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THE CRYSTAL AND MOLECULAR STRUCTURES OF π-ARENE COMPLEXES OF THE ENNEACARBONYLTETRACOBALT CLUSTER WITH *ortho*- AND *meta*-XYLENE (A MIXED CRYSTAL) AND WITH BENZENE

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Summary

Crystal structures of two π-areneenneacarbonyltetracobalt compounds are described. In the first the arene is a disordered 1/1 mixture of *ortho* and *meta* xylenes. The unit cell data are: space group $P2_1/c$ (No. 14), $Z = 4$, $a = 10.03(1)$, $b = 9.86(1)$, $c = 20.24(2)$ Å, β 96.40(5)°, $V = 1991(1)$ Å^3. The final unweighted R value is 5.6% after anisotropic full-matrix refinement for 1883 independent reflections collected on a diffractometer using the $\theta - 2\theta$ scanning technique. The second compound, benzeneenneacarbonyltetracobalt has unit cell data: space group $R\overline{3}$ (No. 148), $Z = 2$, $a = 9.79(3)$ Å, α 82.95(1)°, $V = 920.8$ Å^3. Full-matrix anisotropic refinement using 491 reflections yielded a final R of 3.3%. Both structures consist of a tetrahedral cobalt cluster, one cobalt atom is π bonded to the arene moiety, while the other three are each bonded to two terminal and two bridging carbonyl groups. Base to apex cobalt—cobalt distances average 2.481(2) Å while basal cobalt—cobalt distances average 2.455(2) Å. The distance from the apical cobalt to the arene centroid averages 1.62 Å. The aromatic rings show no very significant distortion from local six-fold symmetry.

Introduction

Since the preparation of dibenzenechromium, similar π-dibenzenoid species have been prepared for about a dozen elements, and monobenzenoid half-sandwich compounds are known for a number of these. By far the most exhaustively studied have been derivatives of benzenetricarbonylchromium. The effect of ring substituents on the orientation of the ring has been of interest [1—6] together with detection of the perturbation, if any, from six-fold symmetry [7, 8].

The preparation of hitherto undetected h^6-benzene complexes with the enneacarbonyltetracobalt cluster [9, 10] has broadened the range of molecules containing a metal carbonyl fragment with local three-fold symmetry* inviting comparisons with the results of investigations of the tricarbonylchromium complexes.

Our interest in these compounds originated with the preparation and crystallographic identification of the mixed xylene complex, a side product in a routine preparation of μ-2,2,5,5-tetramethyl-3-hexynehexacarbonyldicobalt. We were unaware of the work of Pauson et al. [9] at the time, but an earlier brief report of the preparation of 1,2,4,5-tetra-t-butylbenzene [11] using the above acetylenic complex as a catalyst led us to speculate that we might have isolated an intermediate. Disappointingly, more careful investigation revealed that xylenes contaminating our solvent were the precursor of the complex.

Experimental

Suitable crystals were glued on Lindeman glass fibres and subjected to an initial survey comprising zero and first level Weissenberg and precession photographs. The photographic data yielded possible space groups and approximate unit cell dimensions, in addition to confirming the satisfactory quality of the crystals. Accurate cell dimensions were subsequently obtained using a Picker-Nuclear FACS-1 diffractometer, equipped with a molybdenum target tube and a graphite monochromator. For each sample, 12 diffraction maxima, widely separated in χ and θ, were centered by systematically mis-setting 2θ, ω and χ. The process was repeated in the negative 2θ region. Values of 2θ, ω, and χ appropriately averaged were used in the calculation of a refined cell and orientation matrix. Since α_1/α_2 splitting was not resolved, a mean value of λ = 0.71069 Å for the Mo-K_α peak was assumed. The pulse height analyser used in conjunction with a scintillation counter was set to accept 100% of this peak.

During data collection, the $\theta - 2\theta$ scanning technique was employed with a 2θ scan speed of 2°/min. Scan base lengths were selected appropriate to the mosaicity of the crystals, and lengthened in proportion to 2θ in order to allow for α_1/α_2 dispersion. Backgrounds were measured for 40 seconds at the low and high ends of the scan. A group of three reflections, widely separated in reciprocal space, were remeasured every 30 observations in order to monitor instrument stability and crystal stability and alignment.

Data reduction, performed using a locally-written program for the CDC 6400 computer, used the following formulae:

Reflection intensity $I(hkl) = P - (B_1 + B_2)(t_P/t_B)$;
e.s.d of intensity $\sigma[I(hkl)] = [P + (B_1 + B_2)(t_P/t_B)^2 + (0.02P)^2]^{1/2}$

where P is the count accumulated during the scan over a time period t_P, while B_1 and B_2 are the backgrounds counted for a total time t_B. The structure amplitudes $|F(hkl)|$ and their estimated standard deviations $\sigma[F(hkl)]$ were obtained using appropriate Lorentz and polarization corrections. No absorption corrections

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* The crystal structure of one of these complexes, with *para*-xylene, has been determined by Dr. O.S. Mills [10].

were applied, the crystals being rather small and irregularly shaped (but see below). Estimates of the scale factors and overall thermal parameters were obtained by the method of Wilson [12].

