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STRUCTURAL CHARACTERIZATION OF CYCLOPENTADIENYL-(DUROQUINONE)COBALT DIHYDRATE

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SUMMARY

The structure of cyclopentadienyl(duroquinone)cobalt dihydrate, $(C_5H_5)Co[(CH_3)_4C_6O_2]\cdot 2H_2O$, has been determined by three-dimensional X-ray analysis. The crystal structure consists of discrete cyclopentadienyl(duroquinone)cobalt molecules linked together by a complex network of hydrogen bonds between water molecules and duroquinone oxygen atoms. Each $(C_5H_5)Co[(CH_3)_4C_6O_2]$ molecule consists of a cobalt atom sandwiched between a cyclopentadienyl ring and a duroquinone ring. A detailed comparison of the molecular parameters of this complex with those of closely related complexes is given. Crystallographic evidence that the metal–duroquinone interaction in cyclopentadienyl(duroquinone)cobalt dihydrate is considerably stronger than that in the electronically-equivalent 1,5-cyclooctadiene(duroquinone)nickel complex is given not only by the metal–C(olefin) distances being 0.12 Å (av) shorter in the duroquinone–cobalt complex [*viz.*, 2.104(8) Å *vs.* 2.222(7) Å] but also by the much greater C_{2v}-type distortion of the duroquinone ring from the planar D_{2h} configuration in free duroquinone. The compound crystallizes with two formula species in a triclinic unit cell of symmetry $P\bar{1}$ and reduced cell dimensions $a = 8.60$ Å, $b = 9.00$ Å, $c = 10.15$ Å, $\alpha = 87°\ 34'$, $\beta = 84°\ 10'$, $\gamma = 73°\ 44'$. Least-squares refinement yielded final unweighted and weighted discrepancy factors of $R_1 = 10.8\%$ and $R_2 = 12.0\%$, respectively, for 2481 independent diffraction maxima collected photographically.

INTRODUCTION

Several transition metal complexes containing 2,3,5,6-tetramethyl-1,4-benzoquinone (*i.e.*, duroquinone) as one of the ligands have been prepared by Schrauzer, Thyret, and Dewhirst[1–4], and by Gubin and Khandkarova[5]. The structure and bonding of one of the Schrauzer–Thyret complexes, 1,5-cyclooctadiene(duroquinone)nickel[1–3], has been analyzed by Glick and Dahl[6] on the basis of an X-ray diffraction investigation. In order to obtain further detailed information about the nature and

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deformation of a duroquinone ring on complexation with another first row transition metal, a single-crystal X-ray diffraction study of cyclopentadienyl(duroquinone) cobalt was undertaken. This particular complex was of special interest to us in that it was considered highly desirable to compare its molecular parameters with those of cyclopentadienyl(tetramethylcyclopentadienone)cobalt whose structure was previously determined[7] in our laboratories. Since a duroquinone ligand may be formally constructed from a tetramethylcyclopentadienone one by the insertion of a second carbonyl fragment (which effectively functions as an "electron sink") within the tetramethylcyclopentadienone ring, it was deemed important to ascertain the conformational difference between these two rings on metal-complexation with a common $Co(C_5H_5)$ moiety. Subsequent to the completed study[8] reported here, crystallographic investigations of three duroquinone–rhodium complexes were reported by Struchkov and co-workers[5] who concluded that the degree of distortion of the rhodium-coordinated duroquinone ring is apparently not sensitive to the nature of the second metal-attached ligand. Schrauzer and Thyret[3,9] put forward a semi-empirical molecular orbital bonding model to rationalize the spectral and magnetic properties of their quinone–metal complexes. Based on the MO calculations, these workers[3,9] predicted a greater stability for the metal–duroquinone bond in cyclopentadienyl(duroquinone)cobalt than that found in cyclooctadiene(duroquinone)nickel. Our determined structure of cyclopentadienyl(duroquinone)cobalt dihydrate not only appears to substantiate their predictions but also appears to provide an explanation for the unusual doublet character of the IR carbonyl absorption band of the duroquinone group as being due to an unusually large deformation of this ligand upon coordination with a $Co(C_5H_5)$ fragment.

Attempts to prepare a crystalline sample (suitable for X-ray diffraction analysis) of duroquinone(cyclopentadienyl)cobalt, free of water molecules, are also described.

EXPERIMENTAL

X-ray data

A sample of cyclopentadienyl(duroquinone)cobalt was generously supplied to us by Professor G. N. Schrauzer of the University of California, San Diego. Recrystallization of this sample from tetrahydrofuran gave single crystals suitable for X-ray analysis. A well-formed single tetragonal-shaped crystal of dimensions 0.3 × 0.3 × 0.25 mm was mounted inside a thin-walled glass capillary with the 0.25 mm edge parallel to the spindle axis. Preliminary oscillation and Weissenberg X-ray photographs indicated triclinic Laue symmetry C_i–$\bar{1}$. Lattice parameters were measured at room temperature (~22°) from $hk0$ and $0kl$ precession photographs which were each calibrated by the superposition of a zero-level exposure of an NaCl crystal on the same film.

