estimated Standard Deviations of the Last Digit in Parentheses

	x	y	z	B, Å²
Co	0.1282 (1)	0.0082 (1)	0.0466 (1)	
O(1)	0.2424 (6)	0.0390 (4)	−0.0216 (5)	3.67 (17)
O(2)	0.0168 (6)	0.0222 (4)	−0.0822 (5)	3.31 (16)
O(3)	−0.2017 (5)	0.0091 (4)	−0.1835 (5)	3.59 (15)
C(1)	0.2342 (9)	0.0578 (6)	−0.1096 (8)	3.08 (24)
C(2)	0.1388 (10)	0.0604 (6)	−0.1762 (8)	3.68 (26)
C(3)	0.0343 (9)	0.0421 (6)	−0.1637 (8)	2.90 (23)
C(4)	−0.0512 (9)	0.0465 (6)	−0.2454 (8)	3.14 (24)
C(5)	−0.1582 (9)	0.0276 (6)	−0.2518 (8)	3.46 (25)
N(1)	0.1115 (8)	0.1261 (6)	0.0843 (7)	3.97 (22)
N(2)	0.1577 (8)	−0.1087 (6)	0.0139 (7)	4.11 (22)
C(6)	−0.2294 (9)	0.0235 (6)	−0.3490 (8)	3.48 (25)
C(7)	−0.3096 (11)	−0.0306 (7)	−0.3671 (10)	4.89 (31)
C(8)	−0.3741 (13)	−0.0411 (8)	−0.4579 (12)	6.30 (35)
C(9)	−0.3572 (11)	0.0034 (9)	−0.5306 (10)	6.21 (32)
C(10)	−0.2786 (12)	0.0554 (8)	−0.5167 (10)	5.51 (33)
C(11)	−0.2147 (10)	0.0676 (7)	−0.4256 (9)	4.34 (28)
C(12)	0.3379 (9)	0.0779 (6)	−0.1361 (8)	3.23 (24)
C(13)	0.3444 (12)	0.0987 (8)	−0.2274 (10)	5.44 (33)
C(14)	0.4458 (12)	0.1124 (8)	−0.2493 (11)	5.69 (36)
C(15)	0.5355 (11)	0.1065 (7)	−0.1791 (11)	4.99 (32)
C(16)	0.5311 (12)	0.0878 (8)	−0.0877 (11)	5.73 (34)
C(17)	0.4309 (10)	0.0719 (7)	−0.0663 (9)	4.25 (29)
C(18)	0.1268 (11)	0.1791 (8)	0.0234 (10)	4.83 (31)
C(19)	0.1326 (12)	0.2557 (8)	0.0473 (12)	6.12 (34)
C(20)	0.1216 (11)	0.2763 (8)	0.1361 (11)	5.86 (35)
C(21)	0.1060 (11)	0.2232 (8)	0.1970 (10)	5.50 (34)
C(22)	0.1014 (10)	0.1487 (7)	0.1696 (9)	4.47 (29)
C(23)	0.1584 (11)	−0.1612 (8)	0.0782 (10)	6.54 (39)
C(24)	0.1773 (12)	−0.2379 (9)	0.0629 (12)	5.61 (35)
C(25)	0.1963 (12)	−0.2586 (8)	−0.0240 (11)	6.28 (36)
C(26)	0.1959 (12)	−0.2026 (9)	−0.0955 (11)	4.79 (30)
C(27)	0.1759 (10)	−0.1288 (8)	−0.0697 (9)	6.30 (37)
C(28)	−0.0155 (52)	0.0990 (28)	0.4036 (41)	
C(29)	0.0535 (35)	0.0970 (23)	0.4829 (52)	
C(30)	0.0724 (24)	0.1498 (32)	0.5408 (27)	
C(31)	0.0135 (49)	0.2103 (26)	0.5173 (34)	
C(32)	−0.0595 (40)	0.2183 (22)	0.4329 (54)	
C(33)	−0.0809 (38)	0.1547 (46)	0.3729 (32)	
C(34)	0.6011 (33)	0.2168 (25)	0.2757 (15)	
C(35)	0.4952 (49)	0.2402 (13)	0.2548 (23)	
C(36)	0.4170 (21)	0.1905 (36)	0.2104 (24)	
C(37)	0.4516 (39)	0.1211 (27)	0.1934 (18)	
C(38)	0.5557 (50)	0.1070 (16)	0.2138 (26)	
C(39)	0.6272 (21)	0.1556 (29)	0.2538 (18)	
H(1)	0.0849	0.1117	0.2230	
H(2)	0.0913	0.2326	0.2682	
H(3)	0.1162	0.3358	0.1477	
H(4)	0.1448	0.2964	0.0039	
H(5)	0.1208	0.1557	−0.0480	
H(6)	0.1402	−0.1508	0.1557	
H(7)	0.1914	−0.2776	0.1338	
H(8)	0.2236	−0.2109	−0.0091	
H(9)	0.1665	−0.2693	−0.0760	
H(10)	0.1904	−0.0800	−0.1057	
H(11)	0.1506	−0.1144	0.3992	
H(12)	0.2234	−0.1039	−0.4435	
H(13)	0.4089	0.0200	0.6000	
H(14)	0.4694	0.0734	0.4625	
H(15)	0.3253	0.0577	0.3100	
H(16)	0.4323	0.0819	0.0037	
H(17)	0.5874	0.0731	−0.0462	
H(18)	0.5998	0.1062	−0.2097	
H(19)	0.4326	0.1592	−0.3034	
H(20)	0.3059	0.1277	−0.2445	
H(21)	0.1404	0.0680	−0.2307	
H(22)	0.0306	−0.0679	0.3143	