The programs used for the solution and refinement of the structures were: FORDAP by Zalkin, for Fourier and Patterson calculations; REL by Long, used for statistical phasing by the method of Sayre [13, 14]; and SFLS by Prewitt, used for least squares refinement. All programs, extensively modified, were run on a CDC 6400 computer. Scattering factors were taken from the International Tables for X-ray Crystallography [15a] as were the anomalous scattering factors for cobalt [15b]. In least-squares refinement, the function minimized was:

$\Sigma w(|F_o|-|F_c|)^2$ where $w = [\sigma(F_o)]^{-2}$

and the discrepancy indices cited below are:

$R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$
$R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

The standard deviation of an observation of unit weight, the "goodness-of-fit", is:

$[\Sigma w(|F_o|-|F_c|)^2/(m-n)]^{1/2}$

where m and n are the numbers of observations and parameters varied respectively.

$C_6H_4(CH_3)_2Co_4(CO)_9$

The mixture of the two xylene complexes was obtained as a side product (yield < 10%) in the reaction of octacarbonyldicobalt with 2,2,5,5-tetramethyl-3-hexyne to form $(CH_3)_3CC_2C(CH_3)_3Co_2(CO)_6$. The solvent used, n-hexane, had been dried over calcium hydride and deoxygenated, but no further purification had been attempted. Experiments subsequent to the structure elucidation have shown that aromatic impurities present in the solvent were the source of the side product. Thus, the xylene complexes were still formed in the absence of the acetylene, but they were not formed if the n-hexane was washed with a mixture of concentrated sulphuric and nitric acids (which removed aromatic and unsaturated impurities) prior to distillation. No separation of the *ortho*- and *meta*-xylene complexes was obtained by chromatography on silica gel. We were not able to identify the complex by elemental analysis or mass spectrometry, therefore the X-ray crystallographic study was initiated.

Recrystallization of the mixture by the cooling of solutions in n-hexane yielded small rhombohedrally shaped crystals with irregularly "stepped" faces. X-ray photographs of the crystal initially chosen for diffractometry suggested that the space group was indeed rhombohedral; the *hkl*, *klh*, and *lhk* zones appeared identical under visual inspection, with no systematic absences or additional symmetry.. The space groups $R3$ (No. 146) or $R\bar{3}$ (No. 148) were assigned: the refined unit cell paramters were $a = 10.046(5)$ Å, α 85.42(2)°, $V = 1004(1)$ Å^3. For $C_6H_4(CH_3)_2Co_4(CO)_9$, $FW = 593.6$ and $Z = 2$, ρ_{calc} =

1.962 g cm^{-3}. The density of the bulk of the sample was 1.87 g cm^{-3} measure by flotation in aqueous zinc iodide.

Data collection from this crystal was terminated prematurely when the diffraction peaks widened and the intensity of the three check reflections dropped excessively. In addition, it was discovered that the three-fold diffraction symmetry no longer existed and new photographs revealed that only the (Weissenberg) $h0l$ zone was similar to the initial photograph, although it was very diffuse. Attempts to find another rhombohedral crystal in the original batch and recrystallized samples proved fruitless; photographic data on a selection of crystals indicated the space group $P2_1/c$ (No. 14). However, the monoclinic $h0l$ zone appeared identical to the zero levels from the rhombohedral polymorph. At this point the rhombohedral modification was abandone and studies on the monoclinic version were continued.

The unit cell parameters for the mixed monoclinic crystal (ca. 0.15 × 0.1 × 0.1 mm) were: a = 10.03(1), b = 9.86(1), c = 20.24(2) Å, β 96.40(5)°, V = 1991(1) Å^3, ρ_{calc} = 1.980 g cm^{-3} for Z = 4, ρ_{obs} = 1.87(2) g cm^{-3}. Between the limits $4° < 2\theta < 45°$, intensity data were collected for a unique set of 300 reflections, using a base scan of 2.5°. After data reduction, 1883 reflections with $I > 3\sigma(I)$ were retained for subsequent refinement of the structure. A set of 200 normalized structure factors ($E > 1.5$) were phased statistically. Thus, 3 origin-determining reflections, (241, 012, 110) and four others ($01\bar{2}$, 526, 089, 253) were used as a starting set for 16 phase pyramids, the most internall consistent of which yielded an E map showing the four cobalt atoms and sever carbonyl groups.