Multiple-film equi-inclination Weissenberg data were taken of the reciprocal levels $h0l$ through $h10l$, with Zr-filtered Mo-$K\alpha$ radiation. In order to record all accessible independent reflections on the upper half of the film and thereby avoid the problem of spot compaction, two separate sets of data corresponding to the two independent 180° rotation ranges were collected for each of the ten non-zero Weissenberg reciprocal layers. Consequently, only spot extension corrections needed to be applied[10] to the intensity measurements from the top half of each film. Timed-exposure precession photographs were taken for the $hk0$, $hk\bar{1}$, $hk\bar{2}$, $0kl$, $\bar{1}kl$, and $\bar{2}kl$

layers. All intensities were judged[11] by comparison with a set of standard spots taken from the same crystal; averaging of the data and corrections for Lorentz-polarization effects were carried out with the INTAV program[12]. Neither absorption nor extinction corrections were applied to the data. For the particular crystal (whose dimensions and rotation axis are given above), the calculated linear absorption coefficient of 11.8 cm^{-1} for Mo-K_α radiation leads to a $\mu R_{\max}$ value of less than 0.4; hence, the maximum variation in intensity on a given reciprocal layer due to absorption is estimated to be less than 8%. All layers of Weissenberg and precession data were merged onto a single scale factor by a weighted least-squares program[13]. This merging procedure yielded a final total of 2481 independent maxima.

Standard deviations of the individual structure amplitudes were estimated as follows: If $I(hkl)_0 < \sqrt{10}\, I_{\min}$, $\sigma(F(hkl)_0) = [|F(hkl)_0|/20][\sqrt{10}\, I_{\min}/I(hkl)_0]^2$. If $I(hkl)_0 \geqslant \sqrt{10}\, I_{\min}$, $\sigma(F(hkl)_0) = |F(hkl)_0|/20$.

The atomic scattering factors used for all atoms were those compiled by Hanson, *et al.*[14].

Preparation of cyclopentadienyl(duroquinone)cobalt

In an effort to obtain a sample of anhydrous cyclopentadienyl(duroquinone)-cobalt, the original preparation described by Schrauzer and Thyret[3] was carried out with some modifications. In a typical preparation 4.0 g (0.020 mole) of cyclopentadienylcobalt dicarbonyl and 4.0 g (0.024 mole) of duroquinone were reacted with refluxing ethylcyclohexane in a quartz tube under UV irradiation. After about 12 h the reaction was stopped and the solvent removed under vacuum. The dark residue was dissolved in CH_2Cl_2, filtered, and the solvent removed to give about one gram of crude product. The product was crystallized from a chloroform/octane mixture to give pure anhydrous cyclopentadienyl(duroquinone)cobalt identified by its IR and PMR spectra which closely agreed with the published values. Crystals suitable for X-ray examination could only be obtained by prolonged sealed-tube sublimation (at 180° for 10 days) which simultaneously led to substantial decomposition. However, since all of the examined crystals exhibited very irregular X-ray diffraction patterns indicative of twinning or multiple crystal growth, no X-ray data were obtained for anhydrous cyclopentadienyl(duroquinone)cobalt.

All starting materials were used as obtained from the supplier. Solvents were reagent grade and were dried by standard procedures before use. All operations were carried out in an atmosphere of prepurified nitrogen.

CRYSTAL DATA

The measured lattice constants for the reduced triclinic unit cell of (C_5H_5)-$Co[(CH_3)_4C_6O_2]\cdot 2H_2O$ are $a = 8.60 \pm 0.02$ Å, $b = 9.00 \pm 0.02$ Å, $c = 10.15 \pm 0.02$ Å, $\alpha = 87° 34' \pm 10'$, $\beta = 84° 10' \pm 10'$, $\gamma = 73° 44' \pm 10'$. The unit cell volume is 750.7 Å^3. The observed density of 1.49 $\text{g}\cdot\text{cm}^{-3}$ (measured by the standard flotation method in a series of carbon disulfide/carbon tetrachloride solutions) is near that of 1.43 $\text{g}\cdot\text{cm}^{-3}$ calculated on the basis of two formula species per unit cell. The total number of electrons per cell, $F(000)$, is 340. The initial arbitrary choice of the centrosymmetric space group $P\bar{1}(C_i^1)$[15] was confirmed by the solution and successful refinement of the structure. The structural determination required the location of one cobalt, 15 carbon, 4 oxygen, and 21 hydrogen atoms comprising one formula species. Hence, all atoms occupy the general twofold set of positions, $\pm(x, y, z)$, of space group $P\bar{1}$.

DETERMINATION OF THE STRUCTURE

An interpretation of a three-dimensional Patterson function calculated with the corrected intensity data led to the approximate position of the cobalt atom in the asymmetric unit. A Fourier synthesis phased on the cobalt atom revealed the positions of the non-hydrogen atoms of the duroquinone and cyclopentadienyl groups. The oxygen atoms of the duroquinone group were clearly distinguished from the methyl carbon atoms on the basis of the expected general geometry of a metal-

