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Structure of Di- μ -carbonyl-bis[η^5 -methylcyclopentadienylcobalt(II)](Co–Co)

BY PETER LOUCA AND JUDITH A. K. HOWARD

School of Chemistry, The University, Bristol BS8 1TS, England

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Abstract. $[\text{Co}_2(\text{C}_6\text{H}_7)_2(\text{CO})_2]$, $M_r = 332.13$, $C2/m$, $a = 7.989$ (4), $b = 8.573$ (4), $c = 9.934$ (4) Å, $\beta = 114.76$ (1)°, $U = 617.8$ (2) Å³, $Z = 2$, $D_x = 1.79$ Mg m⁻³, $\text{Mo K}\alpha$, $\lambda = 0.71069$ Å, $\mu = 2.67$ mm⁻¹, $F(000) = 336$, $T \sim 220$ K, final $R = 0.037$ and $wR = 0.045$ for 1307 unique reflections with $F \geq 3\sigma(F)$. The structure is isomorphous with the analogous Ni complex, the $2/m$ symmetry reducing the number of unique atoms to 11. The carbonyl ligands asymmetrically bridge the two Co atoms, extending away from the neighbouring methyl substituent on the cyclopentadienyl rings which lie across the crystallographic mirror plane.

Introduction. The deformation electron density of a series of dinuclear organometallic structures is currently being studied (Gregson & Howard, 1984; Howard, Louca & McIntyre, 1987) in order to investigate the nature of metal–metal bonds and the role played by bridging carbonyl ligands. The Ni analogue of this Co complex has revealed no accumulation of electron density between the two metal atoms, the linkage between which has a formal bond order of one, based on simple electron counting rules. As a useful comparison we have chosen to investigate the title complex, first reported by Hersh, Hollander & Bergman (1983), which formally has a bond order of two. This preliminary experiment is intended to confirm that the

complex satisfies certain criteria which would enable us to carry out an accurate deformation electron density study.

Experimental. $[\text{Co}_2(\text{CO})_2(\text{MeCp})_2]$ prepared by a method similar to that proposed by Hersh *et al.* (1983); brown crystals obtained by recrystallization from toluene. Rectangular plane crystal, $0.1 \times 0.25 \times 0.32$ mm, mounted under N_2 in a Lindemann-glass capillary. Intensity data collected using a Nicolet $P3m$ diffractometer with graphite monochromator and N_2 gas-flow cooling device. Cell parameters determined by least-squares refinement using 15 accurately centred reflections in the range $29 \leq \theta \leq 31^\circ$. 1415 unique reflections were recorded using ω - 2θ scan techniques, $2\theta_{\text{max}} = 70^\circ$, 1307 [$F \geq 3\sigma(F)$] used in analysis. h 0– ± 12 , k 0–13, l 0–16. Check reflections showed no systematic variation, Lorentz and polarization factors applied, no absorption correction. Structure solved by heavy-atom method, all atoms located by successive electron-density difference syntheses. Blocked-cascade least-squares refinement using *SHELXTL* (Sheldrick, 1981) on 64 parameters. Isotropic thermal parameters for H, minimized $\sum w(|F_o| - |F_c|)^2$, $w = [\sigma^2(F) + 0.0004F^2]^{-1}$, $\sigma(F)$ from counting statistics, $R = 0.037$, $wR = 0.043$, $S = 1.7$. Max. height in final difference Fourier synthesis 1.5 e \AA^{-3} . Max. shift/e.s.d. = 0.003. Atomic scattering factors including corrections for

Table 1. Fractional atomic positional coordinates for $[\text{Co}_2(\text{CO})_2(\text{MeC}_5\text{H}_4)_2]$

	x	y	z	$U(\text{\AA}^2)$
Co	0.14020 (3)	0	0.10398 (3)	0.0157 (1)*
C	0.0958 (3)	0	-0.0965 (2)	0.0195 (5)*
O	0.1780 (3)	0	0.1714 (2)	0.028 (6)*
C(1)	0.1932 (4)	0	0.4476 (3)	0.0348 (8)*
C(2)	0.2769 (3)	0	0.3385 (2)	0.0226 (6)*
C(3)	0.3252 (2)	0.1336 (2)	0.2776 (2)	0.0244 (4)*
C(4)	0.4084 (2)	0.0826 (2)	0.1827 (2)	0.0254 (4)*
H(11)	0.115 (7)	0.077 (6)	0.442 (6)	0.036 (15)
H(12)	0.229 (7)	0	0.542 (5)	0.034 (10)
H(3)	0.313 (4)	0.237 (4)	0.296 (3)	0.033 (7)
H(4)	0.449 (5)	0.143 (4)	0.119 (3)	0.038 (7)