A Fourier synthesis using phases based on the four cobalt atoms revealed the entire structure excepting the substituents on the benzene ring which were rather indistinct. A further difference synthesis computed after one cycle of refinement of the partial structure showed three peaks, one at approximately $5e^{-}$Å^{-3} and the other two at about $2e^{-}$Å^{-3}. With supporting evidence from the mass spectrum of the compound (a large peak at m/e 106) these peaks were interpreted as methyl groups of a mixture of *ortho*- and *meta*-xylenes arranged with one methyl group coincident. Accordingly, three carbon atoms were included in isotropic least-squares refinement, with occupancy factors of 1.0, 0.5 and 0.5 which were allowed to vary. After 4 cycles, the refinement had converg ed (parameter shifts less than 0.1 of their standard deviations) with R = 0.091 and R_w = 0.090. The three occupancy factors had not changed significantly from their input values. They were fixed and refinement was continued. Anisotropic thermal parameters were used for all atoms except the methyl groups, which were maintained isotropic. The final discrepancy indices after a further 4 cycles of refinement were R = 0.056, R_w = 0.054 and the "goodness-of-fit" was 1.39. Final atomic positions are listed in Table 1*.

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* The tables of structure factors and thermal parameters have been deposited as NAPS Document No. 02358, with ASIS/NAPS, c/o Microfiche Publications, 305 E. 46th Street, New York, New York 10017. A copy may be secured by citing the document and remitting $1.50 for microfiche or $5.00 for photocopies. Advance payment is required. Make cheques payable to Microfiche Publications.

TABLE 1

FINAL POSITIONAL PARAMETERS WITH ESTIMATED STANDARD DEVIATIONS FOR XYLENE-ENNEACARBONYLTETRACOBALT[a]

Atom	*X/a*	*Y/b*	*Z/c*
Co(1)	0.79997(12)	0.28372(14)	0.31044(6)
Co(2)	0.89898(12)	0.16564(14)	0.41097(7)
Co(3)	0.69311(13)	0.07858(13)	0.34877(7)
Co(4)	0.68542(12)	0.29049(14)	0.41342(7)
C(1)	0.4764(10)	0.3323(12)	0.4292(7)
C(2)	0.5408(13)	0.4497(12)	0.4054(7)
C(3)	0.6633(15)	0.4966(13)	0.4434(8)
C(4)	0.7220(13)	0.4246(16)	0.4970(7)
C(5)	0.6569(14)	0.3079(16)	0.5182(7)
C(6)	0.5392(12)	0.2594(13)	0.4834(6)
C(7)	0.3448(16)	0.2824(18)	0.3912(8)
C(8)[b]	0.4804(34)	0.5266(37)	0.3536(17)
C(9)[b]	0.7155(40)	0.6234(44)	0.4172(20)
C(11)	0.8843(12)	0.2265(12)	0.2433(6)
O(11)	0.9392(12)	0.1840(11)	0.2006(5)
C(12)	0.7606(11)	0.4513(12)	0.2799(5)
O(12)	0.7380(10)	0.5573(9)	0.2600(5)
CB(1)	0.9404(12)	0.3395(11)	0.3727(5)
OB(1)	1.0153(9)	0.4306(9)	0.3890(5)
C(21)	1.0264(11)	0.0614(12)	0.3838(6)
O(21)	1.1109(8)	—0.0020(10)	0.3652(5)
C(22)	0.9734(11)	0.2073(11)	0.4935(6)
O(22)	1.0177(10)	0.2376(11)	0.5448(5)
CB(2)	0.7745(9)	0.0363(12)	0.4384(6)
OB(2)	0.7511(9)	—0.0318(9)	0.4835(4)
C(31)	0.7585(13)	—0.0492(13)	0.2990(6)
O(31)	0.8070(11)	—0.1251(9)	0.2658(5)
C(32)	0.5391(14)	0.0022(11)	0.3612(6)
O(32)	0.4416(9)	—0.0510(10)	0.3726(5)
CB(3)	0.6202(12)	0.2146(12)	0.2867(6)
OB(3)	0.5229(9)	0.2451(10)	0.2534(5)
H(4)	0.8081	0.4538	0.5203
H(5)	0.6955	0.2602	0.5583
H(6)	0.5002	0.1740	0.4968

[a] estimated standard deviations in parentheses are right justified to the least significant digits of the preceding number.

[b] refined with an occupancy factor of 0.5

$C_6H_6Co_4(CO)_9$

The benzene complex was obtained by refluxing octacarbonyldicobalt (1.50 g, 4.4 mmoles) in 75 ml of benzene for 21 hours. The product obtained after removal of excess benzene under vacuum was recrystallized from n-hexane. (Found: C, 31.91; H, 1.22; Co. 41.32. $C_{15}H_6Co_4O_9$ calcd.: C, 31.84; H, 1.07; Co, 41.65%.)