	β_{11} or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	0.0050 (1)	0.0028 (1)	0.0035 (1)	−0.0003 (1)	0.0011 (1)	0.0003 (1)
C(28)	0.028 (7)	0.010 (3)	0.014 (4)	−0.003 (3)	0.011 (4)	−0.006 (3)
C(29)	0.018 (4)	0.007 (2)	0.026 (6)	0.002 (2)	0.013 (4)	−0.001 (3)
C(30)	0.013 (2)	0.007 (2)	0.020 (4)	−0.003 (2)	0.006 (2)	0.000 (2)
C(31)	0.027 (6)	0.006 (2)	0.018 (4)	−0.004 (2)	0.011 (4)	−0.003 (2)
C(32)	0.018 (4)	0.007 (2)	0.027 (5)	0.000 (2)	0.011 (4)	0.006 (3)
C(33)	0.022 (5)	0.016 (3)	0.014 (3)	−0.008 (3)	0.003 (3)	0.007 (3)
C(34)	0.018 (4)	0.009 (2)	0.009 (2)	−0.005 (2)	0.004 (2)	−0.003 (1)
C(35)	0.028 (4)	0.005 (1)	0.013 (2)	0.004 (2)	0.011 (3)	0.000 (1)

Table I. (*Continued*)

	β_{11} or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(36)	0.009 (2)	0.016 (3)	0.013 (3)	0.002 (2)	0.004 (2)	0.003 (2)
C(37)	0.018 (4)	0.011 (2)	0.008 (2)	−0.007 (2)	0.005 (2)	−0.001 (2)
C(38)	0.029 (5)	0.005 (1)	0.012 (3)	0.003 (2)	0.011 (3)	0.002 (1)
C(39)	0.013 (3)	0.010 (2)	0.006 (2)	0.003 (2)	0.001 (2)	0.002 (1)

a Anisotropic temperature factors of the form $\exp\{-[\beta_{11}h^2 + \beta_{22}k^2 + 2\beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{23}kl]\}$ were used for the Co(II) ion and the uncoordinated pyridine molecules; the resulting thermal coefficients, with standard deviations of the last significant figure given in parentheses, are given in this table. b The isotropic thermal parameters for the hydrogen atoms were set to 6.0 Å^2.

