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CRYSTAL AND MOLECULAR STRUCTURE OF BIS(PENTAMETHYLCYCLOPENTADIENYL)DICARBONYLDICOBALT

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Summary

The compound $(\eta^5\text{-}Me_5C_5)Co(\mu\text{-}CO)_2Co(\eta^5\text{-}Me_5C_5)$ has been prepared and characterized. The crystal structure has been determined and the Co—Co distance found to be 2.327(2) Å. This structure completes the information on M—M distances in the series of compounds CpM(EO)(E′O)MCp, where Cp = C_5H_5 or Me_5C_5, M = Fe or Co and E = C or N, several members of which were previously studied by others. The EAN rule would predict a double bond here as in the isoelectronic compound $CpFe(NO)_2FeCp$ and the M—M distances are virtually identical in the two molecules. Disordered packing of the molecules limits the accuracy with which the molecular dimensions, other than Co—Co, may be determined. However, the structure is in generally close agreement with those of the other molecules in the set previously mentioned. The crystals are monoclinic with a 7.433(2) Å, b 14.704(8) Å, c 9.671(2) Å, β 101.84(2)° and V 1034.6(7) Å^3; $Z = 2$. The structure was refined to $R_1 = 0.062$ and $R_2 = 0.074$ using a disordered model in space group $P2_1/m$.

Introduction

Since metal—metal multiple bonds [1,2] were first recognized in 1963, with the discovery of Re=Re bonds in $Re_3Cl_{12}^{3-}$ and related species, there has been a constantly increasing stream of discoveries in this field, particularly with respect to triple [3,4] and quadruple bonds [3,5]. Indeed, interest in the latter has nearly eclipsed the slow evolution of knowledge concerning metal-to-metal double bonds. Moreover, all known or suspected examples of the latter suffer from ambiguities attendant upon the presence of bridging ligands. These ambiguities are of two principal types: (1) In some cases, if not all, there is the possibility that diamagnetism arises by coupling of electron spins through the bridging ligands instead by formation of a direct M—M bond. (2) In every case the size and other steric requirements (e.g., preferred bond angles) of the bridging ligands, which change from one such ligand to another, make it unreasonable to expect any simple relationship between M—M distances and bond orders. In spite of these inherent difficulties, there has been steadily increasing interest and activity in M—M double bonds and several have been postulated in the very recent literature [6—8].

An interesting series of compounds began to appear in 1974 when Calderon et al. [9] published the structure of $CpFe(\mu\text{-}NO)_2FeCp$ ($Cp = \eta^5\text{-}C_5H_5$), in which an Fe=Fe bond must be postulated if the metal atoms are to achieve 18-electron valence shell configurations. The Fe—Fe distance found was 2.326(4) Å. In 1976, Bergman and coworkers [10] reported the structure of the $CpCo(\mu\text{-}CO)_2CoCp^-$ ion, for which a bond order of 1.5 might be proposed. The Co—Co distance was found to be 2.372(2) Å, which is not inconsistent with the distance and postulated bond order for the iron compound, although an increase of only ca. 0.045 Å as the bond order decreases by 0.5 is perhaps a little surprising. However, the significance of this is unclear since the Co atom might have a somewhat smaller radius than the Fe atom. A better comparison would be between the two cobalt species $CpCo(\mu\text{-}CO)_2CoCp^n$ where $n = -1$ and 0. We therefore undertook to prepare the neutral molecule and determine its structure.

While this was in progress, Bernal et al., [11] reported results for two other compounds that must be regarded as members of this same group. One is $CpCo(\mu\text{-}CO)(\mu\text{-}NO)CoCp$, which is formally isoelectronic with $CpCo(\mu\text{-}CO)_2CoCp^-$ and has essentially the same Co—Co distance, viz., 2.370(1) Å. The other, $CpCo(\mu\text{-}NO)_2CoCp$, which has still another electron, also has essentially the same Co—Co bond length, namely, 2.372(1) Å.

