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THE SYNTHESIS AND MOLECULAR STRUCTURES OF TWO CYCLOBUTADIENECOBALT COMPLEXES FORMED BY THE REACTION BETWEEN π-CYCLOPENTADIENYLDICARBONYLCOBALT AND PHENYL-2-THIENYLACETYLENE

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Summary

The reaction between h^5-cyclopentadienyldicarbonylcobalt and phenyl-2-thienylacetylene in refluxing xylene has been found to produce 78% yield of (h^5-cyclopentadienyl)(h^4-diphenyldi-2-thienylcyclobutadiene)cobalt, as well as lesser amounts of a cyclotrimerization product, triphenyltri-2-thienylbenzene, and three isomeric cyclopentadienone—cobalt complexes. A single crystal X-ray structural study intended to confirm the disposition of the phenyl and thienyl substituents of the cyclobutadiene ring in the first compound was carried out. The results are inconclusive since there is disorder of these groups in the crystalline lattice. The most likely model involves a mixture of *cis* and *trans* isomers plus phenylthienyl disorder. The atoms of the (h^5-C_5H_5)Co(C_4) moiety are well behaved crystallographically and have molecular parameters which are within accepted values of recent determinations not plagued by disorder or uncertainty of isomeric purity.

A minor biproduct, resulting from the apparent coreaction of phenyl-2-thienylacetylene and diphenyldiacetylene with h^5-cyclopentadienyldicarbonylcobalt, has also been identified by spectral and X-ray diffraction techniques as the novel complex bis [(h^5-cyclopentadienyl)(h^4-*trans*-diphenyl-2-thienylcyclobutadienyl)-cobalt]. The crystallographic study of this compound also revealed disorder in the thienyl groups but it is not as severe as that found for the major product.

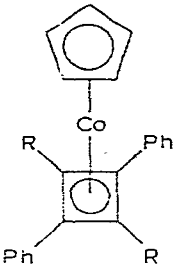
Introduction

In recent studies we have been concerned with the synthesis, mechanism of formation, and structural elucidation of products resulting from reactions between h^5-cyclopentadienyldicarbonylcobalt and various unsymmetrical acetylenes [1—5]. It was of interest to include in this program an acetylene bearing a thiophene ring, since coordination to cobalt could conceivably involve the heterocyclic substituent or the acetylenic carbon atoms. In this paper, we describe in detail the reaction between h^5-cyclopentadienyldicarbonylcobalt and phenyl-2-thienylacetylene, as well as X-ray crystallographic structural determinations of two of the products.

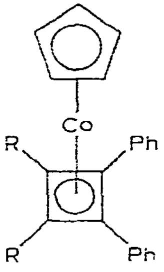
Synthesis and spectral considerations

The reaction between h^5-cyclopentadienyldicarbonylcobalt and phenyl-2-thienylacetylene in refluxing xylene has been found to produce a variety of organic and organometallic compounds, similar to the products described earlier for reactions involving diphenylacetylene [6] and phenylethynylsilane [5]. Separation and purification of the various products were achieved by a combination of column and thin-layer chromatography techniques, as well as by recrystallization.

The major product of the reaction, isolated from the first band in 78% yield, was a cyclobutadienecobalt complex thought to be I or II. As expected for such a complex, the product exhibited a multiplet for the aromatic protons and a singlet for the cyclopentadienyl protons, respectively, at τ 2.3—3.3 and 5.29 ppm (ratio 16/5).



(I)



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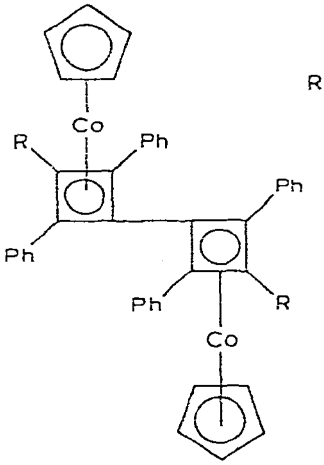
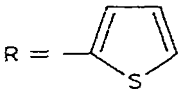


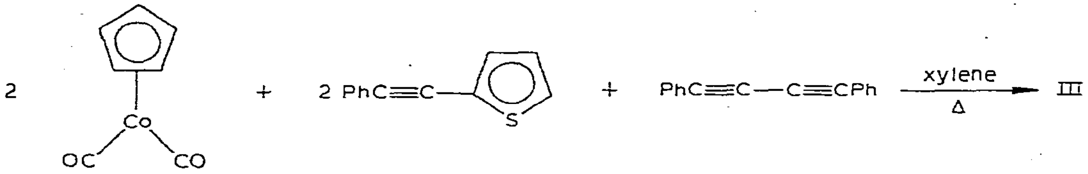
(III)



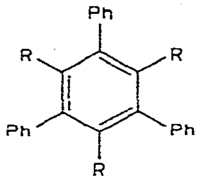
The mass spectrum of the product exhibited strong peaks for the molecular ion (M^+) at *m/e* 492 as well as for the loss of phenylthienylacetylene from M^+ at *m/e* 308. However, moderately strong peaks were also observed at *m/e* 314 and 302, which could correspond to losses of diphenylacetylene and dithienylacetylene, respectively, from M^+. Structural conclusions based on mass spectra of the product were therefore not as evident as in the case of *cis*- and *trans*-isomers of (h^5-cyclopentadienyl)-[h^4-diphenylbis(trimethylsilyl)cyclobutadiene]-cobalt [5]. For this reason, an X-ray crystallographic investigation was undertaken to determine the disposition of the substituents on the complexed cyclobutadiene ring (vide infra).

Continued elution of the column produced a second band which was shown by TLC to contain at least six products. The major product in this mixture was subsequently separated by preparative TLC, and was initially suspected to be the second cyclobutadienecobalt isomer (I or II) on the basis of a singlet cyclopentadienyl proton resonance at τ 5.25 ppm, its infrared spectrum and its melting point (238—239.5°C). However, the mass spectrum of the product indicated an intense molecular ion peak at m/e 818, indicating a more complex structure than either I or II. Consideration of the molecular ion peak at 818, together with a major peak at m/e 634 corresponding to loss of phenylthienylacetylene from M^+, suggested a binuclear structure such as III, which was conclusively verified by an X-ray crystallographic analysis (vide infra).

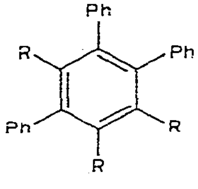
The origin of complex III in this reaction is still not completely clear. Our best explanation at present, however, is that the phenyl-2-thienylacetylene used in this reaction was contaminated with a small amount of diphenyldiacetylene, formed during the synthesis of the former acetylene from 2-iodothiophene and cuprous phenylacetylide [7] *. Diphenyldiacetylene is a common oxidative coupling product in reactions involving cuprous phenylacetylide [8—10], and a coreaction between phenyl-2-thienylacetylene and diphenyldiacetylene with h^5-cyclopentadienyldicarbonylcobalt could account for the formation of III.