Table II. Bond Distances (Å) and Angles (deg) within 1,5-Diphenyl-1,3,5-pentanetrionate

Part A.　Bond Distances

Bond classification	Experimental results		Lit. values (av)
C_t–R	C(5)–C(6)	1.493 (14)	1.524 (3)a
	C(1)–C(12)	1.499 (14)	1.512 (4)b
	Av 1.496 (14)		1.535 (8)c
C_t–C_m	C(4)–C(5)	1.393 (14)	1.390 (3)a
	C(1)–C(2)	1.375 (14)	1.391 (3)b
	Av 1.384 (14)		1.393 (6)c
C_m–C_b	C(3)–C(4)	1.420 (14)	
	C(2)–C(3)	1.423 (14)	
	Av 1.422 (14)		
C_t–O_t	C(5)–O(3)	1.272 (12)	1.274 (3)a
	C(1)–O(1)	1.291 (11)	1.268 (3)b
	Av 1.282 (11)		1.241 (6)c
C_b–O_b	C(3)–O(2)	1.290 (11)	

Part B.　Bond Angles

Angle classification	Experimental results		Lit. values (av)
R–C_t–O_t	C(6)–C(5)–O(3)	115.4 (10)	114.85 (23)a
	C(12)–C(1)–O(1)	114.9 (9)	115.6 (2)b
	Av 115.2 (10)		114.5 (6)c
O_t–C_t–C_m	O(3)–C(5)–C(4)	126.8 (10)	125.30 (26)a
	O(1)–C(1)–C(2)	124.1 (10)	125.7 (2)b
	Av 125.4 (10)		126.1 (5)c
C_m–C_b–O_b	C(4)–C(3)–O(2)	120.2 (10)	
	C(2)–C(3)–O(2)	122.0 (10)	
	Av 121.4 (10)		
C_t–C_m–C_b	C(3)–C(4)–C(5)	127.4 (10)	124.02 (34)a
	C(1)–C(2)–C(3)	128.1 (10)	125.6 (3)b
	Av 127.8 (10)		125.9 (7)c

Part C.　Oxygen–Oxygen Distances$d$

O(1)–O(3)′	3.219 (7)	O(1)–O(2)	2.839 (7)
O(2)–O(2)′	2.617 (7)	O(2)–O(3)	2.862 (7)
		Av	2.851 (7)

a E. C. Lingafelter and R. L. Braun, *J. Amer. Chem. Soc.*, 88, 2951 (1966). b F. A. Cotton and R. Eiss, *ibid.*, 90, 38 (1968). c R. C. Elder, *Inorg. Chem.*, 7, 1117 (1968). d The primed atoms in this and other tables correspond to atoms related to the unprimed atoms by the center of inversion located at the origin.

of papers concerned with the structures of some *oligomeric* cobalt(II) acetylacetonates.[9-11] These are of interest since Co–Co distances in complexes containing edge- and face-shared octahedra can be compared to the Co–Co distance in $Co_2(DBA)_2(py)_4$. Finally, a paper by Elder[12] which reports the structure of $Co(acac)_2(py)_2$ is of obvious interest since the coordinated atoms are identical with those in Co_2-$(DBA)_2(py)_4$.

Table II contains the bond lengths and angles found within the independent chelated ring of $Co_2(DBA)_2(py)_4$ together with the corresponding average values found in three of the literature sources indicated above.[8,10,12] Our values are

(9) F. A. Cotton and R. C. Elder, *Inorg. Chem.*, 4, 1145 (1965).
(10) F. A. Cotton and R. Eiss, *J. Amer. Chem. Soc.*, 90, 38 (1968).
(11) R. A. Cotton and R. C. Elder, *Inorg. Chem.*, 5, 423 (1966).
(12) R. C. Elder, *Inorg. Chem.*, 7, 1117 (1968).

within the range of those literature values surveyed, with two notable exceptions. The C_t–R bond is considerably shorter than when R or R′ is a methyl group, due partially to the fact that an sp^2-like phenyl carbon atom replaces an sp^3-like methyl carbon atom. The C_t–C_m–C_b angle differs from that expected by almost two degrees; this variation is most likely due to distortion of each DBA ligand as it attempts to "fit" around both cobalt atoms.