In the meantime, our efforts to characterize $CpCo(\mu\text{-}CO)_2CoCp$ structurally were unsuccessful because of the extremely reactive nature of this compound. However, it has been possible to obtain crystals and determine the structure of the pentamethylcyclopentadienyl analog, and we report that work here.

Experimental

Reactions were performed under dry, oxygen-free nitrogen or argon in modified Schlenk-type glassware [12]. Reagents and products were manipulated in an argon-filled dry box [13] under conditions where a sodium/potassium alloy mirror persisted for at least 2 min. Toluene was distilled from sodium metal under argon after several hours at reflux. Pentane was distilled from sodium benzophenone ketyl under argon; the blue ketyl was first generated from benzophenone and sodium metal in a small amount of diphenyl ether. Red $\eta^5\text{-}C_5Me_5\text{-}Co(CO)_2$ was prepared from $Co_2(CO)_8$ and acetylpentamethylcyclopentadiene [14].

Proton NMR spectra were obtained on a Varian T-60 spectrometer from samples made up in the dry box and flame-sealed into 5 mm tubes. Infrared spectra were obtained on a Perkin—Elmer PE-283 grating spectrophotometer and mass spectra on an AEI MS-902 double focussing mass spectrometer.

Synthesis of μ-dicarbonylbis[η^5-pentamethylcyclopentadienylcobalt(I)]

η^5-Pentamethylcyclopentadienyldicarbonylcobalt(I), η^5-$C_5Me_5Co(CO)_2$, (0.399 g, 1.59 mmol) was dissolved in 10 ml dry, oxygen-free toluene. As the red solution was refluxed under nitrogen for 24 h, it became dark green. The solvent was removed by vacuum evaporation and unreacted η^5-$C_5Me_5Co(CO)_2$ sublimed from the residue at 20—40°C, 0.01 Torr. The purplish-green residue was extracted with 35 ml dry, oxygen-free pentane and filtered. An insoluble residue was repeatedly washed by distilling back some of the pentane until the washings were only slightly green; four washings were required. The very dark emerald-green filtrate and washings were cooled to —78°C for 4 h. The dark, purplish-black crystals were formed and washed with pentane at —78°C, then vacuum dried. The yield was 0.221 g (62%), m.p. 272—274°C dec. (sealed tube). ^{1}H NMR (C_6D_6): singlet at δ 1.46 ppm. IR (mineral oil mull): strong bridging CO stretch at 1756 cm^{-1}. Mass spectrum (70 eV): strong molecular ion at *m/e* 444 (precise mass: 444.0927; calcd. for $C_{22}H_{30}Co_2O_2$: 444.0910).

The product, $[\eta^5$-$C_5Me_5Co(CO)]_2$, is very sensitive to air. Weak, terminal CO stretching bands at 2004 and 1948 cm^{-1} in the infrared spectrum indicated the presence of traces of η^5-$C_5Me_5Co(CO)_2$. These bands grew as the strong band at 1756 cm^{-1} disappeared when the sample was progressively exposed to air over increasing time intervals. After the 1756 cm^{-1} band of the dinuclear compound had disappeared entirely, the terminal CO bands began gradually to disappear as the monomer was oxidized in turn. Apparently the dimer disproportionates as it oxidizes. The weak bands seen in the first IR spectrum were presumably due to the action of traces of oxygen while the sample was prepared in the dry box.

Ready recapture of CO can account for the low yields of dimer obtained via photolysis. Red solutions of η^5-$C_5Me_5Co(CO)_2$ in sealed NMR tubes (C_6D_6) turn dark green upon exposure to a 275 Watt tungsten flood lamp, then return to red in the dark. In contrast to the behavior of η^5-$C_5H_5Co(CO)_2$ proton NMR spectra obtained immediately after irradiation up to 12 h show only 8% conversion to the dimer as judged from the integrated spectra. Attempts to prepare the dimer via photolysis of solutions of η^5-$C_5Me_5Co(CO)_2$ in toluene using either the tungsten lamp or a 125 Watt low pressure mercury flood lamp (quartz flask) produced the dimer in only 6% isolated yield and most of the starting material was recovered intact.