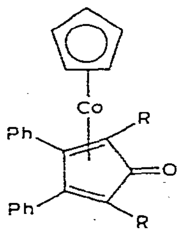
A high melting white solid was also isolated from the second band. The product was identified by elemental and mass spectral analyses as triphenyltri-2-thienylbenzene, a product of the cyclotrimerization of phenyl-2-thienylacetylene. Two isomeric hexasubstituted benzenes (IV and V) are theoretically possible in this reaction [2,4]. It is not known with certainty at the present time if the cyclotrimerization product is a pure isomer or a mixture of IV and V, al-



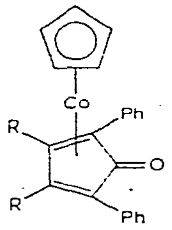
(IV)



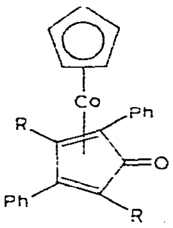
(V)



(VI)



(VII)



(VIII)

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* Phenyl-2-thienylacetylene and diphenyldiacetylene are virtually indistinguishable by TLC, and tend to cosublime when a mixture is heated in vacuo at 60°C. Subsequent preparations of phenyl-2-thienylacetylene by the literature method have invariably produced small amounts of diphenyldiacetylene as a contaminant, as evidenced by gas chromatography of the product [7].

though unsymmetrical products such as V are generally highly favored in reactions of this [11,12].

Elution of the column with benzene finally removed a deep red band which after evaporation of the solvent afforded 40 mg of a dark red solid. Three distinct singlet resonances were observed in the NMR spectrum of the product at τ 5.25, 5.21 and 5.15 ppm, corresponding to the three theoretically possible cyclopentadienonecobalt isomers (VI—VIII). A mass spectrum of the product showed an expected intense molecular ion peak at *m/e* 520 as well as other peaks that are characteristic of such complexes. Further separation of the product into the various isomers was not attempted.

Experimental

All melting points were taken in sealed capillaries under nitrogen and are uncorrected. CAMAG neutral alumina and silica were used for column and for thin-layer chromatography, respectively. h^5-Cyclopentadienyldicarbonylcobalt [6] and phenyl-2-thienylacetylene [7] were prepared according to literature methods. Elemental analyses were carried out by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts. NMR spectra were recorded on a Varian A-60 instrument, IR spectra on a Beckman IR-10 instrument, and mass spectra on a Perkin—Elmer—Hitachi RMU-6L instrument at 70 eV.

Reaction of h^5-cyclopentadienyldicarbonylcobalt and phenyl-2-thienylacetylene

Xylene (250 ml), phenyl-2-thienylacetylene (1.78 g, 10 mmol) and h^5-cyclopentadienyldicarbonylcobalt (869 mg, 5 mmol) were placed in a 500-ml, 3-necked flask equipped with a condenser, nitrogen inlet, bubbler, and magnetic stirrer. The flask was covered with aluminum foil, the mixture was degassed several times under nitrogen, and the contents heated at reflux for 24 h. At the end of this period, TLC indicated that all of the starting acetylene had been consumed. The reaction mixture was then allowed to cool to room temperature, filtered, and the filtrate was concentrated and placed on a 1" by 20" column of alumina which had been packed in hexane.

The first band (yellow) was eluted with a benzene/hexane (1/8) solvent mixture. After evaporation to dryness, band one yielded 1.92 g (78%) of (h^5-cyclopentadienyl)(h^4-*trans*-diphenyldi-2-thienylcyclobutadiene)cobalt (I). An analytical sample of this complex was obtained via recrystallization from benzene/heptane (8/1). After drying in vacuo at 100°C, deep red crystals of m.p. 231—232.5°C were obtained. NMR ($CDCl_3$) τ (ppm) 5.29 (s, 5 H, h^5-C_5H_5), 2.3—3.3 (m, 16 H, aromatic). IR (KBr) 3175—2900m, 1600s, 1500s, 1450m, 1210s, 1000m, 810s, 700s cm^{-1}. Mass spectrum *m/e* (%) 492 (100, M^+), 427 (2, $M - C_5H_5^+$), 368 (1, $M - C_5H_5Co^+$), 314 (30, $M - C_6H_5C_2C_6H_5^+$), 308 (100, $M - C_6H_5C_2C_4H_3S^+$), 302 (44, $M - C_4H_3SC_2C_4H_3S^+$), 190 (7, $C_4H_3SC_2C_4H_3S^+$), 184 (41, $C_6H_5C_2C_4H_3S^+$), 178 (4, $C_6H_5C_2C_6H_5^+$), 124 (100, $C_5H_5Co^+$).

Anal. Found: C, 70.88; H, 4.21; Co, 11.93; S, 13.00. $C_{29}H_{21}CoS_2$ calcd.: C, 70.72; H, 4.30; Co, 11.96; S, 13.02%.

Continued elution of the column with benzene/hexane (1/1) removed a second yellow band, which yielded 170 mg of a product consisting of six compounds as indicated by TLC. This mixture was transferred onto three silica preparative TLC plates (ca. 1.2 mm thickness), and the plates multiply eluted with benzene/hexane (1/1). The most abundant compound was contained in a yellow band of fourth highest R_f. This band was removed, extracted with methylene chloride, and evaporated to dryness. Recrystallization of the product from benzene/heptane followed by drying in vacuo at 100°C produced 15 mg of bis[(h^5-cyclopentadienyl)(h^4-*trans*-diphenyl-2-thienylcyclobutadienyl)cobalt] (III), m.p. 238—239.5°C. NMR ($CDCl_3$) τ (ppm) 5.35 (s, h^5-C_5H_5), 2.2—3.0 (m, aromatic). IR (KBr) 3175—2900m, 1600s, 1500s, 1450m, 1210m, 1000m, 810s, 700m cm^{-1}. Mass spectrum *m/e* (%) 818 (100, M^+), 753 (1, $M - C_5H_5^+$), 694 (5, $M - C_5H_5Co^+$), 634 (10, $M - C_6H_5C_2C_4H_3S^+$), 409 (10, M^{2+}), 184 (4, $C_6H_5C_2C_4H_3S^+$), 124 (36, $C_5H_5Co^+$), 59 (8, Co^+).

Anal. Found: C, 73.62; H, 4.64. $C_{50}H_{36}Co_2S_2$ calcd.: C, 73.34; H, 4.43%.

While attempting to dissolve band two in benzene, a small amount of an insoluble white material precipitated. This solid was dried in vacuo at ca. 100°C, and was found to sublime rather than melt at temperatures greater than 400°C. It has been identified as triphenyltri-2-thienylbenzene (IV and/or V).

Anal. Found: C, 78.20; H, 4.68; mol. wt., 552 (mass spectrometry). $C_{36}H_{24}S_3$ calcd.: C, 78.22; H, 4.38%; mol. wt., 552.

A third band (red) was subsequently eluted with benzene. Evaporation of the solvent produced 40 mg of a residue. The latter was dried in vacuo at ca. 150°C to afford the isomeric complexes of (h^5-cyclopentadienyl)(h^4-diphenyldi-2-thienylcyclopentadienone)cobalt (VI—VIII). NMR ($CDCl_3$) τ (ppm) 5.25 (s, h^5-C_5H_5), 5.21 (s, h^5-C_5H_5), 5.15 (s, h^5-C_5H_5), 1.9—3.0 (m, aromatic). IR (KBr) 3080m, 2910w, 1705m, 1600s, 1450m, 1230w, 820m, 760m, 690s cm^{-1}. Mass spectrum *m/e* (%) 520 (100, M^+), 492 (10, $M - CO^+$), 330 (8, $M - C_4H_3SC_2C_4H_3S^+$), 308 (30, $C_5H_5CoC_6H_5C_2C_4H_3S^+$), 302 (14, $C_5H_5CoC_6H_5C_2C_6H_5^+$), 260 (24, M^{2+}), 190 (20, $C_4H_3SC_2C_4H_3S^+$), 189 (44, $C_{10}H_{10}Co^+$), 184 (14, $C_6H_5C_2C_4H_3S^+$), 178 (32, $C_6H_5C_2C_6H_5$), 124 (40, $C_5H_5Co^+$).