The average oxygen–oxygen (O_t–O_b) distance, referred to as the chelate "bite," of 2.851 (7) Å is well within the range found in the metal acetylacetonates[8] and is almost exactly equal to the intraligand "bite" of 2.880 Å in $Co(acac)_2$-$(py)_2$.[12] The most significant distortion in the molecule is evidenced by the oxygen–oxygen distances between the two ligands, *i.e.*, O_b–O_b and O_t–O_t. The O_b–O_b distance is 2.617 (7) Å and the O_t–O_t distance is 3.219 (7) Å. The interligand O–O distance in $Co(acac)_2(py)_2$ is 2.873 Å which, interestingly, is almost exactly the same distance as the intraligand "bite." The distortion in the four-membered Co_2O_2 ring in $Co_2(DBA)_2(py)_4$ is such that the four-membered ring is flattened, which may be caused by Co–Co repulsion. As a result of this distortion the O_t–O_t contact distance is unusually long relative to the O_b–O_b contact.

The average cobalt–nitrogen bond distance found was 2.200 (10) Å compared with 2.186 (7) Å (av) reported for $Co(acac)_2(py)_2$. Both these values are significantly less than the expected cobalt–nitrogen distance of 2.27 Å calculated from covalent radii. Elder[12] attributed this shortening in $Co(acac)_2(py)_2$ to π bonding between the cobalt atom and the pyridine ring. The intra-ring angles and distances for the coordinated pyridines are given in Table III. The angles agree within two standard deviations of those reported in other complexes, while the bond lengths in Co_2-$(DBA)_2(py)_4$ tend to be some two to four standard deviations higher.

The Co–Co distance in $Co_2(DBA)_2(py)_4$ is of interest in any discussion of magnetic exchange between the two ions. The measured value of 3.272 (3) Å is considerably longer than the Co–Co distance of 2.70 Å calculated from the atomic radius. Therefore, a major contribution of a direct Co–Co interaction in the antiferromagnetism of $Co_2(DBA)_2$-$(py)_4$ is not at all likely. For this reason, it is presumed that the low magnetic moment is caused by a superexchange mechanism involving the bridging oxygens. Since Co_2-$(DBA)_2(py)_4$ comprises two distorted octahedra linked at a common edge, it is interesting to compare the Co–Co distance to those found in $Co_3(acac)_6(H_2O)$.[10] The latter compound contains three octahedra in which the central $Co(acac)_2$ unit shares a common face with a second $Co(acac)_2$ unit and a common edge with a $Co(acac)_2(H_2O)$ unit. The Co–Co distance across the common octahedral face is 2.97 Å, considerably shorter than the Co–Co distance in $Co_2(DBA)_2(py)_4$. On the other hand, the Co–Co distance in $Co_3(acac)_6H_2O$ across a common edge is 3.28 Å which is essentially identical with the Co–Co distance in $Co_2(DBA)_2(py)_4$.

Table III. Distances and Angles in Phenyl and Pyridine Groups

Distances, Å

Coordinated Pyridine Rings

N(1)–C(22)	1.324 (14)	C(22)–C(21)	1.389 (17)
N(1)–C(18)	1.334 (14)	C(18)–C(19)	1.413 (17)
N(2)–C(23)	1.318 (15)	C(23)–C(24)	1.421 (18)
N(2)–C(27)	1.323 (14)	C(26)–C(27)	1.411 (17)
Av	1.324 (16)	Av	1.407 (17)

C(20)–C(21)	1.337 (18)	
C(19)–C(20)	1.366 (18)	
C(24)–C(25)	1.372 (19)	
C(25)–C(26)	1.435 (19)	
	Av 1.435 (18)	

Phenyl Rings

C(12)–C(17)	1.383 (15)	C(6)–C(7)	1.394 (15)
C(16)–C(17)	1.410 (17)	C(7)–C(8)	1.397 (18)
C(15)–C(16)	1.368 (18)	C(8)–C(9)	1.367 (18)
C(14)–C(15)	1.356 (17)	C(9)–C(10)	1.354 (17)
C(13)–C(14)	1.419 (17)	C(10)–C(11)	1.402 (17)
C(12)–C(13)	1.385 (16)	C(6)–C(11)	1.401 (15)
		Av	1.386 (16)

Free Pyridine Rings

C(32)–C(33)	1.410 (39)	C(35)–C(36)	1.393 (32)
C(31)–C(32)	1.373 (37)	C(34)–C(35)	1.378 (32)
C(30)–C(31)	1.318 (34)	C(34)–C(39)	1.208 (28)
C(29)–C(30)	1.253 (34)	C(38)–C(39)	1.306 (30)
C(28)–C(29)	1.286 (38)	C(37)–C(38)	1.319 (31)
C(29)–C(33)	1.313 (40)	C(36)–C(37)	1.360 (33)