TABLE 1

FINAL ATOMIC PARAMETERS WITH THEIR ESTIMATED STANDARD DEVIATIONS[a]

	x	y	z	B
Co	0.2734(1)	0.2905(1)	0.2406(1)	[b]
C(1)[c]	0.2658	0.3097	0.0439	3.4(2)
C(2)	0.1846	0.2004	0.0910	3.9(2)
C(3)	0.0519	0.2749	0.1789	3.5(2)
C(4)	0.0512	0.4299	0.1859	3.3(2)
C(5)	0.1834	0.4514	0.1026	4.1(2)
C(6)	0.4451(10)	0.0950(8)	0.3131(8)	1.9(1)
C(7)	0.3075(10)	0.1429(8)	0.4044(8)	2.1(1)
C(8)	0.2707(11)	0.2916(9)	0.4720(9)	2.7(1)
C(9)	0.3326(10)	0.4093(8)	0.3935(8)	2.1(1)
C(10)	0.4685(10)	0.3650(8)	0.3008(8)	2.2(1)
C(11)	0.5554(10)	0.1991(8)	0.2746(8)	1.9(1)
C(12)	0.5060(12)	−0.0650(10)	0.2552(10)	3.4(2)
C(13)	0.2000(12)	0.0355(10)	0.4531(10)	3.2(2)
C(14)	0.2581(12)	0.5773(10)	0.4284(10)	3.4(2)
C(15)	0.5586(12)	0.4792(10)	0.2270(10)	3.3(2)
O(1)	0.6972(8)	0.1519(7)	0.2094(7)	3.8(1)
O(2)	0.1701(8)	0.3244(7)	0.5751(7)	3.6(1)
O(3)	0.7409(9)	0.2025(8)	−0.0678(8)	4.7(1)
O(4)	0.0508(10)	0.1326(8)	0.7819(8)	5.5(2)

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[a] The estimated standard deviation in parentheses applies to the last significant digit. [b] Anisotropic temperature factors used for the cobalt atom are of the form $\exp\{-[B_{11}\cdot h^2+B_{22}\cdot k^2+B_{33}\cdot l^2+2\,B_{12}\cdot h\cdot k+2\,B_{13}\cdot h\cdot l+2\,B_{23}\cdot k\cdot l]\}$. The resulting thermal coefficients ($\times 10^4$) are as follows: B_{11}, 48(2); B_{22}, 40(1); B_{33}, 23(1); B_{12}, −10(1); B_{13}, −10(1); B_{23}, 2(1). [c] The rigid-body model for the five cyclopentadienyl carbon atoms, C(n) where $n=1$–5, is defined such that the atomic parameters are relative to an orthonormal axis system x', y', z' in which carbon C(1)′ is located at the origin; the $+y'$ direction is along a vector from the midpoint of the C(3)′–C(4)′ vector through the origin; the $+x'$ direction is parallel to the C(2)′–C(5)′ vector; $+z'$ is the vector product of x' and y'. The cyclopentadienyl carbon ring thus lies in the $x'y'$ plane. The rigid-body angles ϕ, θ, and ρ define the position (other than a translation component to the crystallographic origin) of the rigid group coordinate system with respect to the crystallographic axis system in the following manner: an orthonormal basis set of vectors (x, y, z) is chosen with a along x and with b in the x, y plane. The set (x, y, z) is brought into coincidence with (x', y', z') by a rotation of ϕ about z', θ about the resulting x, and ρ about final y. The values of these angles (in degrees are ϕ, −2.2(2); θ, −165.5(2); ρ, −38.4(3).

TABLE 2

INTRAMOLECULAR DISTANCES (Å)

For the cobalt–duroquinone fragment the distances are averaged in accordance with C_{2v} symmetry.

Duroquinone ring		
C=C bonds	C(6)–C(7)	1.397(12)[a]
	C(10)–C(9)	1.398(14)
		1.398(9)
C–C	C(6)–C(11)	1.524(12)
	C(10)–C(11)	1.493(12)
	C(7)–C(8)	1.477(13)
	C(9)–C(8)	1.485(13)
		1.495(8)
$C-CH_3$ bonds	C(6)–C(12)	1.509(13)
	C(7)–C(13)	1.556(14)
	C(9)–C(14)	1.512(12)
	C(10)–C(15)	1.576(15)
		1.538(8)
C=O bonds	C(8)–O(2)	1.269(13)
	C(11)–O(1)	1.295(12)
		1.282(9)
Non-bonding ring distances	C(6)...C(10)	2.492(11)
	C(7)...C(9)	2.464(12)
		2.478(8)
	C(6)...C(9)	2.847(15)
	C(7)...C(10)	2.843(16)
		2.845(11)
	C(8)...C(11)	2.956(20)
Non-bonding $H_3C...CH_3$ distances	C(12)...C(13)	3.093(21)
	C(14)...C(15)	3.074(21)
		3.084(16)
Non-bonding $H_3C...O$ distances	C(12)...O(1)	2.881(16)
	C(15)...O(1)	2.859(15)
	C(13)...O(2)	2.859(15)
	C(14)...O(2)	2.900(16)
		2.875(9)
Distances involving H_2O	O(1)...O(3)	2.835(13)
	O(2)...O(4)	2.945(16)
	O(1)...O(4′)[b]	2.857(18)
	O(3)...O(4″)[c]	2.859(18)

(*Continued*)

TABLE 2 (*continued*)