Crystallographic studies

(h^5-Cyclopentadienyl)(h^4-trans-diphenyldi-2-thienylcyclobutadienyl)cobalt. Crystals suitable for X-ray studies were grown from benzene/heptane mixtures. Preliminary examination by precession and Weissenberg film methods showed that the crystals are monoclinic, space group $P2_1/c$ (systematic absence $h0l$ with l odd and $0k0$ with k odd). The crystal used for data collection was a pentagonal-shaped platelet with one elongated side parallel to the a axis. The long side was 0.25 mm and the directions perpendicular to it 0.20 mm and 0.1 mm. It was mounted on a CAD-4 computer controlled 4-circle diffractometer (Enraf—Nonius) with the a axis approximately parallel to the goniometer axis. Cell dimensions were determined from 25 accurately centered reflections by a least squares technique described previously [13]. The results were a = 10.193(5), b = 19.099(10), c = 12.513(6) Å and β = 112.08(2); V = 2257.3 Å^3. Assuming Z = 4, the calculated density is 1.449 g cm^{-3}. This compares to an observed density of 1.46 g cm^{-3} determined by flotation in an aqueous KI solution.

Intensity data were collected by the $\theta - 2\theta$ scan technique out to a value of $2\theta_{max}$ = 60° with monochromatized (graphite crystal) Mo-K_α (λ 0.7107 Å) radia-

(continued on p. 236)

TABLE I

Positional and Thermal Parameters for Compound I

Atom	x	y	z	β_{11}	β_{22}	β_{33}	$2\beta_{12}$	$2\beta_{13}$	$2\beta_{23}$
Co(1)	0.22066(12)	0.67656(6)	0.41719(9)	98(1)	23.1(3)	45.9(7)	1(2)	62(2)	-3(2)
C(1)	0.1346(13)	0.5987(6)	0.3063(9)	338(27)	57(6)	129(13)	-165(22)	275(31)	-115(15)
C(2)	0.1051(9)	0.6605(7)	0.2521(7)	153(17)	85(7)	61(8)	36(19)	15(19)	-78(13)
C(3)	0.2282(11)	0.6918(6)	0.2638(7)	311(23)	51(6)	57(8)	-18(19)	204(23)	12(11)
C(4)	0.3373(9)	0.6480(6)	0.3251(7)	128(15)	85(7)	80(9)	3(17)	140(20)	-61(13)
C(5)	0.2761(14)	0.5896(6)	0.3519(8)	418(31)	52(5)	78(10)	180(22)	189(30)	18(13)
C(6)	0.1727(7)	0.7591(4)	0.4883(6)	95(12)	19(3)	47(7)	13(10)	71(15)	-9(7)
C(7)	0.3210(7)	0.7378(4)	0.5473(5)	87(12)	22(3)	36(6)	7(10)	42(14)	-1(7)
C(8)	0.1226(7)	0.6944(3)	0.5198(6)	111(12)	14(3)	48(7)	-1(9)	61(15)	-7(7)
C(9)	0.2707(8)	0.6726(4)	0.5804(6)	85(9)	25(3)	39(5)	25(13)	47(11)	2(10)
C(10)	-0.0181(7)	0.6691(5)	0.5103(5)	102(12)	33(4)	42(6)	-11(13)	50(14)	6(9)
C(11)	-0.1299(7)	0.7161(4)	0.5172(6)	41(10)	29(3)	46(7)	-13(9)	44(14)	-8(8)
C(12)	-0.2507(8)	0.6748(6)	0.5052(7)	101(12)	63(5)	74(8)	2(18)	84(16)	-6(15)
C(13)	-0.2389(13)	0.6004(7)	0.4882(8)	273(23)	80(7)	71(10)	-209(22)	30(25)	27(14)
CS(1)	0.9301(4)	0.5885(2)	0.4881(4)	176(8)	30(2)	141(5)	8(6)	132(11)	-1(5)

C(14)	0.3378(8)	0.6141(4)	0.6565(6)	100(13)	22(3)	68(8)	11(11)	76(17)	-4(8)
C(15)	0.2757(9)	0.5792(5)	0.7231(7)	129(15)	33(4)	79(9)	-24(13)	102(19)	4(10)
C(16)	0.3653(15)	0.5242(5)	0.7893(8)	549(38)	20(4)	65(10)	-45(19)	164(32)	27(10)
C(17)	0.5021(14)	0.5196(7)	0.7662(9)	316(27)	66(6)	144(14)	288(23)	-284(30)	-109(16)
CS(18)	0.4902(5)	0.5807(3)	0.6677(4)	159(8)	75(3)	134(6)	41(8)	114(11)	20(7)
C(19)	0.4568(8)	0.7739(4)	0.5754(6)	106(13)	21(3)	89(9)	9(11)	112(18)	-7(9)
C(20)	0.5696(7)	0.7682(4)	0.6900(7)	43(10)	19(3)	96(9)	-25(9)	79(16)	-40(9)
C(21)	0.6812(9)	0.8109(6)	0.6963(7)	168(16)	49(5)	69(8)	78(16)	29(19)	-17(12)
C(22)	0.6841(11)	0.8502(5)	0.6097(10)	199(21)	31(5)	196(15)	15(15)	191(30)	-7(14)
C(23)	0.5801(15)	0.8518(7)	0.5122(10)	419(34)	67(7)	135(14)	172(25)	211(37)	67(16)
C(24)	0.4830(7)	0.8197(4)	0.4934(6)	50(9)	145(2)	62(6)	-28(10)	37(12)	-1(9)
C(25)	0.1068(7)	0.8252(5)	0.4373(6)	104(12)	30(3)	63(7)	17(13)	64(15)	21(10)
CS(26)	0.1588(6)	0.9004(3)	0.4903(5)	309(13)	79(3)	151(7)	-47(11)	193(15)	-16(8)
C(27)	0.0363(16)	0.9529(5)	0.3972(12)	548(39)	19(4)	280(21)	76(21)	654(52)	45(15)
C(28)	-0.0556(12)	0.9078(6)	0.3160(9)	285(25)	52(6)	136(13)	177(20)	179(30)	103(15)
CS(29)	-0.0334(6)	0.8290(3)	0.3247(4)	261(10)	69(3)	172(7)	41(11)	143(14)	70(9)

The form of the thermal ellipsoid here and in Table III is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + \beta_{12}hk + \beta_{13}h\ell + \beta_{23}k\ell)] \times 10^4$

tion at a 4° take-off angle. The scan rate was variable ranging from 6.7°/min for the strongest reflections to 0.67°/min for the weakest. The angular scan width was also variable and amounted to $3 \times (0.7 + 0.3 \tan \theta)^\circ$. The right and left backgrounds were scanned for half the time required for the total peak scan. During data collection an intensity control reflection was recorded every time a set of 24 reflections was collected. The change in intensity of this standard was random with a deviation about the mean amounting to no more than ±3%. A total of 6000 reflections were scanned in the hkl and $hk\bar{l}$ octants. Of these 2436 were found to have intensities equal to or greater than 3σ, where σ = (total counts + background counts)$^{1/2}$, and were considered to be observed. The data were corrected for Lorentz and double polarization effects but not for absorption. Since μR ranges from 0.18 to 0.09, an absorption correction was deemed unnecessary.