* U = equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. Selected bond lengths (\AA) and angles ($^\circ$) for $[\text{Co}_2(\text{CO})_2(\text{MeC}_5\text{H}_4)_2]$

Co—Co	2.326 (1)	C(1)—C(2)	1.492 (4)
Co—C	1.856 (2)	C(2)—C(3)	1.422 (2)
Co—C'	1.871 (2)	C(3)—C(4)	1.431 (3)
Co—C(2)	2.119 (2)	C(4)—C(4')	1.416 (4)
Co—C(3)	2.082 (2)	C(1)—H(11)	0.90 (6)
Co—C(4)	2.074 (2)	C(1)—H(12)	0.96 (4)
C—O	1.180 (4)	C(3)—H(3)	0.92 (3)
Cp—Co	1.699 (2)	C(4)—H(4)	0.97 (4)
Co—C—O	143.0 (2)	C(1)—C(2)—C(3)	126.4 (1)
Co'—C—O	139.7 (1)	C(2)—C(3)—C(4)	108.6 (2)
Co—C—Co'	77.2 (1)	C(3)—C(4)—C(4')	107.8 (1)
Co'—Co—C	51.7 (1)	C(3)—C(2)—C(3')	107.3 (2)
Co'—Co—C(2)	146.9 (1)	C(2)—C(3)—H(3)	129 (2)
C—Co—C(2)	95.2 (1)	C(4)—C(3)—H(3)	123 (2)
C'—Co—C(2)	142.0 (1)	C(3)—C(4)—H(4)	130 (2)
C—Co—C(3)	112.9 (1)	C(4')—C(4)—H(4)	123 (2)
C'—Co—C(3)	129.4 (1)	H(11)—C(1)—H(12)	112 (4)
C—Co—C(4)	152.5 (1)	H(11)—C(1)—H(11)	95 (8)
C'—Co—C(4)	96.1 (1)	H(11)—C(1)—C(2)	118 (4)
		H(12)—C(1)—C(2)	103 (4)
Cp—Co—Co'	178.9 (1)		

Atom n' is related to atom n by a twofold rotation axis; atom n'' is related to atom n by a mirror plane. Cp is the centroid of the methylcyclopentadienyl ring.

anomalous dispersion taken from *International Tables for X-ray Crystallography* (1974).*

Discussion. Final positional parameters and selected bond lengths and angles are given in Tables 1 and 2, respectively. The molecular geometry and atom labelling scheme are shown in Fig. 1. The longer of the two Co—C(O) bonds lies *trans* to the ring C atom which carries the electron-donating methyl group and is consistent with the effect expected due to the *trans* influence. The Co—Co separation is 2.326 (1) \AA compared with 2.3957 (6) \AA found by neutron diffraction for Ni—Ni, implying as expected that the Co—Co bond order is higher than that of the Ni—Ni bond.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44119 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

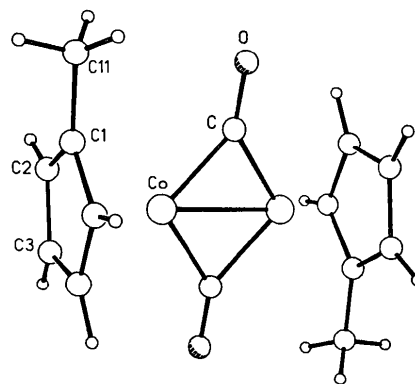


Fig. 1. Molecular structure of $[\text{Co}_2(\text{CO})_2(\text{MeCp})_2]$, with only the crystallographically unique atoms labelled.

The question then arises as to how the bonding differs between the two compounds and to what extent is either the Co—Co or Ni—Ni interaction delocalized through the bridging carbonyl ligands. The results of the deformation electron density study on the Ni complex were interpretable in the immediate vicinity of the metal atoms only in terms of crystal-field-type destabilization of the $3d$ orbitals. Any M — M bonding we wish to observe is likely to be very small and highly delocalized relative to the changes which occur in the metal $3d$ orbitals, and thus may become masked. However, a comparison with a similar analysis on the Co complex is expected to reveal more information about the nature of metal—metal bonds than either of the individual deformation density studies would do.

This structural study has shown that since the title complex has no problems with disorder at low temperature and has relatively few structural parameters, it is eminently suitable for a more accurate X-ray diffraction experiment and is also worthy of a more detailed analysis of the density using a multipole formalism (Hirshfeld, 1971).

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