Co–(duroquinone ring)	Co–C(6)	2.117(14)
	Co–C(10)	2.124(11)
	Co–C(7)	2.075(12)
	Co–C(9)	2.100(11)
		2.104(8)
	Co–C(8)	2.350(11)
	Co–C(11)	2.390(12)
		2.370(9)
	Co–mp(1)[d]	1.975(15)
	Co–mp(2)[d]	1.993(15)
		1.984(11)
Co–(cyclopentadienyl ring)	Co–C(1)	2.054(13)
	Co–C(2)	2.119(13)
	Co–C(3)	2.121(15)
	Co–C(4)	2.038(14)
	Co–C(5)	2.033(13)
		2.073(6)
	Co–centroid	1.672(15)

[a] The estimated standard deviation in parentheses applies to the last significant digit. [b] Equivalent position $1-x, -y, 1-z$. [c] Equivalent position $1+x, y, -1+z$. [d] mp(1) and mp(2) are defined as the midpoints of the olefinic bonds C(6)–C(7) and C(10)–C(9), respectively.

complexed duroquinone group[4]. Three cycles of full-matrix least-squares refinement* resulted in discrepancy factors* of $R_1=16.5\%$ and $R_2=23.0\%$. A three-dimensional difference Fourier map phased on the resulting parameters revealed the presence of an electron-density peak at approximately 2.9 Å from each of the two duroquinone oxygen atoms. The obvious assumption that these two peaks were due to the oxygen atoms of two water molecules was evidenced by an infrared spectrum (KBr pellet) of the recrystallized sample. Since this electron-density difference synthesis also indicated anisotropic thermal motion of the cobalt atom, anisotropic thermal parameters for the cobalt atom were utilized in subsequent least-squares cycles. The cyclopentadienyl ring was treated as a rigid-body of D_{5h} symmetry with an assumed C–C bond length of 1.40 Å. A description of the utilized rigid-body system is outlined in Table 1[16]. Three cycles of rigid-body anisotropic–isotropic least-squares refinement** led to final discrepancy factors of $R_1=10.8\%$ and $R_2=12.0\%$. No irregularities were observed on a final difference Fourier map. Since peaks characteristic of hydrogen atoms were not clearly resolved in the expected positions on this map, no further attempt was made

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* All least-squares refinements were based on the minimization of the quantity $\Sigma w_i(\Delta F_i)^2$; the w_i were assigned according to the estimated standard deviations of the structure factors. The unweighted and weighted reliability factors, R_1 and R_2, are defined as follows: $R_1=[\Sigma w||F_0|-|F_c||/|F_0|]\times 100$; $R_2=[\Sigma w||F_0|-|F_c||^2/\Sigma w|F_0|^2]^{\frac{1}{2}}\times 100$.

** Isotropic least-squares refinement cycles were carried out with unmerged Weissenberg data; separate scale factors were varied as well as atomic parameters. Anisotropic–isotropic refinement cycles were carried out with merged Weissenberg and precession data; the single scale factor which resulted from the merging operations was varied as well as the atomic parameters.

to locate them. Anomalous dispersion corrections were not deemed necessary for this centrosymmetric crystalline compound in that for Mo–K_α radiation small corrections to the atomic scattering factors (*viz.*, $\Delta f' = 0.4$, $\Delta f'' = 1.1$ for cobalt)[17] have been found in our laboratories not to affect significantly the atomic coordinates for centrosymmetric space groups.

The final atomic parameters with their estimated standard deviations, obtained from the output of the last cycle, are given in Table 1*. Tables 2 and 3 give interatomic distances and bond angles, calculated with the Busing–Martin–Levy function-and-error program[18], along with estimated standard deviations obtained from the full inverse matrix (including the uncertainties in lattice parameters). The "best" molecular

TABLE 3

BOND ANGLES (°)

For the cobalt–duroquinone fragment the bond angles are averaged in accordance with C_{2v} symmetry

Duroquinone ring		*Co–(duroquinone ring)*	
C(6)–C(11)–C(10)	111.4(7)[a]	mp (1)–Co–mp (2)	77.3(7)
C(7)–C(8)–C(9)	112.6(8)		
	112.0(5)	*Angles involving H_2O*	
		O(3)---O(1)---O(4')[b]	96.5(8)
C(11)–C(6)–C(12)	114.3(8)	O(1)---O(3)---O(4'')[c]	123.8(9)
C(11)–C(10)–C(15)	112.7(8)	O(2)---O(4)---O(1')[b]	105.8(9)
C(13)–C(7)–C(8)	115.3(8)	O(2)---O(4)---O(3')[d]	127.9(9)
C(14)–C(9)–C(8)	117.7(9)	O(1')[b]---O(4)---O(3')[d]	126.1(9)
	115.0(5)		
C(11)–C(6)–C(7)	121.2(7)		
C(11)–C(10)–C(9)	121.9(8)		
C(8)–C(7)–C(6)	121.3(8)		
C(8)–C(9)–C(10)	121.1(8)		
	121.4(5)		
C(12)–C(6)–C(7)	124.3(8)		
C(15)–C(10)–C(9)	124.9(7)		
C(13)–C(7)–C(6)	122.9(7)		
C(14)–C(9)–C(10)	120.8(9)		
	123.2(5)		
C(6)–C(11)–O(1)	123.6(7)		
C(10)–C(11)–O(1)	124.2(8)		
C(7)–C(8)–O(2)	122.9(9)		
C(9)–C(8)–O(2)	123.3(8)		
	123.5(5)		

[a] The estimated standard deviation in parentheses applies to the last significant digit. [b] Equivalent position $1-x$, $-y$, $1-z$. [c] Equivalent position $1+x$, y, $z-1$. [d] Equivalent position $x-1$, y, $1+z$.