Solution and refinement of the structure. A three-dimensional Patterson map was prepared from which the positional parameters of the cobalt atom were deduced. After these initial parameters were subjected to a cycle of refinement $R(F)$ was 0.38. The posiitons of the other non-hydrogen atoms were then determined from successive Fourier and difference syntheses. However, difficulty was encountered in precisely defining the sulphur atoms of the thiophene rings as well as a carbon atom in one of the assumed phenyl rings. This difficulty was resolved by recognizing that the abnormal phenyl ring behaved, in reality, as a thiophene ring and that the sulfur atoms were disordered. The disorder was resolved by using a scattering factor of $\frac{1}{2}fc + \frac{1}{2}fs$ for atoms in certain ring positions. In ring 1 this hybrid scattering factor was applied to atom number 1, in ring 2 to atom 18 and in ring three to atoms 26 and 29. These atoms are designated in Table I as CS(1), CS(18), etc. Refinement, by the block diagonal least squares method with isotropic temperature factors *, now proceeded smoothly to an $R(F) = 0.10$. A difference synthesis revealed the positions of all the hydrogens and these were placed in their ideal positions [14]. Hydrogen atoms were not placed at positions required for bonding to CS type atoms. Refinement was now continued with anisotropic temperature factors for the heavy atoms and isotropic temperature factors, one unit higher than the heavy atom to which they were bonded, for the hydrogens. The final residual $R(F) = \Sigma||F_0| - |F_c||/\Sigma|F_0|$ was 0.06 and the weighted residual $Rw(F) = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{1/2}$ was 0.05. The function minimized in the refinement was $\Sigma w(|F_0| - |F_c|)^2$ with weights w assigned by the expression $w = 1/\{1 + [(|F_0| - 95)/50]^2\}$.

A final difference Fourier map revealed almost zero electron densities at atomic positions and a number of small peaks ($< 0.4\ e\text{Å}^{-3}$) randomly distributed throughout the map.

Neutral atom scattering factors for Co were taken from Cromer and Waber [15] and for the remaining atoms from the International Tables [16].

Table I contains the final positional parameters for the non-hydrogen atoms together with the anisotropic thermal parameters. Table II lists the final parameters for the hydrogen atoms calculated on the assumption of a carbon—hydro-

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* The programs used in this work were those of F.R. Ahmed, S.R. Hall, M.E. Pippy and C.P. Huber, NRC Crystallographic programs for the IBM 360, Division of Pure Physics, National Research Council, Ottawa, Canada, 1968.

TABLE II

Positional and Thermal Parameters for Hydrogen Atoms of Compound I

Atom	x	y	z	Biso
H (1)*	0.0624	0.5659	0.3098	7.49
H (2)	0.0122	0.6807	0.2110	6.19
H (3)	0.2358	0.7388	0.2526	5.31
H (4)	0.4386	0.6575	0.3460	5.98
H (5)	0.3268	0.5492	0.3948	7.76
H(11)	-0.1213	0.7669	0.5286	3.31
H(12)	-0.3367	0.6982	0.5064	6.12
H(13)	-0.3122	0.5655	0.4805	7.82
H(15)	0.1808	0.5916	0.7237	5.11
H(16)	0.3332	0.4959	0.8416	7.85
H(17)	0.5708	0.4838	0.8086	9.32
H(20)	0.5672	0.7389	0.7546	3.92
H(21)	0.7670	0.8108	0.7680	6.51
H(22)	0.7668	0.8817	0.6259	8.17
H(23)	0.5986	0.8834	0.4535	9.56
H(24)	0.4114	0.8239	0.4168	3.33
H(27)	0.0286	1.0034	0.3959	8.28
H(28)	-0.1426	0.9255	0.2506	7.97

*The numbers on the hydrogen atoms in this table and Table IV correspond to those of carbon atoms to which they are attached.

gen bond distance of 0.95 Å and ideal geometry. The numbering scheme used throughout is shown in Fig. 1 [17]. A table of structure factors is available *.

Bis[(h^5-cyclopentadienyl)(h^4-trans-diphenyl-2-thienylcyclobutadienyl)cobalt]. The experimental procedure was essentially the same as described above. The crystals are monoclinic, space group $C2/c$ based upon the systematic absences $h0l$ with l odd and hkl with $h + k$ odd. The unit cell dimensions are $a = 27.367(8)$, $b = 10.998(5)$, $c = 15.860(6)$ Å, $\beta = 128.45(2)°$ and $V = 4197.1$ Å^3. With $Z = 4$ the calculated density is 1.294 g cm^{-3} which compares to a measured density of 1.284 g cm^{-1}. Of 4500 reflections scanned out to $2\theta_{max} = 60°$, 1934 were found to have intensities greater than $3\sigma(I)$ and considered to be observed. The crystal used for the data collection was a rectangular parallelopiped 0.25 × 0.14 × 0.10 mm^3 and was mounted along a random direction but roughly parallel to the a axis.

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* The table of observed and calculated structure factors has been deposited as NAPS Document No. 03026. Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. A copy may be secured by citing the document number, remitting $ 6.00 for photocopies or $ 3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications.

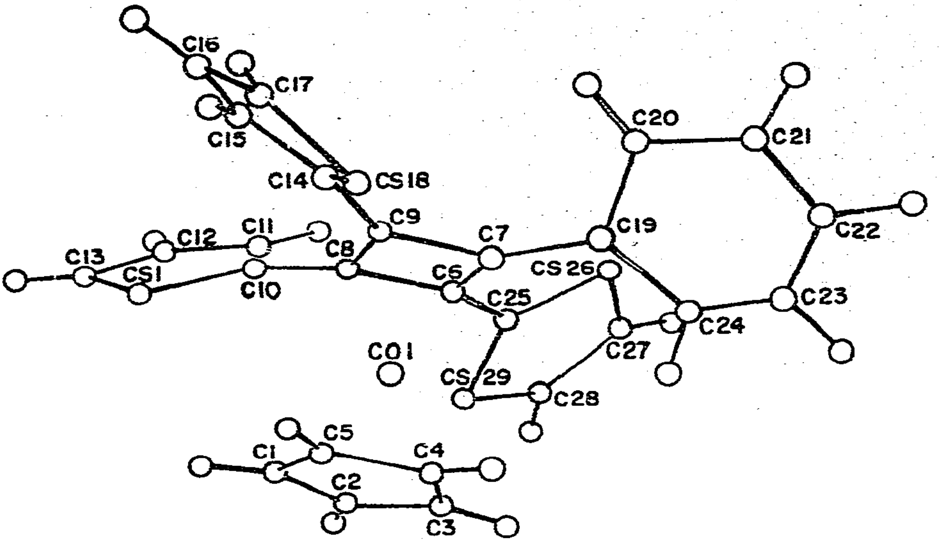

Fig. 1. Molecular structure and numbering scheme for compound I.

Solution and refinement of the structure. The positions of the cobalt atoms were obtained from a three dimensional Patterson map and those for the remaining non-hydrogen atoms from successive Fourier and difference maps. Hydrogen atom positions were calculated as before and assigned temperature factors one unit higher than those of the atoms to which they were bonded. Refinement with isotropic temperature factors converged to a final $R(F) = 0.094$. Inclusion of anisotropic thermal parameters reduced $R(F)$ to 0.055 and $Rw(F)$ to 0.05. The weighting scheme used was

$$w = 1/\{1 + [(|F_0| - 150)/50]^2\}$$

The final difference map showed only a random distribution of residual density with the highest peaks being in the order of 0.4 e Å^{-3}. In this crystal also the sulfur atoms were disordered so that a combination scattering factors $\frac{1}{2}fs + \frac{1}{2}fc$ had to be used.