While in most batches the crystals were fine needles quite unsuitable for single crystal studies, one batch gave small crystals similar to those obtained for the mixed xylene complex. Such a crystal (ca. 0.1 × 0.1 × 0.1 mm) was chosen and the crystal and molecular structure was determined. Just as for the original crystal of the mixed compound, the photographic evidence indicated space group $R3$ (No. 146) or $R\bar{3}$ (No. 148). The refined cell parameters were: $a = 9.798(3)$ Å, α 82.95(1)°, $V = 920.8$ Å^3, $\rho_{calc} = 2.04$ g cm^{-3} for $Z = 2$ and $FW = 565.78$, while $\rho_{obs} = 1.99(1)$ g cm^{-3}. A careful examination of the diffraction symmetry using the diffractometer revealed differences between the intensities of symmetry related reflections which, at the time seemed too large to be due to absorption. The average relative error among symmetry related groups of $|F_o|$ was ± 7% ranging up to about 10% for a very few strong groups of reflections, and 20% for some weak groups. The linear absorption coefficient of 37.26 cm^{-1} yields estimated transmission factors from about 0.68 to 0.78 or about ± 3% in $|F_o|$. The resulting suspicion that the crystal might be triclinic, coupled with the rather low diffraction intensity from the small crystal, prompted us to collect a complete hemisphere of data. Hexagonal indices were used for convenience, and in the portion of the sphere having positive h and $4^\circ < 2\theta < 45^{\circ 6}$, 2693 reflections were collected of which 1887 reflections above the 3σ limit were retained. A base scan of 2.0° was used.

The positions of the cobalt atoms were deduced from a three-dimensional Patterson synthesis. The first Fourier synthesis, based on data phased by these four atoms, showed the remaining non-hydrogen atoms. The positional and isotropic thermal parameters were refined to convergence (3 cycles) using both space groups $P\bar{1}$ and $R\bar{3}$. The discrepancy indices were $R = 0.085$, $R_w = 0.079$ for the triclinic, and $R = 0.085$, $R_w = 0.080$ for the rhombohedral space group at this point; a statistically insignificant difference [16]. The parameters refined in the triclinic space group showed no significant deviation from rhombohedral symmetry. Thus it was felt that absorption effects probably contributed significantly to the apparent breakdown of diffraction symmetry. Unfortunately the sample crystal was rather too cratered in appearance for an accurate absorption correction to be feasible, and the possibility of growing better crystals appeared remote. No absorption correction was applied, but the symmetry equivalent reflections were averaged. Unless at least 3 of a group of symmetry related reflections were above the 3σ limit, they were not included in the merged data set. This affected about 200 reflections. The merged set of 491 reflections was used for 5 cycles of anisotropic refinement in the rhombohedral space group. Anomalous dispersion factors were applied to the cobalt scattering factors, and hydrogen atoms, placed in calculated positions, were included in the structure factor calculations. Final discrepancy indices were: $R = 0.033$, $R_w = 0.030$; "goodness-of-fit" = 1.25. Final atomic positions appear in Table 2.

TABLE 2

FINAL POSITIONAL PARAMETERS WITH STANDARD DEVIATIONS FOR BENZENEENNEACARBONYLTETRACOBALT

Atom	*X/a*	*Y/b*	*Z/c*
Co(1)	0.30627(11)	0.18002(10)	0.39772(11)
Co(4)	0.18692(10)	0.18692(10)	0.18692(10)
C(1)	0.0364(13)	0.2263(10)	0.0444(14)
C(2)	−0.0213(10)	0.1596(14)	0.1682(14)
C(11)	0.3949(10)	0.2320(8)	0.5264(9)
O(11)	0.4494(8)	0.2707(7)	0.6107(7)
C(12)	0.2750(9)	0.0094(10)	0.4754(10)
O(12)	0.2536(7)	−0.0958(6)	0.5260(7)
CB(1)	0.4545(10)	0.1185(9)	0.2615(8)
OB(1)	0.5342(7)	0.0260(7)	0.2379(6)
H(1)	−0.0011	0.2975	0.0126
H(2)	−0.0887	0.1944	0.2136

Discussion

The structure determinations indicate that the molecules are related to dodecacarbonyltetracobalt, $Co_4(CO)_{12}$, by removal of the three terminal carbonyl groups and their replacement by a benzenoid system at the apical cobalt atom of the cluster (Figs. 1 and 2). Such molecular parameters as have been obtained crystallographically from the disordered $Co_4(CO)_{12}$ [17] and by normal coordinate analysis of the infrared spectrum of $XCo_4(CO)_9$ where X = toluene, mesitylene and tetralin [18] are substantiated by this work. (An interesting confirmation might be to use the molecular geometry of the $Co_4(CO)_9$ fragment to fit the crystal data for $Co_4(CO)_{12}$.)

