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# CRYSTAL AND MOLECULAR STRUCTURE OF $[\eta^5\text{-}C_5(CH_3)_5]Co(O_2C_6H_4)$, A COBALT(*o*-CATECHOLATE) COMPLEX

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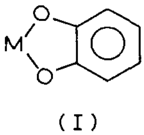
## Summary

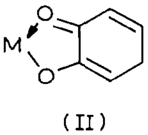
$[\eta^5\text{-}C_5(CH_3)_5]Co(O_2C_6H_4)$ crystallizes in the orthorhombic space group *Pnma* with $a$ 12.942(4), $b$ 12.902(4), $c$ 8.543(3) Å, $V$ 1426(1) Å$^3$, and $Z = 4$. Least-squares refinement of 1688 independent observed reflections, $F(_{\text{obs}}) \geqslant 2.5\sigma(F_{\text{obs}})$, gives $R_F$ 3.79 and $R_{wF}$ 3.72%. The cyclopentadienyl ring contains two short (1.412(3) Å) and three longer (⟨av⟩ 1.430(4) Å) C–C bond lenghts, consistent with a slight preference for diolefin bonding. The $O_2C_6H_4$ fragment is best described as a catecholate with a C–O bond distance of 1.338(3), and a Co–O distance of 1.837(2) Å.

## Introduction

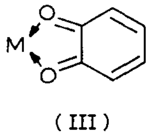
The ground-state electronic structure of $CpCo(bb'C_6H_4)$ complexes in which b,b′ = O, N, S has been of interest to us [1,2] and others [3–5]. The possibility of electron delocalization and the various bonding modes of the five-membered metallacycle formed by the $Cobb'C_2$ fragment [3–7] as well as the redox behavior [8] of quinone-metal complexes [9] are central issues in previous studies. Electron distributions giving rise to I (catecholate), II (semiquinone), and III (benzoquinone) can be imagined for quinone ligands in transition metal complexes. Crystal structure determinations provide evidence for all three forms [10]. However, the only quinone structure closely related to the complex of interest here, IV, is the Rh homologue [11] in which the $Rh(O_2C_6H_4)$ fragment was found to have form I.



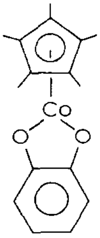
(I)



(II)



(III)



(IV)

Metallocyclopentadienyl complexes containing unequal C–C bond distances are known [12–14]. Imbalanced population of the HOMOs of the Cp ring stemming from bonding to a non-cylindrically symmetric metal-ligand fragment or Jahn-Teller effects are thought to be responsible.

The appropriate electronic description of the $Co(O_2C_6H_4)$ fragment and the nature of the bonding within the Cp ring are important in connection with anomalies that appear when comparing the $^{59}Co$ nuclear quadrupole resonance spectra of the $CpCobb'C_6H_4$ complexes with the analogous $[\eta^5-C_5(CH_3)_5]Co-(bb'C_6H_4)$ series [15]. We, therefore, report here a determination of the crystal and molecular structure of IV.

## Experimental

### *Preparation and characterization of* $[\eta^5-C_5(CH_3)_5]Co(O_2C_6H_4)$

Reagent-grade solvents were dried over Linde 4 Å molecular sieves and used without further purification. All reactions and manipulations were performed under nitrogen. Catechol (Aldrich) was sublimed prior to use (80–83 °C/≈ 3 mmHg). $[\eta^5-C_5(CH_3)_5]CoI_2(CO)$ was prepared as before [16]. NMR spectra were obtained on a Bruker WA 250. Elemental analyses were performed by MicroAnalysis, Wilmington, Delaware.

Disodium catecholate was prepared by dropwise addition of catechol (titer: 0.42 mmol $ml^{-1}$ anhydrous ethanol) to a sodium ethoxide solution (titer: 0.67 mmol Na $ml^{-1}$ anhydrous ethanol). The catecholate solution (33.8 ml) was slowly added to $[\eta^5-C_5(CH_3)_5]CoI_2(CO)$ (3.06 g, 6.30 mmol) in methylene chloride (150 ml). After stirring for 24 h, the solvent was removed and the crude product sublimed (170 °C/2 mmHg) to produce dark purple, air-stable crystals of IV (0.97 g, 50.8%): m.p. 195–197 °C (dec.); $^1H$ NMR ($CDCl_3$): $\delta$ 1.96 ppm (s, 15, $CH_3$) 6.5–7.20 (m, 4, $C_6H_4$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 9.80 ppm ($C_5(CH_3)_5$), 87.10 ($C_5(CH_3)_5$), 116.0, 118.10, 161.50 ($C_6H_4$). Anal. Found: C, 64.14; H, 6.36. $C_{16}H_{19}CoO_2$ calcd.: C, 63.58; H, 6.34%.