The final positional parameters and anisotropic temperature factors are listed in Table III and the hydrogen atom positions in Table IV. *

Description of the crystal structures. For this discussion the trithienyl complex, originally thought to be either I or II, will still be referred to as compound I and the dimer as compound III. The molecular configuration of compound I is shown in Fig. 1 and its thermal motion in Fig. 2. Bond distances and angles are given in Table V. Similar information for compound III is shown in Figs. 3 and 4 and Table VII. As in other similar structures [5, 18, 19] the cyclopentadiene and cyclobutadiene rings of the present compounds are bonded to the metal in the *hapto* mode. The cyclobutadiene rings are planar (Tables VI and VIII) and square within the accuracy of the data. The average carbon—carbon bond distances in the 4-membered rings are 1.464(5) and 1.463(6) Å * for compounds I and III,

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* The values in parentheses following average values in the text are standard deviations of the mean calculated as $[\Sigma(X_i - \bar{X})^2/m(m-1)]$.

TABLE III

Positional and Thermal Parameters for Compound III

Atom	x	y	z	β_{11}	β_{22}	β_{33}	$2\beta_{12}$	$2\beta_{13}$	$2\beta_{23}$
Co(1)	0.14741(5)	-0.14599(10)	0.40921(8)	15.8(2)	51.8(8)	56.2(8)	7(1)	4.2(7)	14(2)
CS(1)	-0.04330(21)	-0.3345(5)	0.3828(4)	36(1)	115(6)	129(5)	2(5)	102(5)	23(9)
C(1)	0.1404(3)	-0.2224(7)	0.2876(6)	18(2)	45(7)	67(7)	3(7)	55(7)	6(12)
C(2)	0.1635(3)	-0.3090(6)	0.3767(6)	17(2)	46(8)	55(7)	2(7)	43(7)	-4(12)
C(3)	0.2211(3)	-0.2406(6)	0.4459(6)	14(2)	42(7)	66(7)	4(7)	49(6)	4(12)
C(4)	0.1982(3)	-0.1515(7)	0.3604(6)	18(2)	47(6)	62(6)	0(8)	53(6)	7(14)
C(5)	0.2265(4)	-0.0483(7)	0.3436(6)	22(2)	63(8)	48(7)	-19(7)	46(7)	-14(12)
C(6)	0.2834(4)	-0.0636(8)	0.3621(7)	18(2)	69(9)	79(8)	-5(8)	50(8)	12(13)
C(7)	0.1987(3)	0.0736(6)	0.3111(6)	24(2)	30(7)	68(7)	6(6)	68(7)	52(11)
C(8)	0.3080(4)	0.0373(9)	0.3494(7)	25(3)	133(12)	79(9)	-26(10)	59(9)	15(15)
C(9)	0.2784(5)	0.1410(9)	0.3193(7)	50(4)	90(10)	68(8)	-41(13)	68(9)	10(19)
C(10)	0.2219(5)	0.1471(14)	0.3003(8)	48(4)	278(19)	76(9)	128(18)	56(11)	-40(28)
C(11)	0.0866(4)	-0.0067(8)	0.3680(7)	25(3)	83(9)	81(8)	40(8)	69(8)	44(15)
C(12)	0.1465(4)	0.0273(7)	0.4594(7)	25(3)	51(8)	83(8)	9(8)	62(8)	-18(14)
C(13)	0.1642(4)	-0.0574(8)	0.5397(6)	24(3)	92(9)	55(7)	7(8)	49(8)	-14(14)
C(14)	0.0675(4)	-0.1124(8)	0.3916(7)	18(2)	94(11)	92(8)	14(8)	63(8)	13(15)
C(15)	0.1152(4)	-0.1420(9)	0.4978(6)	25(2)	96(9)	69(7)	17(10)	70(7)	21(18)
C(16)	0.0021(5)	-0.2915(13)	0.5103(9)	14(2)	358(3)	145(11)	42(13)	44(9)	391(29)
C(17)	-0.0232(4)	-0.1652(12)	0.5100(7)	50(4)	268(20)	79(9)	-178(16)	106(11)	-222(25)
C(18)	-0.0769(3)	-0.1263(7)	0.4011(5)	13(2)	74(9)	37(5)	12(7)	26(6)	-28(12)
C(19)	-0.0892(3)	-0.2228(7)	0.3274(6)	14(2)	66(8)	60(7)	-10(7)	42(7)	8(13)
C(21)	0.1420(4)	-0.4304(7)	0.3792(6)	18(2)	54(8)	46(7)	-10(7)	30(7)	-1(12)
C(22)	0.0860(3)	-0.4503(6)	0.3710(6)	14(2)	29(7)	70(7)	-12(6)	43(6)	-7(12)
C(23)	0.0698(5)	-0.5550(11)	0.3712(9)	33(4)	192(17)	122(12)	21(13)	80(11)	47(25)
C(24)	0.1006(5)	-0.6503(10)	0.3807(8)	40(3)	93(10)	131(10)	-27(13)	81(10)	-24(24)
C(25)	0.1524(6)	-0.6385(10)	0.3908(8)	49(4)	119(12)	145(12)	80(14)	117(12)	26(25)
C(26)	0.1743(4)	-0.5386(7)	0.3836(7)	18(2)	43(8)	110(9)	13(7)	63(7)	81(15)

TABLE IV

Positional and Thermal Parameters for Hydrogen Atoms

Atom	x	y	z	Biso
H (6)	0.3059	-0.1440	0.3847	5.04
H (7)	0.1604	0.0905	0.2998	2.77
H (8)	0.3476	0.0325	0.3621	5.48
H (9)	0.3003	0.2098	0.3147	7.18
H(10)	0.2013	0.2328	0.2631	9.07
H(11)	0.0622	0.0547	0.2983	5.48
H(12)	0.1702	0.0971	0.4659	4.78
H(13)	0.2046	-0.0574	0.6129	4.97
H(14)	0.0276	-0.1554	0.3408	5.05
H(15)	0.1148	-0.2098	0.5365	4.45
H(16)	0.0391	-0.3297	0.5767	8.19
H(17)	-0.0078	-0.1119	0.5726	7.26
H(18)	-0.0995	-0.0488	0.3794	3.44

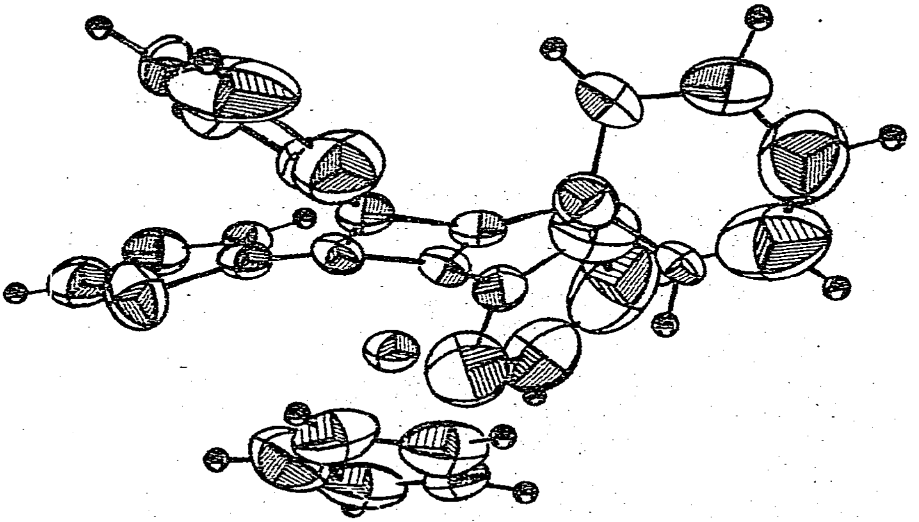

Fig. 2. Thermal ellipsoid plot at the 50% probability level for compound I.