Angles, Deg

Coordinated Pyridine Rings

C(18)–N(1)–C(22)	116.6 (12)	
C(27)–N(2)–C(23)	117.8 (11)	
	Av 117.2 (12)	

N(1)–C(22)–C(21)	123.4 (12)	C(22)–C(21)–C(20)	120.1 (14)
N(1)–C(18)–C(19)	122.6 (13)	C(18)–C(19)–C(20)	118.7 (14)
N(2)–C(23)–C(24)	123.8 (13)	C(23)–C(24)–C(25)	118.2 (15)
N(2)–C(27)–C(26)	124.8 (13)	C(27)–C(26)–C(25)	116.1 (14)
Av	123.6 (13)	Av	118.3 (14)

C(21)–C(20)–C(19)	118.7 (15)	
C(24)–C(25)–C(26)	119.3 (14)	
	Av 119.0 (14)	

Phenyl Rings

C(12)–C(17)–C(16)	120.2 (13)	C(6)–C(11)–C(10)	119.7 (11)
C(17)–C(16)–C(15)	119.2 (13)	C(11)–C(10)–C(9)	120.5 (13)
C(16)–C(15)–C(14)	121.9 (14)	C(10)–C(9)–C(8)	121.6 (14)
C(15)–C(14)–C(13)	119.0 (14)	C(9)–C(8)–C(7)	118.4 (14)
C(14)–C(13)–C(12)	120.2 (14)	C(8)–C(7)–C(6)	122.0 (12)
C(13)–C(12)–C(17)	119.3 (14)	C(7)–C(6)–C(11)	117.6 (11)
		Av	120.0 (13)

C(13)–C(12)–C(1)	122.9 (11)	
C(17)–C(12)–C(1)	117.7 (10)	
C(11)–C(6)–C(5)	123.3 (10)	
C(7)–C(6)–C(5)	118.9 (10)	
	Av 120.6 (10)	

Free Pyridine Rings

C(33)–C(32)–C(31)	116.8 (32)	C(36)–C(35)–C(34)	118.4 (23)
C(32)–C(31)–C(30)	123.8 (29)	C(35)–C(34)–C(39)	122.7 (25)
C(31)–C(30)–C(29)	115.5 (34)	C(34)–C(39)–C(38)	120.3 (27)
C(30)–C(29)–C(28)	125.0 (41)	C(39)–C(38)–C(37)	123.2 (27)
C(29)–C(28)–C(33)	124.5 (42)	C(38)–C(37)–C(36)	119.2 (26)
C(28)–C(33)–C(32)	113.8 (41)	C(37)–C(36)–C(35)	115.7 (25)

If the magnetic exchange takes place by means of a super-exchange mechanism involving the bridging oxygen, it should be sensitive to Co–O bond lengths and O–Co–O bond angles. The Co–O$_t$ and Co–O$_b$ bond distances are measurably different (see Figure 4), although this difference is not nearly as great as between the "primary" and bridging Co–O bond distances in the acetylacetonate oligomers.[9] It is worth

Table IV. Description of Cobalt Coordination Sphere

Part A. Bond Distances

Bond classification	Results		
Co–O$_t$	Co–O(3')		2.012 (7)
	Co–O(1)		2.005 (7)
		Av	2.008 (7)
Co–O$_b$	Co–O(2')		2.097 (7)
	Co–O(2)		2.091 (7)
		Av	2.094 (7)
Co–Co			3.272 (3)
Co–N	Co–N(1)		2.203 (10)
	Co–N(2)		2.197 (10)
		Av	2.200 (10)