### *Structure determination*

Regularly-shaped single crystals grown by sublimation were mounted on glass fibers with epoxy cement. By the use of a Nicolet R3 diffractometer, final unit-cell parameters (Table 1) were determined from the angular settings of 25 well-centered reflections ($20° \leqslant 2\theta \leqslant 30°$). An orthorhombic space group, *Pnma* or $Pn2_1a$, was indicated by systematic absences. The centric alternative, *Pnma*, was initially chosen on the basis of *E*-statistics and subsequently confirmed by the successful and chemically reasonable solution and refinement of the structure. Data collection, solution, and refinement employed routines in the P3 and SHELXTL (version 3.0) program packages (Nicolet Corp.). Correction for Lorentz and polarization effects were applied to the intensity data. An empirical absorption correction was not needed based on the absorption coefficient (12.5 $cm^{-1}$), regular crystal shape, and $\psi$-scan data. Redundant data were averaged ($R(I)$ 2.79%). The cobalt atom was located from a sharpened Patterson map. Least-squares refinement of the metal atom position followed by a Fourier synthesis located all remaining nonhydrogen atoms. After anisotropic refinement of the nonhydrogen atoms, all hydrogen atoms were located and refined isotropically by blocked-cascade, least-squares methods. $GOF$ was 1.519 for 1416 unique reflections with $|F_0| > 2.5\sigma|F_0|$. The largest peak in the final difference map was 0.3 $eÅ^{-3}$ located 0.07 Å from C(1). The final positional and thermal parameters are presented in Tables 2 and 3.

## Results and discussion

The molecular structure and atom labelling for $[\eta^5\text{-}C_5(CH_3)_5]Co(O_2C_6H_4)$ appear in Fig. 1. The unit cell consists of four molecules in a head-to-tail arrangement (Fig. 2). The mirror plane of the space group bisects the C(1)–C(1a) and C(3)–C(3a) bonds of the phenylene ring and the C(4)–C(4a) bond of the cyclopentadienyl ring. Co, C(6), C(9), and H(9b) lie on the mirror plane. The metallacycle ring is planar

TABLE 1

CRYSTAL AND REFINEMENT DATA

| | |
|---|---|
| Formula | $C_{16}H_{19}CoO_2$ |
| Formula weight | 302.24 |
| Crystal system | orthorhombic |
| Space group | *Pnma* |
| $a$ (Å) | 12.942(4) |
| $b$ (Å) | 12.902(4) |
| $c$ (Å) | 8.543(3) |
| $V$ (Å$^3$) | 1426(1) |
| $Z$ | 4 |
| $\rho$ (calcd) (g $cm^{-3}$) | 1.41 |
| Temp. (°C) | 25 |
| Crystal dimension (mm) | 0.32×0.44×0.44 |
| Radiation | Graphite-monochromated Mo-$K_\alpha$ ($\lambda$ 0.71073 Å) |
| Diffractometer | Nicolet R3 |
| Abs. Coeff. ($cm^{-1}$) | 12.5 |
| Scan speed (deg $min^{-1}$) | Variable 4–10 |
| $2\theta$-Scan range (°) | $4° \leqslant 2\theta \leqslant 55°$ |
| Scan technique | $\theta/2\theta$ |
| Data collected | $+h, +k, +l$ |
| Scan width (°) | $1.0 + \Delta(\alpha_1 - \alpha_2)$ |
| Ignorance factor ($G$)[a] | 0.0017 |
| Unique data | 1688 rflns (1852 collected) |
| Unique data with ($F_{obs}$) > $2.5\sigma(F_{obs})$ | 1416 |
| Std. rflns. | 3/200 (no decay observed) |
| $R_F$ | 3.79 |
| $R_{wF}$ | 3.72 |

[a] Weight = $[\sigma^2(F) + g(F^2)]^{-1}$.