TABLE V

Interatomic Distances (Å) and Angles (°) for Compound I

Bond	Dist.	Bond	Dist.
Co-C(1)	1.997(11)	C(6)-C(25	1.461(11)
C(2)	1.980(8)	C(7)-C(19)	1.458(11)
C(3)	1.972(9)	C(8)-C(10)	1.475(11)
C(4)	2.018(10)	C(9)-C(14)	1.460(11)
C(5)	2.023(11)		
C(6)	1.960(7)	Thiophene ring 1	
C(7)	1.953(7)	C(10)-C(11)	1.478(11)
C(8)	1.931(7)	C(11)-C(12)	1.421(12)
C(9)	1.911(7)	C(12)-C(13)	1.448(17)
		C(13)-CS(1)	1.739(14)
C(1)-C(2)	1.340(16)	CS(1)-C(10)	1.617(10)
C(2)-C(3)	1.347(16)		
C(3)-C(4)	1.372(14)	Thiophene ring 2	
C(4)-C(5)	1.379(16)	C(14)-C(15)	1.392(12)
C(5)-C(1)	1.348(19)	C(15)-C(16)	1.435(14)
		C(16)-C(17)	1.529(21)
C(6)-C(7)	1.468(11)	C(17)-CS(18)	1.668(13)
C(7)-C(9)	1.466(11)	CS(18)-C(14)	1.635(9)
C(8)-C(9)	1.472(11)		
C(6)-C(8)	1.448(10)	Thiophene ring 3	
		C(25)-CS(26)	1.587(11)
C(19)-C(20)	1.467(11)	CS(26)-C(27)	1.682(15)
C(20)-C(21)	1.379(13)	C(27)-C(28)	1.390(17)
C(21)-C(22)	1.327(14)	C(28)-CS(29)	1.520(13)
C(22)-C(23)	1.282(17)	CS(29)-C(25)	1.587(9)
C(23)-C(24)	1.111(16)		
C(24)-C(19)	1.458(10)		
Bond Angles			
C(5)-C(1)-C(2)	109(1)	C(8)-C(6)-C(7)	91.7(6)
C(1)-C(2)-C(3)	108(1)	C(6)-C(7)-C(9)	88.5(6)
C(2)-C(3)-C(4)	108.5(9)	C(7)-C(9)-C(8)	90.9(6)
C(3)-C(4)-C(5)	106.4(9)	C(9)-C(8)-C(6)	89.0(6)
C(4)-C(5)-C(1)	107(1)		
CS(1)-C(10)-C(11)	112.3(6)	CS(18)-C(14)-C(15)	113.2(7)
C(10)-C(11)-C(12)	108.2(6)	C(14)-C(15)-C(16)	111.3(8)
C(11)-C(12)-C(13)	116.3(9)	C(15)-C(16)-C(17)	111.2(9)
C(12)-C(13)-CS(1)	105.4(9)	C(16)-C(17)-CS(18)	106.3(9)
C(13)-CS(1)-C(10)	97.4(6)	C(17)-CS(18)-C(14)	97.7(9)
CS(29)-C(25)-CS(26)	112.2(6)	C(24)-C(19)-C(20)	116.3(6)
C(25)-CS(26)-C(27)	101.8(7)	C(19)-C(20)-C(21)	110.2(7)
CS(26)-C(27)-C(28)	105(1)	C(20)-C(21)-C(22)	124.0(9)
C(27)-C(28)-CS(29)	121(1)	C(21)-C(22)-C(23)	122(1)
C(28)-CS(29)-C(25)	99.7(6)	C(22)-C(23)-C(24)	123(1)
		C(23)-C(24)-C(19)	124.9(9)
C(6)-C(25)-CS(29)	122.7(6)	C(6)-C(8)-C(10)	133.6(7)
C(6)-C(25)-CS(26)	125.0(6)	C(6)-C(7)-C(19)	134.3(7)
C(7)-C(19)-C(20)	122.1(6)	C(7)-C(6)-C(25)	134.9(7)
C(7)-C(19)-C(24)	121.4(7)		
C(8)-C(10)-C(11)	123.0(6)	C(7)-C(9)-C(14)	135.0(7)
C(8)-C(10)-CS(1)	123.5(6)	C(8)-C(6)-C(25)	134.9(7)
C(9)-C(14)-C(15)	123.3(5)	C(8)-C(9)-C(14)	135.0(7)
C(9)-C(14)-CS(18)	123.0(6)	C(9)-C(7)-C(19)	136.5(6)
		C(9)-C(8)-C(10)	133.6(7)

(Continued)

TABLE V

Interatomic Distances (Å) and Angles (°) for Compound I (continued)

Torsion Angles	
C(6)-C(7)-C(19)-C(20)	-46.4
C(8)-C(6)-C(25)-CS(26)	-52.8
C(8)-C(9)-C(14)-C(15)	-54.4
C(9)-C(8)-C(10)-C(11)	-46.5

respectively and the average bond angles are 90.0° in both structures. These values compare very favorably with previously published data [5,18]. The average cobalt—carbon (C(4)) distances are 1.939(10) Å for compound I and 1.985(9) Å for compound III.

The cyclopentadiene rings are also planar and regular. Average Co—C and car-

TABLE VI

Mean Planes for Compound I with Deviations in Å Therefrom

A. Plane Containing C(1), C(2), C(3), C(4), C(5)
$0.3030x - 0.4350y - 0.8479z = -8.0057 \quad \chi^2 = 1.21$

C(1)	-0.002 (11)	C(4)	0.005 (9)
C(2)	0.005 (9)	C(5)	-0.003 (10)
C(3)	-0.006 (9)		

B. Plane Containing C(6), C(7), C(8), C(9)
$0.3300x - 0.4300y - 0.8403z = -11.1659 \quad \chi^2 = 1.59$

C(6)	-0.004 (7)	C(10)	-0.154 (7)
C(7)	0.004 (7)	C(14)	-0.157 (7)
C(8)	0.004 (7)	C(19)	-0.146 (8)
C(9)	-0.004 (7)	C(25)	-0.191 (7)

C. Thiophene ring 1
$0.0037x + 0.1552y - 0.9879z = -3.8301 \quad \chi^2 = 49.6$

C(10)	-0.043 (7)	C(13)	0.000(10)
C(11)	0.011 (7)	CS (1)	0.007 (5)
C(12)	0.025 (9)		

D. Thiophene ring 2
$-0.1851x - 0.6420y - 0.7441z = -13.2461 \quad \chi^2 = 15.7$

C(14)	-0.017 (8)	C(17)	-0.015(13)
C(15)	0.008 (9)	CS(18)	0.018 (6)
C(16)	0.007(10)		

E. Thiophene ring 3
$0.8268x + 0.0708y - 0.5580z = -2.5169 \quad \chi^2 = 1.25$

C(25)	-0.006 (7)	C(28)	0.004(12)
CS(26)	-0.003 (7)	CS(29)	-0.006 (6)
C(27)	0.000(16)		

F. Phenyl ring
$0.5761x - 0.7534y - 0.3170z = -12.1128 \quad \chi^2 = 0.79$

C(19)	-0.000 (8)	C(22)	0.004(10)
C(20)	-0.001 (7)	C(23)	-0.007(13)
C(21)	-0.001(10)	C(24)	0.004 (7)