Part B. Bond Angles

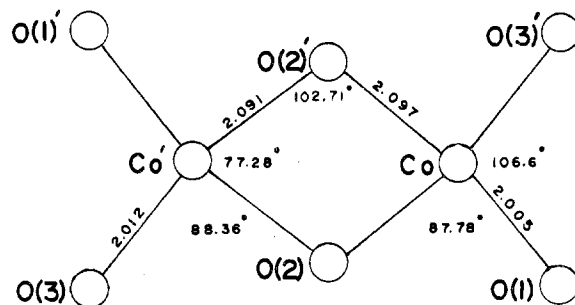| Angle classification	Results		
O$_t$–Co–O$_b$	O(1)–Co–O(2)		87.78 (29)
	O(3')–Co–O(2')		88.36 (27)
		Av	88.07 (28)
O$_t$–Co–O$_t$	O(1)–Co–O(3')		106.60 (30)
O$_b$–Co–O$_b$	O(2)–Co–O(2')		77.28 (29)
Co–O$_b$–Co	Co–O(2)–Co'		102.71 (29)

Figure 4. Important bond distances and angles within the cobalt coordination sphere.

noting that the average Co–O$_b$ distance of 2.094 (7) Å is 0.060 Å longer than the "normal" Co–O distance of 2.034 Å in the Co(acac)$_2$(py)$_2$ monomer, while the average Co–O$_t$ distance of 2.008 (7) Å is only slightly shorter. Thus, the Co–O bond distances in Co$_2$(DBA)$_2$(py)$_4$ are not unusual when compared with Co(acac)$_2$(py)$_2$. The O–Co–O bond angles, however, are considerably different from those in the parent monomer. Although the O$_t$–Co–O$_b$ bond angles are close to the expected 90°, the O$_b$–Co–O$_b$ bond angles are reduced to 77.28 (29)°. As a result, the O$_t$–Co–O$_t$ bond angles are increased to 106.60 (30)°. The important bond angle from the viewpoint of a superexchange mechanism is Co–O$_b$–Co. Its value of 102.71 (29)° is nearly midway between a 90° angle expected for σ bonds involving oxygen p orbitals and a 120° angle compatible with σ bonds involving sp^2-type oxygen orbitals.

Another important structural feature of the Co$_2$(DBA)$_2$-(py)$_4$ molecule is the planarity of the Co(DBA)$_2$ fragment. We have predicted earlier[1b] that it would be reasonable to assume that the triketonates are nearly planar since the chelate ring carbon atoms of the ligand must be essentially sp^2 hybridized. In addition, the electron-delocalized system that presumably extends throughout the ligand should enhance planarity and molecular rigidity. Experimentally, we find the chelate rings and the cobalt atoms to be essentially coplanar. Table V shows the best plane through the chelate rings and the perpendicular displacements of the intra-ring C, O, and Co atoms from this mean plane. The fact that both cobalt atoms are situated in the mean plane of the two

Table V. Analysis of Mean Planes

Cobalts and Oxygens
$0.1943X - 0.9660Y - 0.2199Z = 0$

Atom	Dev from planarity, Å	Atom	Dev from planarity, Å
Co	−0.00689	O3	−0.01672
Co'	0.00689	O1'	0.01288
O1	−0.01288	O2'	−0.03645
O2	0.03645	O3'	0.01671

Cobalts and Chelate Framework
$0.2004X - 0.9546Y - 0.2204Z = 0$

Atom	Dev from planarity, Å	Atom	Dev from planarity, Å
Co	−0.01587	O(1')	0.03323
O(1)	−0.03323	O(2')	−0.03252
O(2)	0.03252	O(3')	0.00588
O(3)	−0.00588	C(1')	0.01668
C(2)	0.02590	C(2')	−0.02590
C(3)	0.02745	C(3')	−0.02745
C(4)	0.01946	C(4')	−0.01946
C(5)	−0.05455	C(5')	0.05455
C(1)	−0.01668	Co'	0.01587

triketonate ligands is in marked contrast to the results reported for the cobalt 1,3-diketonate complexes[9,11-13] where in each case the Co atom is appreciably removed from the plane of the chelate rings. Indeed, even in Co(acac)$_2$(py)$_2$ where the donors are the same as in Co$_2$(DBA)$_2$(py)$_4$ the Co atom was found to be displaced 0.131 Å from the plane of the four oxygens toward one of the pyridine nitrogens.