X-ray crystallography

Data collection. The crystals were covered with dry, degassed mineral oil and examined under a microscope. Several well-shaped crystals were isolated and kept immersed in mineral oil. The crystals were then coated with a quick-setting epoxy cement and wedged in capillaries. A crystal measuring approximately 0.53 × 0.35 × 0.02 mm was placed on a Syntex $P\bar{1}$ automated diffractometer. Preliminary examination showed that the crystal was probably monoclinic and of good quality. ω scans of several intense reflections had widths at half-height of less than 0.25°. Fifteen reflections in the range $20° < 2\theta(\text{Mo-}K_\alpha) < 30°$ were used to determine unit cell parameters, which are: *a* 7.433(2) Å, *b* 14.704(8) Å, *c* 9.671(2) Å, β 101.84(2)° and *V* 1034.6(7) Å^3. The volume indicates two molecules in the unit cell. The procedures preliminary to data collection have been described previously [16].

All data were collected using Mo-K_α radiation taken from an incident-beam graphite monochromator. A total of 1539 unique reflections with $0 < 2\theta(\text{Mo-}K_\alpha) \leqslant 45°$ were collected at 23 ± 2°C using the $\theta - 2\theta$ scan technique with a variable scan rate of 4.0 to 24.0° per minute depending on the intensity of a reflection. A scan range from 1.0° above to 1.0° below the expected positions of the K_{α_1} and K_{α_2} peaks was used. Background measurements were made at both limits of each scan, with equal time intervals for background and peak counting. Intensities of three standard reflections measured periodically showed no significant variation during data collection. Lorentz and polarization corrections were applied *. Due to the shape of the crystal and the inability to describe the faces accurately an empirical absorption correction was applied using data from ψ scans at $\chi = 90°$.

The intensity data showed that the crystal symmetry could not be higher than monoclinic and the only systematic absence observed, $0k0$ for k odd, indicated space groups $P2_1$ or $P2_1/m$. The correct space group was assumed to be $P2_1/m$ and this choice was validated by the successful solution and refinement of the structure, now to be described. The lower symmetry, though it does not require the assumption of any disorder, does not allow a successful refinement, as shown by exhaustive trials.

Solution and refinement. Direct methods, as embodied in the program MULTAN, were used to determine the positions of the cobalt atoms. With the y coordinates of Co(1) and Co(2) fixed, the remaining heavy atom coordinates were refined by least squares. After refining both cobalt positions, difference Fourier maps revealed the approximate positions of all other non-hydrogen atoms. It was found that the Me_5C_5 rings and the CO groups were each subject to a two-fold disorder, necessitating refinement of twice the expected number of atoms, each at half weight. The disordered structure was refined to convergence by full-matrix least squares to give final discrepancy factors of

$$R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0| = 0.062$$

$$R_2 = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{1/2} = 0.074$$

The function $\Sigma w(|F_0| - |F_c|)^{1/2}$ was minimized with the weighting factor, w, equal to $4F_0^2/\sigma(F_0^2)^2$. All structure factor calculations and least squares refinements were excuted using only those 782 reflections for which $F_0^2 > 3\sigma(F_0^2)^3$. Atomic scattering factors were those of Cromer and Waber [17]. Anomalous dispersion effects were included in the scattering factors of cobalt [18]. The error in an observation of unit weight was 1.541. With anisotropic thermal parameters for Co(1) and Co(2), which lie in a mirror plane, the final data/parameter ratio is 7.2. A final difference Fourier map was essentially featureless. A table of observed and calculated structure factors is available **.

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* All crystallographic calculations were performed using the Molecular Structure Corporation PDP-11/45 computer and the Enraf-Nonius Structure Determination Package.

** The table of structure factors has been deposited as NAPS Document No. 03297. Please contact ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017.