(maximum deviation from planarity is 0.0009 Å) and is coplanar with the phenylene ring (dihedral angle 1.6°). The O–Co–O bond angle of 86.9(1)° in IV is similar to that in $Co[O_2C_6H_2(t\text{-}Bu)_2]_2(bpy)$ (87.4(3)°) [22].

*Cp ring*

The cyclopentadienyl ring is planar (maximum deviation from planarity is 0.0008 Å) and forms a dihedral angle of 91.7° with the metallacycle fragment. Previous

TABLE 2

ATOM COORDINATES ($\times 10^4$) FOR IV

| Atom | *x/a* | *y/b* | *z/c* | *U*(iso) [a] |
|---|---|---|---|---|
| Co | 2080(1) | 2500 | 1970(1) | [b] |
| O | 1335(1) | 3480(1) | 892(2) | [b] |
| C(1) | 655(2) | 3045(2) | −88(2) | [b] |
| C(2) | −36(2) | 3580(2) | −1040(3) | [b] |
| C(3) | −720(2) | 3034(2) | −1965(3) | [b] |
| C(4) | 3512(2) | 3057(2) | 2523(3) | [b] |
| C(5) | 2774(2) | 1607(2) | 3628(3) | [b] |
| C(6) | 2314(3) | 2500 | 4322(4) | [b] |
| C(7) | 4191(2) | 3719(3) | 1539(4) | [b] |
| C(8) | 2499(4) | 492(4) | 3938(6) | [b] |
| C(9) | 1538(4) | 2500 | 5609(6) | [b] |
| H(2) | −36(20) | 4291(20) | −1011(28) | 57(7) |
| H(3) | −1196(20) | 3404(19) | −2577(30) | 61(7) |
| H(7a) | 4917(28) | 3693(24) | 2014(35) | 95(10) |
| H(7b) | 3959(30) | 4402(29) | 1524(41) | 122(15) |
| H(7c) | 4263(22) | 3444(25) | 487(3) | 93(10) |
| H(8a) | 2866(28) | 260(30) | 4779(54) | 122(14) |
| H(8b) | 1791(36) | 498(31) | 4211(53) | 155(18) |
| H(8c) | 2503(54) | 116(62) | 3310(80) | 231(33) |
| H(9a) | 1071(30) | 1883(29) | 5635(43) | 136(15) |
| H(9b) | 1843(43) | 2500 | 6597(68) | 129(20) |

[a] Å$^2 \times 10^3$. [b] Refined anisotropically, see Table 3.

TABLE 3

ANISOTROPIC TEMPERATURE FACTORS (Å$^2 \times 10^3$) [a] FOR IV

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Co | 35(1) | 54(1) | 35(1) | 0 | −5(1) | 0 |
| O | 51(1) | 48(1) | 48(1) | 2(1) | −10(1) | −5(1) |
| C(1) | 37(1) | 52(1) | 31(1) | 1(1) | 1(1) | −1(1) |
| C(2) | 53(1) | 55(1) | 43(1) | 6(1) | −2(1) | 4(1) |
| C(3) | 46(1) | 79(2) | 37(1) | 4(1) | −6(1) | 8(1) |
| C(4) | 37(1) | 60(1) | 37(1) | −1(1) | −8(1) | −3(1) |
| C(5) | 44(1) | 78(2) | 45(1) | 17(1) | −12(1) | −8(1) |
| C(6) | 38(2) | 119(4) | 35(2) | 0 | −1(2) | 0 |
| C(7) | 58(2) | 78(2) | 62(2) | 13(2) | −8(1) | −16(2) |
| C(8) | 79(2) | 99(3) | 108(3) | 57(3) | −30(2) | −28(2) |
| C(9) | 50(3) | 238(9) | 40(2) | 0 | 7(2) | 0 |

[a] The anisotropic temperature factor exponent takes the form $-2\pi^2(h^2a^{\star 2}U_{11}{}^2 + k^2b^{\star 2}U_{22}{}^2 + \ldots + 2hka^\star b^\star U_{12}{}^2 + \ldots)$.