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* The table of structure factors has been deposited as NAPS Document No. 01784, with ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 Third Avenue, New York, New York 10022. A copy may be secured by citing the document number and remitting $ 2.00 for a microfiche or $ 5.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.

planes formed by specified sets of atoms and perpendicular distances of atoms from these planes were calculated with the least-squares program of Smith[19] and are given in Table 4.

TABLE 4

EQUATIONS OF LEAST-SQUARES PLANES AND DISTANCES (Å) FROM THESE PLANES[a]

A. Plane containing mp(1), Co, mp(2)

$0.6745X - 0.2885Y - 0.6796Z + 0.1370 = 0$

B. Plane containing C(6), C(7), C(8), C(9), C(10), C(11), O(1), O(2), C(12), C(13), C(14), C(15)

$-0.6368X + 0.2041Y - 0.7435Z + 5.0565 = 0$

C(6)	0.09	C(13)	0.28
C(7)	0.11	C(14)	0.10
C(8)	−0.22	C(15)	0.23
C(9)	0.10	O(1)	−0.44
C(10)	0.10	O(2)	−0.50
C(11)	−0.19	Co	1.65
C(12)	0.20		

C. Plane containing C(6), C(7), C(9), C(10)

$-0.6332X + 0.2009Y - 0.7475Z + 4.9640 = 0$

C(6)	−0.005	C(15)	0.13
C(7)	0.005	O(1)	−0.52
C(9)	−0.005	C(8)	−0.33
C(10)	0.005	C(13)	0.18
Co	1.55	C(14)	0.14
C(11)	−0.28	O(2)	−0.62
C(12)	0.11		

D. Plane containing C(6), C(10), C(11), O(1)

$-0.4446X + 0.1187Y - 0.8878Z + 4.6718 = 0$

C(6)	0.02	C(11)	0.02
C(10)	−0.05	O(1)	0.02

E. Plane containing C(6), C(11), C(10)

$-0.3754X + 0.0909Y - 0.9224Z + 4.4853 = 0$

F. Plane containing C(7), C(8), C(9), O(2)

$-0.8083X + 0.2832Y - 0.5161Z + 4.5280 = 0$

C(7)	0.02	C(9)	0.02
C(8)	−0.07	O(2)	0.03

G. Plane containing C(7), C(8), C(9)

$-0.8549X + 0.3057Y - 0.4192Z + 4.2412 = 0$

H. Plane containing C(1), C(2), C(3), C(4), C(5)[b]

$-0.6126X + 0.2198Y - 0.7593Z + 1.6539 = 0$

Co	−1.67

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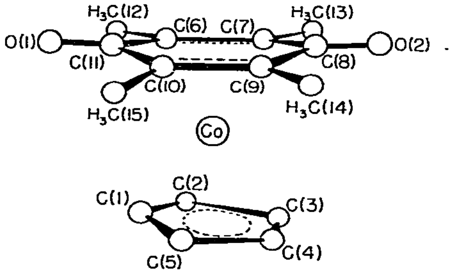
[a] The Smith least-squares plane program was utilized to obtain the equations of best planes formed by the atoms indicated and also the perpendicular distances of these and other atoms from the planes. Unit weighting was used in the calculations. The equation of the least-squares plane is expressed in orthogonal coordinates X, Y, Z, which are related to the triclinic cell coordinates by the transformation: $X = a\cdot x + b\cdot(\cos\gamma)\cdot y + c\cdot(\cos\beta)\cdot z$; $Y = [b\cdot(1-\cos^2\gamma)^{\frac{1}{2}}]\cdot y + [c\cdot(\cos\alpha - \cos\beta\cdot\cos\gamma)/(1-\cos^2\gamma)^{\frac{1}{2}}]z$; $Z = c[1-\cos^2\beta - (\cos\alpha - \cos\beta\cdot\cos\gamma)^2/\sin^2\gamma]^{\frac{1}{2}}z$. [b] The cyclopentadienyl ring was constrained to D_{5h} symmetry in rigid-body refinement.

The Blount program[20] was used to calculate the Patterson and all Fourier maps. The full-matrix rigid-body least-squares refinement was carried out with a locally modified version of the Busing–Martin–Levy ORFLS program[21].

RESULTS AND DISCUSSION

General description of the structure

The solid-state structure determined for cyclopentadienyl(duroquinone)-cobalt dihydrate is comprised of monomeric $(C_5H_5)Co[(CH_3)_4C_6O_2]$ molecules linked together by a complex network of hydrogen bonds between water molecules and the quinoid oxygen atoms of the cobalt-complexed duroquinone. Each monomeric unit of cyclopentadienyl(duroquinone)cobalt (Fig. 1) consists of a cobalt atom sandwiched between the cyclopentadienyl and tetramethyl-*p*-benzoquinone rings. This diamagnetic complex conforms to the 18-electron rule[22] by a formal contribution to the zerovalent cobalt atom of five electrons from the cyclopentadienyl radical and four electrons from the two olefinic bonds of the duroquinone ring.