TABLE VII
Interatomic Distances (Å) and Angles (°) for Compound III

Bond	Dist.	Bond	Dist.
Co-C(1)	1.995(9)	C(1)-C(2)	1.477(10)
C(2)	1.982(8)	C(2)-C(3)	1.448(12)
C(3)	2.002(9)	C(3)-C(4)	1.458(10)
C(4)	1.961(9)	C(4)-C(1)	1.470(12)
C(11)	2.041(10)		
C(12)	2.065(8)	C(11)-C(12)	1.402(14)
C(13)	2.058(9)	C(12)-C(13)	1.394(12)
C(14)	2.052(11)	C(13)-C(15)	1.408(14)
C(14)	2.064(10)	C(15)-C(14)	1.381(12)
		C(14)-C(11)	1.414(14)
C(21)-C(22)	1.470(15)	C(5)-C(6)	1.401(16)
C(22)-C(23)	1.231(15)	C(6)-C(8)	1.372(14)
C(23)-C(24)	1.289(18)	C(8)-C(9)	1.301(15)
C(24)-C(25)	1.323(22)	C(9)-C(10)	1.376(21)
C(25)-C(26)	1.289(16)	C(10)-C(7)	1.104(18)
C(26)-C(21)	1.453(13)	C(7)-C(5)	1.463(11)
CS(1)-C(19)	1.573(10)	C(1)-C(19)	1.450(11)
C(19)-C(18)	1.452(11)	C(2)-C(21)	1.463(11)
C(18)-C(17)	1.469(12)	C(4)-C(5)	1.483(13)
C(17)-C(16)	1.546(19)	C(3)-C(3')	1.451(10)
C(16)-CS(1)	1.649(12)		
Bond Angles			
C(4)-C(1)-C(2)	88.8(6)	C(14)-C(11)-C(12)	109.2(8)
C(1)-C(2)-C(3)	90.4(6)	C(11)-C(12)-C(13)	106.6(8)
C(2)-C(3)-C(4)	90.4(6)	C(12)-C(13)-C(15)	108.6(8)
C(3)-C(4)-C(1)	90.4(6)	C(13)-C(15)-C(14)	108.7(8)
		C(15)-C(14)-C(11)	106.9(8)
C(26)-C(21)-C(22)	116.7(8)		
C(21)-C(22)-C(23)	119.6(9)	C(16)-CS(1)-C(19)	101.1(6)
C(22)-C(23)-C(24)	123(1)	CS(1)-C(19)-C(18)	114.4(7)
C(23)-C(24)-C(25)	120(1)	C(19)-C(18)-C(17)	107.1(8)
C(24)-C(25)-C(26)	126(1)	C(18)-C(17)-C(16)	112.5(9)
C(25)-C(26)-C(21)	113.3(9)	C(17)-C(16)-CS(1)	104.9(9)
C(7)-C(5)-C(6)	116.6(8)		
C(5)-C(6)-C(8)	116.8(9)		
C(6)-C(8)-C(9)	120.6(9)		
C(8)-C(9)-C(10)	119(1)		
C(9)-C(10)-C(7)	127(1)		
C(10)-C(7)-C(5)	119.9(9)		
C(1)-C(19)-C(18)	124.6(8)	C(1)-C(2)-C(21)	131.1(6)
C(1)-C(19)-CS(1)	121.0(7)	C(3)-C(2)-C(21)	135.7(6)
C(2)-C(21)-C(22)	122.9(8)	C(2)-C(1)-C(19)	133.8(8)
C(2)-C(21)-C(26)	120.3(8)	C(4)-C(1)-C(19)	134.9(7)
C(4)-C(5)-C(6)	120.3(7)	C(3)-C(4)-C(5)	134.9(7)
C(4)-C(5)-C(7)	123.0(8)	C(1)-C(4)-C(5)	133.5(7)
		C(3)-C(3')-C(2')	135.7(8)
		C(3)-C(3')-C(4')	133.8(8)
Torsion Angles			
C(2)-C(1)-C(19)-CS(1)	-0.29		
C(4)-C(3)-C(3')-C(2')	-4.5		
C(1)-C(2)-C(21)-C(26)	-38.5		
C(1)-C(4)-C(5)-C(6)	-65.1		

TABLE VIII

Mean Planes for Compound III with Deviations in Å Therefrom

A. Plane Containing C(1), C(2), C(3), C(4)

$0.7825x - 0.5384y - 0.3127z = 0.9734$ $x^2 = 8.2$

C (1)	0.013(10)	C(3')	0.104(10)
C (2)	-0.013 (9)	C(5)	0.176(10)
C (3)	0.013 (9)	C(21)	0.219(9)
C (4)	-0.013 (9)	C(19)	0.175(10)

B. Cyclopentadiene ring

$0.7592x - 0.5772y - 0.3072z = -2.2743$ $x^2 = 0.80$

C(11)	-0.003(11)	C(14)	0.005(11)
C(12)	-0.000(10)	C(15)	-0.006(10)
C(13)	0.004(11)		

C. Phenyl ring containing C(5), C(6), C(7), C(8), C(9), C(10)

$0.1383x - 0.2510y - 0.9571z = -3.5573$ $x^2 = 7.51$

C (5)	0.002 (7)	C (8)	-0.007 (9)
C (6)	0.009 (8)	C (9)	-0.005 (9)
C (7)	-0.012 (8)	C(10)	0.016(10)

D. Phenyl ring containing C(21), C(22), C(23), C(24), C(25), C(26)

$0.0684x - 0.0507y - 0.9963z = -4.4128$ $x^2 = 45.1$

C(21)	-0.020 (7)	C(24)	0.005(10)
C(22)	-0.008 (8)	C(25)	-0.038(11)
C(23)	0.018(11)	C(26)	0.042 (9)

E. Thiophene ring

$0.8895x + 0.4395y - 0.1250z = 6.6006$ $x^2 = 0.18$

C(16)	-0.002(10)	C(19)	-0.002(10)
C(17)	-0.001(14)	CS (1)	0.002 (7)
C(18)	0.002 (9)		

bon—carbon distances are 1.998(10), 1.357(6) and 2.056(4), 1.400(6) Å for compounds I and III, respectively and both rings have average bond angles of 108.0°. The cobalt ring centroid distances are Co—R(C(4)), 1.639 Å and Co—R (C(5)), 1.630 Å for compound I and 1.694 Å and 1.676 Å for compound III. These bond distances in the case of compound I are somewhat low as are other interatomic distances in this complex. This may stem in part from the disorder and in part from the relatively high thermal motion exhibited by this complex. The cyclobutadiene and cyclopentadiene rings are nearly parallel making dihedral angles of 1.76° and 2.73° for compounds I and III, respectively.

The bond distances and angles observed for the groups attached to the cyclobutadiene ring deviate significantly from expected values. This undoubtedly stems from the severe disorder exhibited by the crystals. In spite of this disorder some interesting facts emerge from the data. All the rings are planar and are positioned such that the carbons bonded to the cyclobutadiene ring are below the plane of this ring in the direction away from the cyclopentadiene ring. These rings are also twisted about the carbon—carbon bonds linking them to the cyclobutadiene ring. The angle of twist is given as the appropriate torsion angle in