Results and discussion

The atomic positional and thermal parameters are listed in Table 1. C(1)—O(1) and C(2)—O(2) are the two half-weight CO groups. The carbon atoms C(101)—C(105) and C(201)—C(205) constitute one pair of crystallographically indendent half-weight C_5 rings while C(106)—C(110) and C(206)—C(210) are the two sets of methyl carbon atoms. Tables 2 and 3 list interatomic distances and angles, respectively. The mirror plane with respect to which the molecules are disordered contains the Co—Co axis. Figure 1 shows the two sets of ligand atoms, one set with open circles and the other with hatched circles, which lie, pairwise, on opposite sides of this plane. The methyl carbon atoms are omitted from this drawing for clarity. Figure 2 shows a molecule in one of the two orientations and defines the numbering scheme. The Co(μ-CO)$_2$Co unit is planar within experimental error.

It is evident from the variations in individual distances within sets of those which ought to be chemically equivalent that the problem of disorder has led to some sizeable inaccuracies. However, the results are useful and credible. Consider first the Co—Co distance. Since the metal atoms lies in the plane about which the disordering occurs, they are ordered and their positions should not be significantly affected by errors arising from inadequate treatment of the disorder problem. Thus, the Co—Co distance obtained, 2.327(2) Å, and its esd are presumably as reliable as the Co—Co distances in other structures, mentioned in the introduction, with which we wish to compare it.

Second, when the average values of other important distances are considered, they are found to be in good agreement with the expected values. Thus, the average Co—C(ring) distance and the associated mean deviation are 2.09 ± 0.06 Å, which may be compared with values of 2.09 and 2.10 Å in the other neutral molecules. Similarly, the mean C—C distance in the five-membered rings is

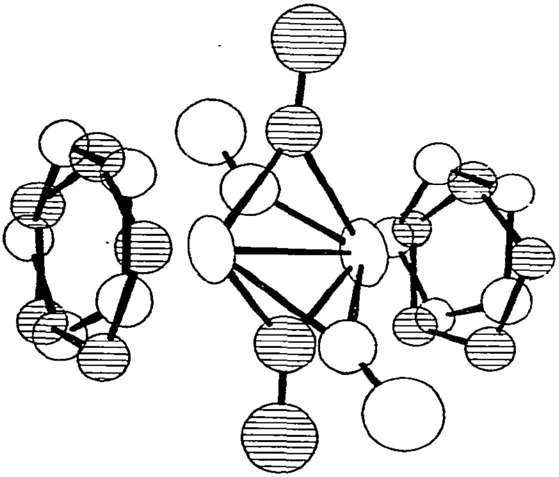

Fig. 1. ORTEP drawing with 50% probability ellipsoids showing the disorder as it exists in the crystal. Methyl groups have been omitted. Hatched C and O atoms belong to one halfmolecule, open ones to the other. The mirror plane coincides, approximately, with the plane of the paper.

TABLE 1

POSITIONAL AND THERMAL PARAMETERS [a] AND THEIR ESTIMATED STANDARD DEVIATIONS

Atom	X	Y	Z	$B_{1,1}$	$B_{2,2}$	$B_{3,3}$	$B_{1,2}$	$B_{1,3}$	$B_{2,3}$
Co(1)	0.2170(2)	0.7500(0)	0.7931(2)	3.40(7)	5.7(1)	1.96(6)	0	0.92(5)	0
Co(2)	0.1490(2)	0.7500(0)	1.0175(2)	3.69(8)	6.8(1)	2.12(6)	0	1.07(6)	0
O(1)	0.347(2)	0.58(1)	0.956(2)	6.0(4)					
O(2)	0.042(2)	0.902(1)	0.863(2)	6.6(4)					
C(1)	0.267(2)	0.650(1)	0.929(2)	3.3(4)					
C(2)	0.115(3)	0.825(1)	0.884(2)	4.3(4)					
C(101)	0.270(2)	0.841(1)	0.631(2)	2.2(3)					
C(102)	0.423(2)	0.780(1)	0.679(2)	2.5(3)					
C(103)	0.356(2)	0.690(1)	0.657(2)	2.5(3)					
C(104)	0.164(2)	0.694(1)	0.595(2)	2.8(3)					
C(105)	0.112(2)	0.787(1)	0.580(2)	2.4(3)					
C(106)	0.298(3)	0.943(2)	0.630(2)	5.6(6)					
C(107)	0.615(3)	0.810(2)	0.737(2)	5.0(5)					
C(108)	0.466(3)	0.606(2)	0.699(3)	6.3(6)					
C(109)	0.033(3)	0.620(2)	0.544(2)	5.1(5)					
C(110)	−0.078(3)	0.831(2)	0.511(2)	4.2(4)					
C(201)	−0.056(2)	0.798(1)	1.132(2)	2.7(3)					
C(202)	−0.003(2)	0.703(1)	1.151(2)	2.1(3)					
C(203)	0.178(2)	0.689(1)	1.204(2)	3.0(4)					
C(204)	0.254(2)	0.783(1)	1.229(2)	2.4(3)					
C(205)	0.107(2)	0.847(1)	1.184(2)	3.0(4)					
C(206)	−0.236(2)	0.843(1)	1.083(2)	3.5(4)					
C(207)	−0.146(3)	0.623(2)	1.118(2)	4.9(5)					
C(208)	0.282(3)	0.601(2)	1.236(3)	6.2(6)					
C(209)	0.451(3)	0.809(2)	1.297(2)	5.9(5)					
C(210)	0.135(3)	0.950(2)	1.203(2)	4.4(5)					