structure determinations of $\eta^5$-$C_5(CH_3)_5$ complexes reveal that the methyl groups are displaced from the ring plane away from the metal by 0.037 to 0.205 Å [13]. The larger displacements are attributed to steric crowding around the metal [13]. In accordance, the methyl groups in IV are not coplanar with the cyclopentadienyl ring, but C(8) and C(8a) are displaced toward the metal (0.066 Å) while C(7), C(7a) (0.022 Å) and C(9) (0.076 Å) are displaced away. An inward twist of the orbital framework on C(5) and C(5a) may increase overlap between the carbon $\pi$ orbital and the appropriate metal *d* orbital while tilting C(8) and C(8a) toward the metal. Such behavior has been discussed by Elian et al. [17].

The orientation of the methyl groups is shown in Fig. 1. C(8), C(8a), and C(9) each have two protons residing on the metal side of the ring. C(7) and C(7a) have one proton on the metal side and one proton approximately in the plane of the Cp ring. While other methyl group orientations have been observed [18,19], the config-

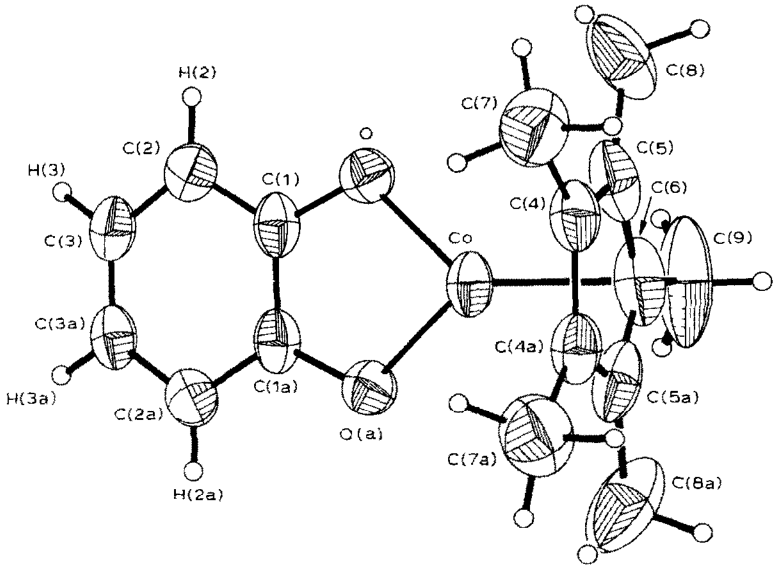


Fig. 1. Molecular structure and labelling scheme for $[\eta^5$-$C_5(CH_3)_5]Co(O_2C_6H_4)$. The hydrogen atoms are depicted with an arbitrary radius.

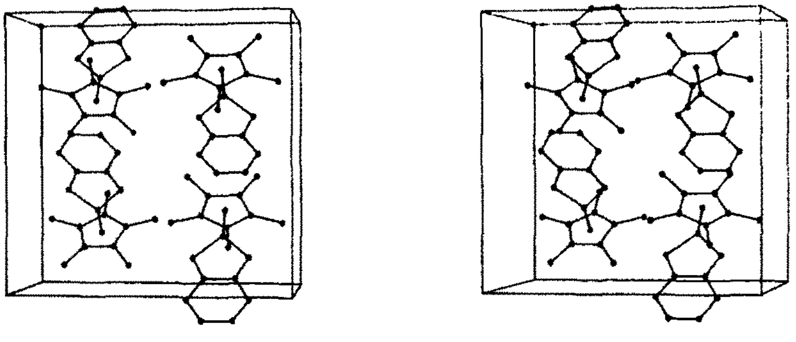
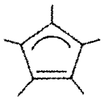
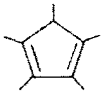


Fig. 2. A stereoview of the unit cell packing of IV viewed along the *b* axis.

uration adopted by IV is one in which nonbonded interactions are probably minimized.