Figure 3 shows the unit cell packing of the mixed complex projected down the unique monoclinic axis. The relation between the monoclinic and rhombohedral polymorphs is also illustrated in Fig. 3. The similarity of the Weissenberg zero levels, noted above, results because the structures are identical in projection down the monoclinic unique axis and the rhombohedral axis, respectively.

The bond lengths and angles for the two structures, displayed side by side in Table 3, show that the $Co_4(CO)_9$ portions of the molecules are essentially identical. The average basal Co—Co distance 2.455(1) Å differs little from the average Co(*n*)—Co(4) distance 2.481(4) Å; both bond lengths being quite normal. It appears in general that the presence of a bridging carbonyl has little effect on the cobalt—cobalt bond length. This is perhaps to be expected since, in cases where Co—Co bonds could be bridged or unbridged, no clearly defined

(continued on p. 112)

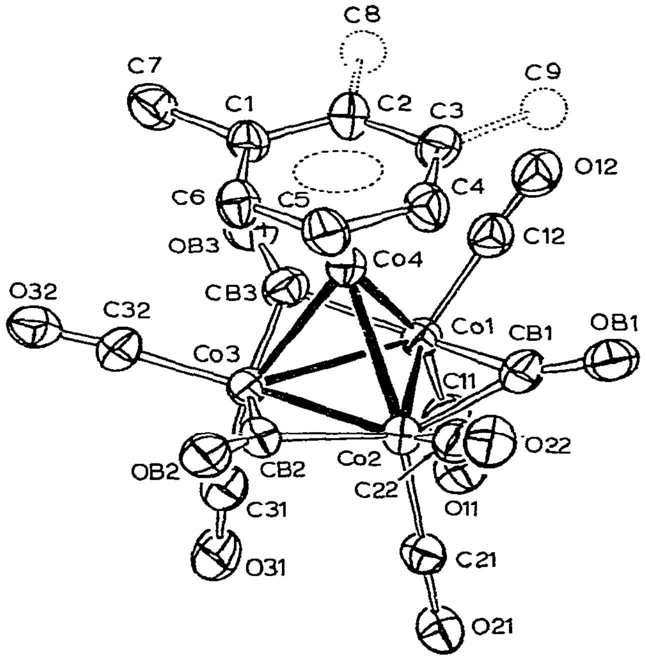

Fig. 1. Xyleneenneacarbonyltetracobalt viewed down the crystallographic *c* axis. The labelling shown in Figures 1 and 2 applies also to the benzene complex.

TABLE 3

BOND LENGTHS (Å) AND ANGLES (°) [a] IN ENNEACARBONYLTETRACOBALT COMPLEXES WITH BENZENE AND XYLENE

Benzene		Xylene				
Bond lengths (Å)						
Co(1)—Co(4)	2.485(1)	2.491(2)	Co(2)—Co(4)	2.477(2)	Co(3)—Co(4)	2.472(2)
Co(1)—Co(2)	2.457(2)	2.456(2)	Co(2)—Co(3)	2.451(2)	Co(3)—Co(1)	2.456(2)
Co(1)—C(11)	1.771(9)	1.772(13)	Co(2)—C(21)	1.774(11)	Co(3)—C(31)	1.783(12)
Co(1)—C(12)	1.795(10)	1.794(12)	Co(2)—C(22)	1.800(13)	Co(3)—C(32)	1.763(13)
Co(1)—CB(3)	1.956(9)	1.938(12)	Co(2)—CB(1)	1.946(11)	Co(3)—CB(2)	1.949(11)
Co(1)—CB(1)	1.939(9)	1.865(12)	Co(2)—CB(2)	1.911(10)	Co(3)—CB(3)	1.926(12)
C(11)—O(11)	1.160(12)	1.154(17)	C(21)—O(21)	1.152(14)	C(31)—O(31)	1.150(16)
C(12)—O(12)	1.120(12)	1.134(14)	C(22)—O(22)	1.122(16)	C(32)—O(32)	1.155(16)
CB(1)—OB(1)	1.148(11)	1.194(15)	CB(2)—OB(2)	1.178(12)	CB(3)—OB(3)	1.161(16)
Co(4)—C(1)	2.122(10)	2.195(11)	Co(4)—C(3)	2.141(13)	Co(4)—C(5)	2.178(14)
Co(4)—C(2)	2.122(13)	2.132(12)	Co(4)—C(4)	2.147(15)	Co(4)—C(6)	2.171(12)
C(1)—C(2)	1.387(18)	1.436(17)	C(3)—C(4)	1.373(21)	C(5)—C(6)	1.391(19)
C(2)—C(3)	1.394(18)	1.452(21)	C(4)—C(5)	1.413(22)	C(6)—C(1)	1.402(18)
					C(1)—C(7)	1.533(20)
					C(2)—C(8)	1.377(37)
					C(3)—C(9)	1.477(44)
Bond angles (°)						
Co(1)—Co(4)—Co(2)	59.25(4)	59.27(5)	Co(2)—Co(4)—Co(3)	59.38(5)	Co(3)—Co(4)—Co(1)	59.33(5)
Co(4)—Co(1)—Co(2)	60.37(4)	60.08(5)	Co(4)—Co(2)—Co(3)	60.22(5)	Co(4)—Co(3)—Co(1)	60.71(5)
Co(4)—Co(1)—Co(3)	60.37(4)	59.96(5)	Co(4)—Co(2)—Co(1)	60.65(5)	Co(4)—Co(3)—Co(2)	60.40(5)
Co(4)—Co(1)—CB(3)	76.7(3)	73.3(4)	Co(4)—Co(2)—CB(1)	78.0(4)	Co(4)—Co(3)—CB(2)	73.9(4)
Co(4)—Co(1)—C(12)	98.9(3)	99.2(4)	Co(4)—Co(2)—C(22)	97.9(4)	Co(4)—Co(3)—C(32)	101.9(4)
Co(4)—Co(1)—CB(1)	77.0(3)	79.1(4)	Co(4)—Co(2)—CB(2)	74.4(3)	Co(4)—Co(3)—CB(3)	74.0(4)
Co(4)—Co(1)—C(11)	161.3(3)	162.8(4)	Co(4)—Co(2)—C(21)	161.6(4)	Co(4)—Co(3)—C(31)	158.7(4)
Co(3)—Co(1)—CB(3)	50.6(3)	50.3(4)	Co(1)—Co(2)—CB(1)	48.4(3)	Co(2)—Co(3)—CB(2)	49.9(3)
Co(3)—Co(1)—C(12)	140.3(3)	141.4(4)	Co(1)—Co(2)—C(22)	138.4(4)	Co(2)—Co(3)—C(32)	141.1(4)
Co([illegible])—Co(1)—CB(1)	110.3(3)	110.7(3)	Co(1)—Co(2)—CB(2)	109.9(4)	Co(2)—Co(3)—CB(3)	109.1(4)