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[a] The form of the anisotropic thermal parameter is: $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

TABLE 2

BOND DISTANCES (Å) [a]

Co(1)—Co(2)	2.327(2)	C(101)—C(102)	1.44(2)
C(1)	1.95(2)	C(102)—C(103)	1.41(3)
C(2)	1.68(2)	C(103)—C(104)	1.43(3)
C(101)	2.16(2)	C(104)—C(105)	1.42(2)
C(102)	2.11(1)	C(105)—C(101)	1.42(2)
C(103)	2.03(2)	C(101)—C(106)	1.52(3)
C(104)	2.05(2)	C(102)—C(107)	1.49(2)
C(105)	2.11(2)	C(103)—C(108)	1.50(3)
Co(2)—C(1)	1.99(2)	C(104)—C(109)	1.47(3)
C(2)	1.67(2)	C(105)—C(110)	1.57(2)
C(201)	2.18(2)	C(201)—C(202)	1.45(2)
C(202)	2.00(2)	C(202)—C(203)	1.35(3)
C(203)	1.99(2)	C(203)—C(204)	1.50(3)
C(204)	2.09(1)	C(204)—C(205)	1.44(2)
C(205)	2.22(2)	C(205)—C(201)	1.41(2)
C(1)—O(1)	1.17(2)	C(201)—C(206)	1.48(3)
C(2)—O(2)	1.25(2)	C(202)—C(207)	1.57(3)
		C(203)—C(208)	1.51(3)
		C(204)—C(209)	1.53(2)
		C(205)—C(210)	1.53(3)

[a] Numbers in parentheses are esd's in the last significant digits.

1.43 ± 0.03 Å, which is similar to values of 1.39 and 1.41 Å found in the other cobalt compounds. Finally, though individual Co—CO distances vary greatly, the average, 1.82 Å, is about equal to those, 1.83 Å, found elsewhere. Thus, despite the scatter in individual values, it seems safe to say that the overall structure has been reliably determined.

TABLE 3

BOND ANGLES (°) [a]