The planes of the two phenyl groups in Co$_2$(DBA)$_2$(py)$_4$ are rotated by 34° (C(6)···C(11)) and by 4° (C(12)···C(17)) from the mean plane of the Co(DBA)$_2$ fragment. The large difference between these two dihedral angles no doubt is a consequence of packing forces.

The temperature dependence of the magnetic susceptibility of octahedral or distorted octahedral d^7 ions is relatively complicated. A theoretical expression for the magnetic moment requires a knowledge or estimation of several parameters. For this reason, calculations on even more complicated systems in which magnetic exchange is important seem fruitless at this time. It is, however, instructive to compare the magnetic results obtained for Co$_2$(DBA)$_2$(py)$_4$ with those for monomeric Co(II) complexes in distorted octahedral environments. This comparison is shown in Table VI. It is obvious from these data that the low moment of Co$_2$(DBA)$_2$(py$_4$) is not simply due to distortion of the octahedra, since many of the monomeric complexes listed are highly distorted and their magnetic behavior is completely different. In addition, the sharp decrease in the magnetic moment with decreasing temperature found in Co$_2$(DBA)$_2$(py)$_4$·4py must be due to antiferromagnetism since in no case does a monomeric complex exhibit such a strong temperature dependence. In fact, Hunter and Webb[14] have now extended the temperature range for Co(acac)$_2$-

(13) F. A. Cotton and J. S. Wood, *Inorg. Chem.*, **3**, 245 (1964).
(14) P. W. W. Hunter and G. A. Webb, *J. Cryst. Mol. Struct.*, **1**, 173 (1971).

Table VI. Comparison of the Magnetic Moments (BM) of Selected Monomeric Co(II) Complexes and Co$_2$(DBA)$_2$(py)$_4$

Complex	Temp, °K			Ref
	300	190	77	
Co(acac)$_2$(H$_2$O)$_2$	4.96	4.84	4.60	a, b
Co(H$_2$O)$_4$Cl$_2$	4.92	4.77	4.45	a
Co(py)$_4$(ClO$_4$)$_2$	5.03	4.98	4.74	a
Co(bipy)$_3$$^{2+}$	4.83	4.75	4.52	a, b
Co$_2$(DBA)$_2$(py)$_4$	4.28	4.07	3.36	c

^{a} F. A. Cotton and J. S. Wood, *Inorg. Chem.*, **3**, 245 (1964). ^{b} B. N. Figgis, M. Gerlock, J. Lewis, F. Mobbs, and G. A. Webb, *J. Chem. Soc. A*, 2086 (1968). ^{c} This work.

(H$_2$O)$_2$ down to 4.2°K, and only in this very low temperature region is the moment of the monomer as low as the values measured for Co$_2$(DBA)$_2$(py)$_4$ at much higher temperatures.

The mechanism of magnetic exchange between the Co atoms is of interest in terms of testing the phenomenological rules for exchange postulated by Anderson.[15] At present there is little definitive experimental verification of these rules. A critical point is that the Co-O$_b$-Co bond angle is 103° and that the metal and oxygen atoms are coplanar. Anderson's mechanism predicts ferromagnetic exchange for 90° bridging angles and antiferromagnetism when they reach 180°. The 103° bridging angle in Co$_2$(DBA)$_2$(py)$_4$·4py indicates a contribution due to s atomic orbitals on the bridging oxygens. If one accepts Anderson's superexchange mechanism, it would be argued that the s-orbital contribution is responsible for the antiferromagnetism by providing a pathway for direct exchange between the cobalts. Another point to keep in mind is that two of the three unpaired electrons on each Co atom have different symmetries and as a result presumably give rise to different exchange possibilities. Two unpaired electrons on each Co are directed at the donor atoms and, therefore, interact directly with the bridging oxygen. The third unpaired electron is expected to be directed between the donor atoms; *i.e.*, it has π-type symmetry. Thus, it may interact directly with its counterpart on the other Co atom or indirectly through the π or π* orbitals (O p$_z$) of the bridging oxygens. The importance of these separate mechanisms or whether they exist at all cannot be assessed at present. A partial solution to such problems may be obtained by studying the structure and magnetism of different metal triketonate systems.

(15) P. W. Anderson, *Phys. Rev.*, **115**, 2 (1959); *Magnetism*, **1**, 25 (1963).