$[C_5H_5][(CH_3C_2CH_3)_2(CO)_2]Co$

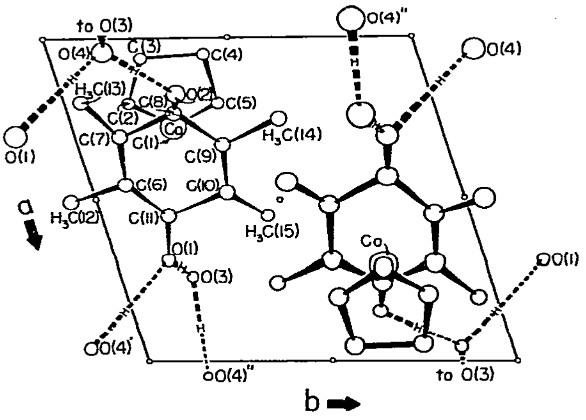


Fig. 1. Molecular configuration of $(C_5H_5)Co[(CH_3)_4C_6O_2]$.

Fig. 2. Projection of the triclinic unit cell of $(C_5H_5)Co[(CH_3)_4C_6O_2] \cdot 2\,H_2O$.

The packing of the two cyclopentadienyl(duroquinone)cobalt molecules and four water molecules in the triclinic unit cell is illustrated in Fig. 2. Although not experimentally located, the hydrogen atoms of the water molecules are illustrated in their most probable positions to indicate the nature of the hydrogen bonding in the crystal structure. These positions were arrived at by a consideration of (i) the observed O...O distances and O...O...O angles, and (ii) the statement made by Donohue[23] (and confirmed by compiled structural results[24,25]), following an examination of hydrogen bonds in organic crystals, that "only in very exceptional cases does a hydrogen atom bonded to a nitrogen or oxygen atom occupy a position such that hydrogen bond formation is impossible". One quinoid oxygen of the independent duroquinone group is involved in one hydrogen bond and the other quinoid oxygen in two hydrogen bonds to water molecules. Of the two crystallographically independent water molecules, one water oxygen atom, O(4), bridges via hydrogen bonds to two quinoid oxygen atoms, while the other water oxygen atom, O(3), bridges via hydrogen bonds to one quinoid oxygen and to the other independent water molecule. The resulting hydrogen bond network in the crystal structure gives rise to chains stretched approximately along the [$\bar{1}$01] direction; as shown in Fig. 2, a chain is built up from a segment comprised of the crystallographically independent cyclopentadienyl(duroquinone)cobalt molecule whose quinone oxygen atoms are interconnected by hydrogen bonding of water molecules to a centrosymmetric counterpart in the adjacent unit cell. The three independent O(water)... O(quinone) distances of 2.835(13), 2.857(18), and 2.949(16) Å and the one O(water)... O(water) distance of 2.859(18) Å are all within the observed range of values for O–H...O bonds in hydrated organic crystals (*viz.*, 2.5–3.0 Å with a weighted average of 2.84 Å for 180 examples[24]). The O(quinone)... O(water)...O(quinone) angle is 105.8(9)°, while the O(water)...O(water)...O(quinone) angles range from 123.8(9)° to 127.9(9)°. The O(water)...O(quinone)...O(water) angle was found to be 96.5(8)°, much less than the angles subtended by water oxygen atoms.

Schrauzer and Dewhirst[4] have attributed the alteration in the electronic spectra of this complex with change of solvent from chloroform to water to a weak solvation of the cobalt atom by water. Although in general significant differences may exist between solid and solution state, the solid-state structure instead suggests relatively strong hydrogen bonding of the negative quinoid oxygen in aqueous media rather than hydration of the cobalt atom as being responsible (at least partly) for the change in electronic spectra.

Stereochemistry of the π-cyclopentadienyl–cobalt fragment

The parameters and bonding of the cyclopentadienyl–cobalt part of the molecule are not significantly different from those observed in other similar π-cyclopentadienyl metal complexes. The cobalt–(ring centroid) length of 1.672(15) Å and the average Co–C(cyclopentadienyl) length of 2.07 Å are well within the range of similar observed values; *e.g.*, 1.67 Å and 2.07 Å in $(C_5H_5)Co[(CH_3)_4C_5O]$[7], 1.67 Å and 2.06 Å in $(C_5H_5)Co[C_5H_5(C_6H_5)]$[26], and 1.68 Å and 2.08 Å in $(C_5H_5)Co[(CF_3)_4C_5O]$[27]. The presumably significant deviations in the Co–C(cyclopentadienyl) distances [*viz.*, 2.119(13) and 2.121(15) Å for Co–C(2) and Co–C(3), respectively, *vs.* 2.033(13), 2.038(14), and 2.054(13) Å for the other three Co–C(cyclopentadienyl) distances] have also been observed in $(C_5H_5)Co[C_5H_5(C_6H_5)]$ as well as in other cyclopentadienyl–metal complexes; this slight tilting may be ascribed to crystal packing effects.