Co(1)—Co(2)—C(1)	53.1(5)	C(201)—C(202)—C(203)	115(2)
C(2)	46.3(6)	C(202)—C(203)—C(204)	103(2)
Co(2)—Co(1)—C(1)	54.7(5)	C(203)—C(204)—C(205)	109(1)
C(2)	45.9(6)	C(204)—C(205)—C(201)	108(2)
Co(1)—C(1)—O(1)	145(1)	C(205)—C(201)—C(202)	105(2)
Co(1)—C(2)—O(2)	137(1)	C(205)—C(201)—C(206)	123(2)
Co(2)—C(1)—O(1)	142(1)	C(202)—C(201)—C(206)	132(2)
Co(2)—C(2)—O(2)	135(1)	C(201)—C(202)—C(207)	122(2)
C(101)—C(102)—C(103)	107(1)	C(203)—C(202)—C(207)	123(2)
C(102)—C(103)—C(104)	109(2)	C(202)—C(203)—C(208)	130(2)
C(103)—C(104)—C(105)	107(2)	C(204)—C(203)—C(208)	127(2)
C(104)—C(105)—C(101)	108(2)	C(203)—C(204)—C(209)	127(1)
C(105)—C(101)—C(102)	108(1)	C(205)—C(204)—C(209)	125(1)
C(105)—C(101)—C(106)	131(1)	C(204)—C(205)—C(210)	122(1)
C(102)—C(101)—C(106)	121(2)	C(201)—C(205)—C(210)	129(2)
C(101)—C(102)—C(107)	125(1)		
C(103)—C(102)—C(107)	128(1)		
C(102)—C(103)—C(108)	125(2)		
C(104)—C(103)—C(108)	128(2)		
C(103)—C(104)—C(109)	131(2)		
C(105)—C(104)—C(109)	122(2)		
C(104)—C(105)—C(110)	130(2)		
C(101)—C(105)—C(110)	121(1)		

[a] Numbers in parentheses are esd's in the last significant digits.

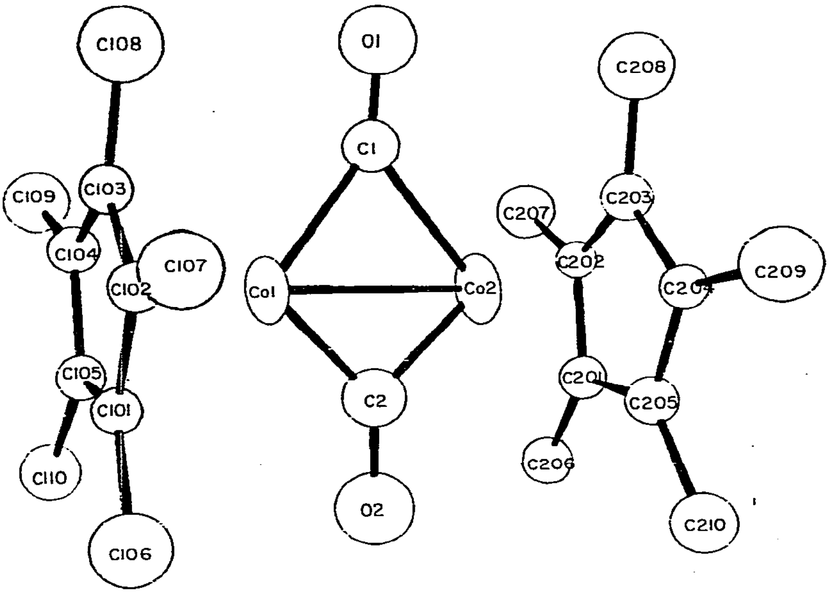

Fig. 2. ORTEP drawing showing one orientation of the disordered molecule and the numbering system used.

The Co—Co distance in our compound is effectively identical to that in the isoelectronic CpFe(μ-NO)$_2$FeCp. Thus, the question of whether a straightforward comparison of the Fe—Fe distance in the latter compound with Co—Co distances in the dicobalt compounds is justified can be answered in the affirmative, or set aside in favor of confining the discussion entirely to dicobalt molecules.

As Bernal et al. [11] have already noted, the observed Co—Co bond length do not appear to support the simple idea that attainment of an effective atomic number of 18 at each metal atom leads to bond orders ranging from 1 to 1.5 to 2 in the series of CpCo(μ-EO)(μ-E'O)CoCp molecules. Evidently, there is a more complex, or simply different, pattern of molecular orbitals involved in this series of compounds than that envisioned in the simple theory that has previously been expected to work in these cases. It does not seem reasonable that the change from Co=Co to Co—Co could cause an increase of only about 0.045 Å in bond length, and particularly that essentially equal bond lengths should occur for bond orders of both 1.0 and 1.5. Metal—metal, metal—ligand and ligand-based orbitals must all be mixed to an important degree in these molecules.

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