Slight inequivalence in the C–C bond distances within the cyclopentadienyl ring results from the lack of cylindrical symmetry in IV. Librational motion corrections [12,21] were applied to IV, but did not change the pattern of the C–C bond distances. The HOMOs of the cyclopentadienyl ring, $e_1^-$ and $e_1^+$, interact slightly


$e_1^-$


$e_1^+$

differently with the $Co(O_2C_6H_4)$ fragment. The C–C bond distance variations of the Cp ring of IV are similar in size and arrangement to those in $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ where the distortion was attributed to enhanced electron population of $e_1^+$ over $e_1^-$. The same situation appears to exist in IV and in $[\eta^5\text{-}C_5(CH_3)_5]Rh(O_2C_6H_4)$ [11]. It is interesting to find that $e_1^-$ is apparently more populated in two structures related to IV, $[\eta^5\text{-}C_5(CH_3)_5]Co(CO)_2$ [13] and $[\eta^5\text{-}C_5(CH_3)_5]Co[(NH)_2C_6H_4]$ [15]. Apart from packing constraints, subtle electronic effects originating in the metallacycle may determine the predominance of $e_1^-$ or $e_1^+$.

*The catecholate*

The bond distances in the $O_2C_6H_4$ fragment are consistent with the catecholate form, I. The C(1)–O distance of 1.338(3) Å in IV (see Table 4) compares with an average C–O bond length of 1.358(10) Å in $Co[O_2C_6H_2(t\text{-}Bu)_2]_2(bpy)$ [22]. In addition, the C(1)–O distance in IV is closer to the C–O length in free catechol

TABLE 4

SELECTED BOND DISTANCES AND ANGLES FOR $[\eta^5\text{-}C_5(CH_3)_5]Co(O_2C_6H_4)$ (IV)

| | | | |
|---|---|---|---|
| Co–O | 1.837(2) | C(4)–C(5) | 1.412(3) |
| C(1)–O | 1.338(3) | C(4)–C(4a) | 1.436(5) |
| C(1)–C(1a) | 1.408(4) | C(5)–C(6) | 1.426(3) |
| C(1)–C(2) | 1.392(3) | C(4)–C(7) | 1.487(4) |
| C(2)–C(3) | 1.379(4) | C(5)–C(8) | 1.505(6) |
| C(3)–C(3a) | 1.379(5) | C(6)–C(9) | 1.489(6) |
| C(2)–H(2) | 0.918(25) | Co–C(4) | 2.043(2) |
| C(3)–H(3) | 0.939(26) | Co–C(5) | 2.035(3) |
| C(7)–H(7a) | 1.024(35) | Co–C(6) | 2.032(3) |
| C(7)–H(7b) | 0.932(39) | C(9)–H(9a) | 1.002(38) |
| C(7)–H(7c) | 0.970(32) | C(9)–H(9b) | 0.932(57) |
| C(8)–H(8a) | 0.912(42) | | |
| C(8)–H(8b) | 0.944(46) | | |
| C(8)–H(8c) | 0.723(76) | | |
| O–Co–O(a) | 86.9(1) | O–C(1)–C(1a) | 114.8(1) |
| Co–O–C(1) | 111.8(1) | C(1a)–C(1)–C(2) | 119.7(1) |
| C(1)–C(2)–C(3) | 119.6(2) | C(2)–C(3)–C(3a) | 120.7(2) |
| C(4a)–C(4)–C(5) | 107.9(1) | C(4)–C(5)–C(6) | 108.2(2) |
| C(5)–C(6)–C(5a) | 107.8(3) | | |

(1.371(4) Å) [23] than *o*-benzoquinone (1.220(2) Å) [24]. [$\eta^5$-$C_5(CH_3)_5$]Rh($O_2C_6H_4$) [11] has C–O bond lengths averaging 1.387(18) Å. The slightly longer C–O bonds in the rhodium analogue may result from hydrogen bonding between the O atom of the complex and catechol molecules of solvation in the lattice.

Further support for the catecholate form in IV lies in the absence of an alternating pattern of bond lengths in the phenylene ring. The bond length of 1.407(4) Å in IV is comparable to the distance between carbons bearing the O atoms in other catecholate complexes [10]. A slightly longer C–C length (⟨av⟩ 1.44(1) Å) is observed for the same type of bond in semiquinone chelates [10].

*Supplementary material.* Table 5 contains a listing of observed and calculated structure factors and is available from the authors on request.

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