Co(3)—Co(1)—Co(2)	60.00(4)	59.86(5)	Co(1)—Co(2)—Co(3)	60.06(5)	Co(2)—Co(3)—Co(1)	60.07(5)
CB(3)—Co(1)—C(12)	93.8(4)	94.3(5)	CB(1)—Co(2)—C(22)	94.8(5)	CB(2)—Co(3)—C(32)	93.3(5)
CB(3)—Co(1)—CB(1)	153.2(4)	152.0(5)	CB(1)—Co(2)—CB(2)	151.6(5)	CB(2)—Co(3)—CB(3)	147.7(5)
CB(3)—Co(1)—Co(2)	109.7(3)	108.5(4)	CB(1)—Co(2)—Co(3)	108.0(4)	CB(2)—Co(3)—Co(1)	108.5(4)
C(12)—Co(1)—CB(1)	95.4(4)	94.7(5)	C(22)—Co(2)—CB(2)	95.7(4)	C(32)—Co(3)—CB(3)	96.6(5)
C(12)—Co(1)—Co(2)	142.0(3)	140.9(4)	C(22)—Co(2)—Co(3)	142.7(4)	C(32)—Co(3)—Co(1)	144.9(4)
CB(1)—Co(1)—Co(2)	51.2(3)	51.3(3)	CB(2)—Co(2)—Co(3)	51.3(3)	CB(3)—Co(3)—Co(1)	50.8(4)
C(11)—Co(1)—Co(3)	103.0(3)	104.0(4)	C(21)—Co(2)—Co(1)	104.9(4)	C(31)—Co(3)—Co(2)	101.3(4)
C(11)—Co(1)—CB(3)	99.7(4)	102.0(5)	C(21)—Co(2)—CB(1)	101.2(5)	C(31)—Co(3)—CB(2)	103.4(5)
C(11)—Co(1)—C(12)	99.6(4)	97.7(5)	C(21)—Co(2)—C(22)	100.4(5)	C(31)—Co(3)—C(32)	99.3(6)
C(11)—Co(1)—CB(1)	103.4(4)	102.9(5)	C(21)—Co(2)—CB(2)	102.7(5)	C(31)—Co(3)—CB(3)	105.1(5)
C(11)—Co(1)—Co(2)	105.0(3)	107.5(4)	C(21)—Co(2)—Co(3)	103.5(4)	C(31)—Co(3)—Co(1)	101.7(4)
Co(1)—C(11)—O(11)	177.3(8)	177(1)	Co(2)—C(21)—O(21)	178(1)	Co(3)—C(31)—O(31)	175(1)
Co(1)—C(12)—O(12)	178.6(8)	179(1)	Co(2)—C(22)—O(22)	178(1)	Co(3)—C(32)—O(32)	176(1)
Co(1)—CB(3)—OB(3)	139.3(7)	139(1)	Co(2)—CB(1)—OB(1)	135(1)	Co(3)—CB(2)—OB(2)	138(1)
Co(1)—CB(1)—OB(1)	142.4(7)	144(1)	Co(2)—CB(2)—OB(2)	143(1)	Co(3)—CB(3)—OB(3)	142(1)
Co(1)—CB(1)—Co(2)	78.2(3)	80.2(4)	Co(2)—CB(2)—Co(3)	78.8(4)	Co(3)—CB(3)—Co(1)	78.9(5)
Co(1)—Co(4)—C(1)	129.8(4)	131.6(4)	Co(2)—Co(4)—C(1)	159.9(3)	Co(3)—Co(4)—C(1)	108.8(3)
Co(1)—Co(4)—C(2)	107.8(3)	109.2(4)	Co(2)—Co(4)—C(2)	161.4(3)	Co(3)—Co(4)—C(2)	130.1(4)
Co(1)—Co(4)—C(3)	106.8(4)	109.6(4)	Co(2)—Co(4)—C(3)	126.5(4)	Co(3)—Co(4)—C(3)	164.5(4)
Co(1)—Co(4)—C(4)	126.8(3)	128.4(4)	Co(2)—Co(4)—C(4)	104.5(4)	Co(3)—Co(4)—C(4)	157.8(4)
Co(1)—Co(4)—C(5)	159.1(4)	160.0(4)	Co(2)—Co(4)—C(5)	105.5(4)	Co(3)—Co(4)—C(5)	126.7(4)
Co(1)—Co(4)—C(6)	162.5(3)	161.8(3)	Co(2)—Co(4)—C(6)	126.3(3)	Co(3)—Co(4)—C(6)	106.8(3)
C(1)—C(2)—C(3)	120(1)	120(1)	C(2)—C(3)—C(4)	121(1)	C(4)—C(5)—C(6)	121(1)
C(6)—C(1)—C(2)	120(1)	118(1)	C(3)—C(4)—C(5)	119(2)	C(5)—C(6)—C(1)	120(1)
					C(1)—C(2)—C(8)	122(2)
					C(3)—C(2)—C(8)	120(2)
					C(2)—C(3)—C(9)	113(2)
					C(4)—C(3)—C(9)	126(2)
					C(6)—C(1)—C(7)	121(1)
					C(2)—C(1)—C(7)	119(1)