Stereochemistry of the duroquinone–cobalt fragment

The most important structural feature is the conformational change of the duroquinone ring in cyclopentadienyl(duroquinone)cobalt from the idealized D_{2h} configuration in free duroquinone[28] to an idealized C_{2v} configuration in the cobalt–duroquinone fragment. Although this resulting geometry is similar to that of the nickel–duroquinone fragment in 1,5-cyclooctadiene(duroquinone)nickel[6] and to those of the rhodium–duroquinone fragments in the cyclopentadienyl-, indenyl-, and acetylacetonato(duroquinone)rhodium complexes[5], significant differences in the degrees of distortion and molecular parameters do exist (*vide infra*). The observed deformation results from the two carbonyl groups bending out of the mean plane of olefinic carbon atoms away from the cobalt atom by an average of 21°. This value represents the dihedral angle between the plane of four olefinic carbon atoms and the plane comprised of the carbonyl carbon atom and its two bonded carbon atoms. The carbonyl oxygen atom does not lie in this latter plane but rather is displaced towards the cobalt atom such that the angle between the plane and the C–O bond vector is 9° (av). The four methyl carbon atoms are bent out of the mean plane of the olefinic carbon atoms *toward* the cobalt atom. These distortions of the duroquinone group are considerably greater in magnitude than those observed for the duroquinone ring in 1,5-cycloocta-diene(duroquinone)nickel but are comparable to those observed in the duroquinone rings in the rhodium complexes. In the duroquinone–nickel molecule, the carbonyl groups are bent only 7.5° out of the plane of the olefinic carbon atoms away from the nickel atom, while the carbonyl oxygen is displaced toward the nickel atom such that the C–O vector makes an average angle of 25° with the plane defined by the three above-mentioned carbon atoms. In cyclopentadienyl(duroquinone)cobalt the perpendicular displacements of the methyl groups from the plane of the olefinic carbon atoms *toward* the metal range from 0.11 to 0.18 Å, while in 1,5-cyclooctadiene(duroquinone)-nickel the corresponding perpendicular displacements of the methyl groups *toward* the metal are only 0.03 to 0.06 Å; in the duroquinone–rhodium complexes these perpendicular displacements range from 0.05 to 0.18 Å.

The effect of the hydrogen bonding on the deformations of the duroquinone ring in the cobalt complex is difficult to assess. It has been observed that in the crystal structure of tetrahydroxy-*p*-benzoquinone[29] the quinone groups are linked in chains by a network of hydrogen bonds between water molecules and hydroxy groups of the quinone ring and by hydrogen bonds between the quinoid oxygen atom and hydroxy groups. In this case the entire quinone molecule was observed to maintain its planarity. On this basis it is assumed that the distortion of the duroquinone group is due mainly to complexation by the metal atom.

Similar distortions of the carbonyl groups have been observed in several cyclopentadienone metal complexes, but the substituent atoms directly attached to the olefinic carbon atoms in the five-membered cyclopentadienone ring containing one carbonyl group are deformed in a more irregular manner with their perpendicular displacements from the mean plane of olefinic carbon atoms being *away from* as well as *toward* the metal atom. For example, in $(C_5H_5)Co[(CH_3)_4C_5O]$[7] the carbonyl portion is tilted 8° out of the diene carbon plane away from the cobalt atom with perpendicular displacements of the methyl carbon atoms being +0.01, +0.03, +0.08, and −0.06 Å (+ signifies away from the metal atom and − toward the metal atom); in both $(C_5H_5)Co[(CF_3)_4C_5O]$[27] and in $(OC)_3Fe[(CF_3)_4C_5O]$[30,31] the corresponding carbonyl tilt is 20°, while the perpendicular displacements are −0.01, +0.04, +0.04, and −0.01 Å in the former molecule and −0.14, −0.14, +0.24 and +0.09 Å in the latter molecule. It is apparent from the present study of cyclopentadienyl(duroquinone)cobalt that a much greater deviation from planarity occurs upon interaction of the cyclopentadienyl–cobalt fragment with the six-membered duroquinone ring, containing two electron–withdrawing carbonyl sinks that conjugate two olefinic groups, than occurs when an identical cyclopentadienyl–cobalt fragment complexes with the five-membered tetramethylcyclopentadienone ring containing only one carbonyl sink that cyclyzes a *cis*-butadiene system.

The splitting of the single infrared carbonyl absorption band at 1629 cm^{-1} in free duroquinone into two IR carbonyl bands at 1563 and 1536 cm^{-1} (KBr pellet)[3] in cyclopentadienyl(duroquinone)cobalt* was suggested by Schrauzer and Dewhirst[4] to arise from a significant distortion of the cobalt-complexed duroquinone ring from the planar D_{2h} symmetry of the uncomplexed ring. Our observations in cyclopentadienyl-duroquinone-cobalt of a relatively large 21° tilt of the carbonyl group away from the plane of olefinic carbon atoms are in accord with this prediction. The much smaller analogous distortion observed for cyclooctadiene(duroquinone)nickel may account for the observation[2] of only a single IR carbonyl absorption at 1553 cm^{-1} for this complex. The previous observations of carbonyl bond lengths and IR absorptions [*e.g.*, free duroquinone, 1.232(2) Å and 1629 cm^{-1}; $(C_5H_5)Co[(CH_3)_4C_5O]$, 1.231(13) Å and 1569 cm^{-1}] indicate an insensitivity of the C–O bond lengths to changes in frequency (and in bond order). However, the average C–O bond length of 1.282(10) Å in cyclopentadienyl(duroquinone)cobalt appears to be longer (on the borderline of statistical significance); this increase in C–O bond length may be attributed at least partly to the hydrogen bonding by the water molecules. In the three rhodium complexes the average duroquinone C–O bond lengths are 1.27 Å (cyclopentadienyl), 1.22 Å (indenyl), and 1.24 Å (acetylacetonato)[5].