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[a] Corresponding or pseudo-symmetry related bond lengths or angles for the benzene and xylene complexes are shown on the same line.

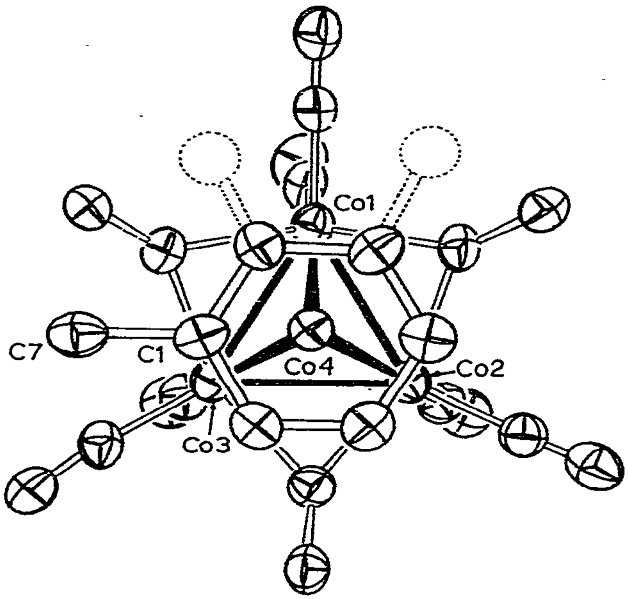

Fig. 2. Xyleneenneacarbonyltetracobalt viewed down the normal to the aromatic ring.

trends have emerged [20]; the bridging carbonyl does not appear to be required to "buttress" a Co—Co bond. Perhaps there is rather subtle interplay between relative σ-donor and π-acceptor strengths for carbonyl groups in bridging and non-bridging situations.

The following minor differences between structures appear: the distances

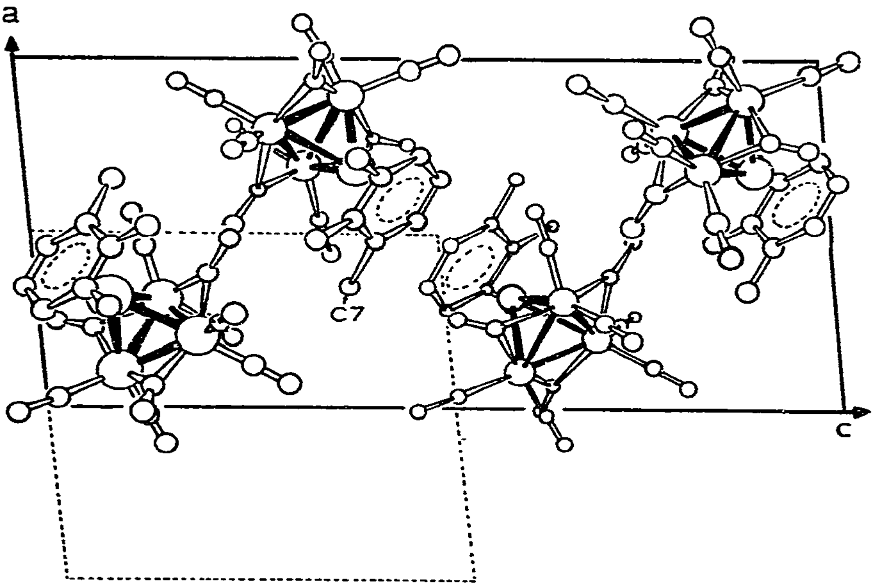

Fig. 3. Contents of the unit cell of xyleneenneacarbonyltricobalt. The unit cell of the benzene complex is shown with a dotted line.

from the centroid of the ring to the apical cobalt atom are 1.64(1) Å for the xylene complex and 1.603(2) Å for the benzene complex. For comparison, a distance of 1.61 Å is observed in π-mesitylenephenylmethinylhexacarbonyltricobalt [21], while cyclopentadiene rings average 1.67 Å from cobalt [22].

The angle between the plane of the basal cobalt atoms and the planes defined by the bridging carbonyl groups and the two cobalt atoms to which they are attached has an average value of 14.3(5)° in the xylene structure and 11.7(3)° in the benzene compound.

The bridging carbonyl groups are not perfectly symmetrically bonded to the basal cobalt atoms. Thus, the $Co_4(CO)_9$ fragments in both structures have approximate C_3 but not C_{3v} symmetry. There are two sets of cobalt to carbon bond lengths; Co(*n*)—CB(*n*) which average 1.91(1) Å, and Co(*n*)—CB(*n*—1) which average 1.947(3) Å. The angles Co(*n*)—CB(*n*)—OB(*n*) average 142.9(4)°, while the angles Co(*n*)—CB(*n*—1)—OB(*n*—1) average 138(1)°. (Where CB(0) and OB(0) are equivalent to CB(3) and OB(3) respectively.) This feature of the molecular geometry seems to represent the beginning of a structural change which is nearly complete (for example) in $[Fe_3(CO)_{13}]^{2-}$ [23].

$C_6H_4(CH_3)_2Co_4(CO)_9$

A detailed examination of bond lengths (Table 2) determined for the 1/1 mixture of xylene complexes reveals the following anomalies. The three "equivalent" base-to-apex cobalt—cobalt distances apparently differ significantly; Co(1)—Co(4) 2.491(2) Å as compared to Co(2)—Co(4) and Co(3)—Co(4), 2.477(2) and 2.472(2) Å respectively. Also distances between ring carbon atoms and the apical cobalt atom vary from 2.19(1) to 2.13(1) Å, these extremes being to the adjacent carbon atoms carrying the full methyl group and the *ortho* half methyl group, respectively. The most likely interpretation is that the distortions from local three-fold symmetry are an artefact of the disorder, but other tempting explanations exist. In complexes of tricarbonylchromium with polycyclic arenes [24—27], the shortest carbonyl to chromium distance is that *trans* to a ring junction, while among the atoms of the ring, the carbon atoms of the junction are furthest from the chromium atom. Comparing the xylene complex, we find the longest cobalt—cobalt apex to base distance *trans* to the bond C(1)—C(2); both substituted with methyl groups in the *ortho*-xylene component of the mixture. However, we do not observe that this part of the ring is significantly more remote from the apical cobalt atom. The deviation from planarity of the ring could be a consequence of repulsions between methyl groups in the *ortho*-xylene component: similar repulsions have been suggested to explain distortions in hexamethylbenzenetricarbonylchromium [28]. Clearly this kind of speculation would have to be substantiated by an analysis of the structure of the pure *ortho*-xylene complex.

$C_6H_6Co_4(CO)_9$

The distances and angles for this complex are included in Table 2 beside those for the xylene compound. While the geometries are very closely similar, the results for the benzene complex should probably be considered more reliable.

Of particular note is the apparent equality of the two structurally non-equivalent bond lengths in the benzene moiety. The 1.39(2) Å distance is equal to that in unpertubed benzene (uncorrected for thermal libration). The carbo atoms are not markedly anisotropic despite an apparent low barrier to rotatio of < 2.7 kcal mole^{-1} [29] in the solid state. We expect to repeat the data col tion for this complex at low temperature in the near future in an attempt to discover a difference in the carbon—carbon distances comparable with those tained for benzenetricarbonylchromium.

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