Glick and Dahl[6] observed for the cyclooctadiene(duroquinone)nickel complex that the major bond length alteration in the duroquinone ring parameters upon metal complexation is an average lengthening of the olefinic carbon–carbon bonds from 1.341(2) Å in free duroquinone to 1.401(10) Å in the nickel-complexed ring. This bond length increase of 0.06 Å was ascribed mainly to a decrease in the π-bond order of the olefinic bond upon coordination to the metal. The observed olefinic carbon–carbon length in cyclopentadienyl(duroquinone)cobalt averages 1.398(10) Å; this bond length suggests that the duroquinone olefin π-bond orders are close in both the cobalt– and nickel–duroquinone complexes.

In general, the other molecular parameters of the cobalt-complexed duroquinone ring are similar to those observed in free duroquinone, cyclooctadiene (duroquinone)nickel, and the duroquinone–rhodium complexes with the notable exception of the duroquinone ring angle whose vertex is the quinoid carbon atom. This bond angle, which averages 119.7(1)° in free duroquinone and 117.5(6)° in cyclooctadiene-(duroquinone)nickel, has decreased to an average value of 112.0(5)° in cyclopentadienyl(duroquinone)cobalt. Since the average nonbonding distances between the terminal olefinic ring carbon atoms defining this angle are virtually identical in both the duroquinone–nickel and duroquinone–cobalt complexes (*viz.*, 2.485 Å *vs.* 2.478 Å), this angular decrease is primarily a consequence of the average decrease of 0.04 Å in the C–C single bond length of 1.454(8) Å in the duroquinone–nickel complex compared to that of 1.495(7) Å in the duroquinone–cobalt complex; in free duroquinone the average C–C single bond length is 1.492(1) Å.

A comparison of corresponding metal–duroquinone distances between cyclopentadienyl(duroquinone)cobalt and cyclooctadiene(duroquinone)nickel also reveals significant differences which suggest a greater stability of the metal–duroquinone bonding in the cobalt complex. The average cobalt to olefinic carbon distance of 2.104(8) A is considerably shorter than the average nickel to olefinic carbon distance

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* The IR spectra (KBr pellet) of cyclopentadienyl(duroquinone)rhodium and cyclopentadienyl-(duroquinone)iridium likewise show a doublet in the carbonyl region at 1580 and 1532 cm^{-1} and at 1660 and 1600 cm^{-1}, respectively[4].

of 2.222(7) Å; the average metal–olefin bond midpoint distance is 1.984 Å in the cobalt complex compared to 2.109 Å for the analogous distance in the nickel complex. These differences in bond lengths are also reflected in the large decrease of 0.14 Å in the perpendicular distance from the metal atom to the plane of the four olefinic carbon atoms on replacement of the (C_8H_{12})Ni fragment (1.69 Å) with the (C_5H_5)Co fragment (1.55 Å). The resultant increase in the angle formed by the two olefin bond midpoints and the metal atom as vertex is from 72° for the nickel complex to 77° for the cobalt complex. The metal to quinoid carbon distances are somewhat closer to each other, 2.370(9) Å for the cobalt complex and 2.314(8) Å for the nickel complex, a consequence of the much greater distortion in the duroquinone ring of the cobalt complex. This experimental evidence for a stronger metal–duroquinone interaction in the cobalt complex than in the nickel complex is in accord with the predictions of Schrauzer and co-workers[3,4,9,32] based on a semi-empirical MO model which involved experimental term-level schemes resulting from assignments of electronic absorption bands.

On the other hand, it is not appropriate to utilize a comparison of the cobalt–duroquinone distances in cyclopentadienyl(duroquinone)cobalt with the cobalt–tetramethylcyclopentadienone distances in cyclopentadienyl(tetramethylcyclopentadienone)cobalt as a means of gauging bond strength, since for two different ligands (*i.e.*, the duroquinone ring *vs.* the cyclopentadienone ring) the metal–ring distances may be controlled to a large extent by the stereochemical requirements of the particular ligands relative to the metal atoms in order to achieve maximum orbital overlap (or more rigorously minimum molecular energy). Glick and Dahl[6], besides making a detailed stereochemical analysis of the observed geometrical differences between the duroquinone ligand in 1,5-cyclooctadiene(duroquinone)nickel and free duroquinone, also compared the ligand deformations of the duroquinone ligand in this nickel complex with those of the metal-complexed cyclopentadienone ligand and rationalized the results in terms of bonding considerations. Qualitative MO symmetry arguments have also been utilized primarily by Mason and collaborators[31,33] and by Schrauzer and co-workers[32,34] in attempts to rationalize the bonding sources giving rise to the observed varying degrees of distortions of the cyclopentadienone ligand in several metal–cyclopentadienone complexes whose structures were determined from X-ray analyses.

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