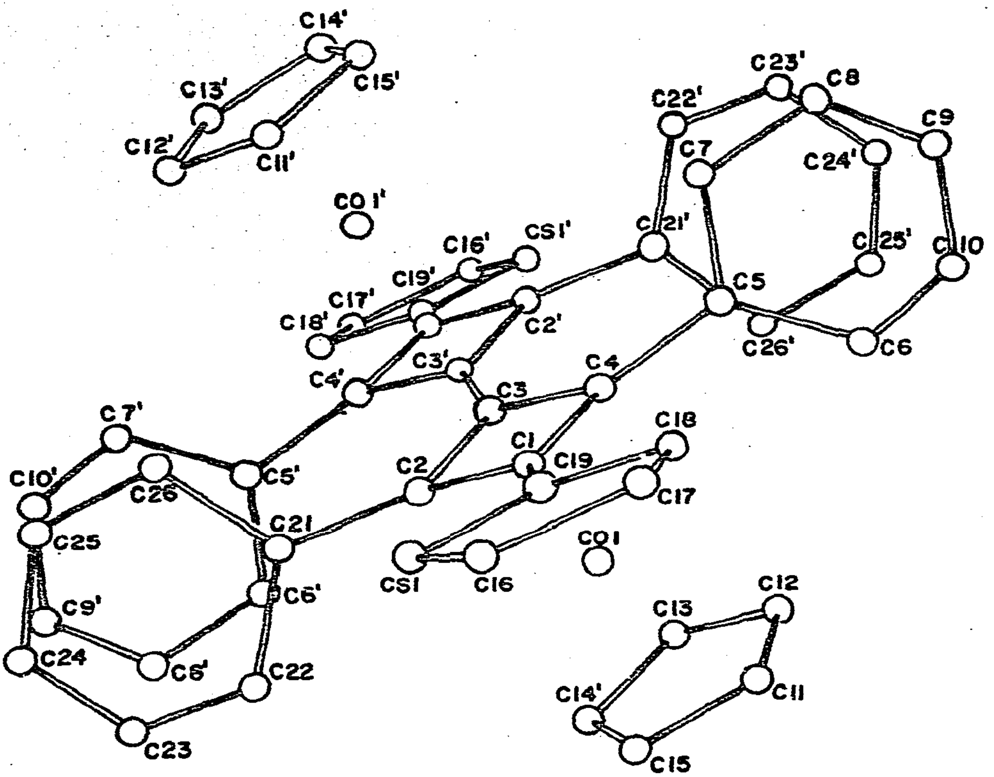

Fig. 3. Molecular structure and numbering scheme for compound III.

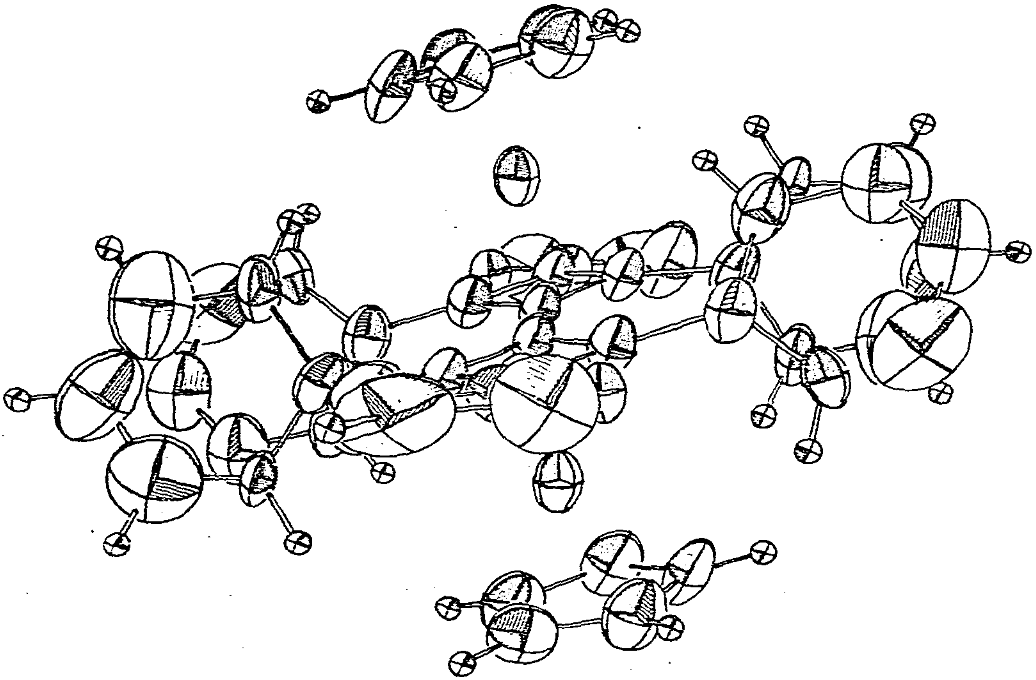

Fig. 4. Thermal ellipsoid plot at the 50% probability level for compound III.

Tables V and VII. A positive angle indicates clockwise rotation about the carbon—carbon bond when viewed from the cyclobutadiene group outward.

Some aspects of the disorder require comment. In the electron-density maps for compound I two rings attached to the cyclobutadiene group had one carbon atom each of higher electron density than the others. A third ring contained two such atoms. Placement of a full sulfur atom at the high density positions followed by refinement always resulted in a deep negative well at these positions. Thus, the hybrid scattering factor was adopted and this allowed normal refinement to proceed. In no case was it possible to identify any superposition of rings. However, examination of temperature factors is quite revealing in this respect. Carbon atoms C(20) and C(24) in the identifiable phenyl ring have much smaller temperature factors than the other ring atoms. On the other hand the atoms designated CS in the thienyl rings exhibit very high thermal motion for heavy atoms such as sulfur. These abnormal thermal parameters indicate a disorder involving phenyl and thienyl rings. That is, the actual ring distribution is two phenyls and two thienyls in harmony with analytical and mass spectroscopic data. However, the rings are scrambled in such a way as to give the observed electron densities.

One possible model indicated by the results is a mixture of *cis* and *trans* isomers. If rings in these positions are superposed, then two of the rings combine phenyl with a thienyl (or vice versa) and two rings are doubly weighted thienyl or phenyl. These doubly weighted rings are *cis* to each other corresponding to the thienyl group containing two CS type atoms and the phenyl ring in Fig. 1. Additional phenyl-thienyl disorder between these two groups is also indicated by the thermal parameters.

The observed bond distances and angles in the phenyl and thienyl rings reflect the disorder. All the CS—carbon bond distances except CS(1)—C(13) in compound I are shorter than expected for thiophene [20]. This shortening is to be expected for superposition of a phenyl group with a thienyl ring. At the same time some of the carbon—carbon bond lengths are longer than expected [20,21],

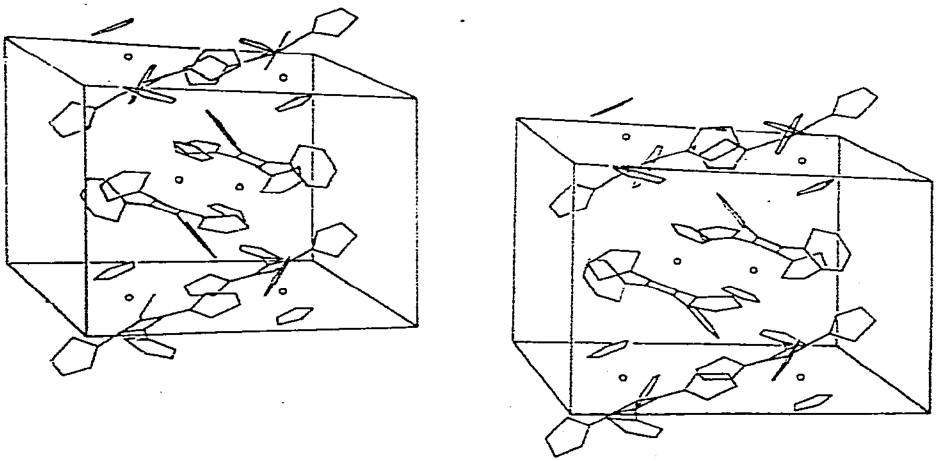

Fig. 5. Stereoview of packing in the unit cell of compound I.

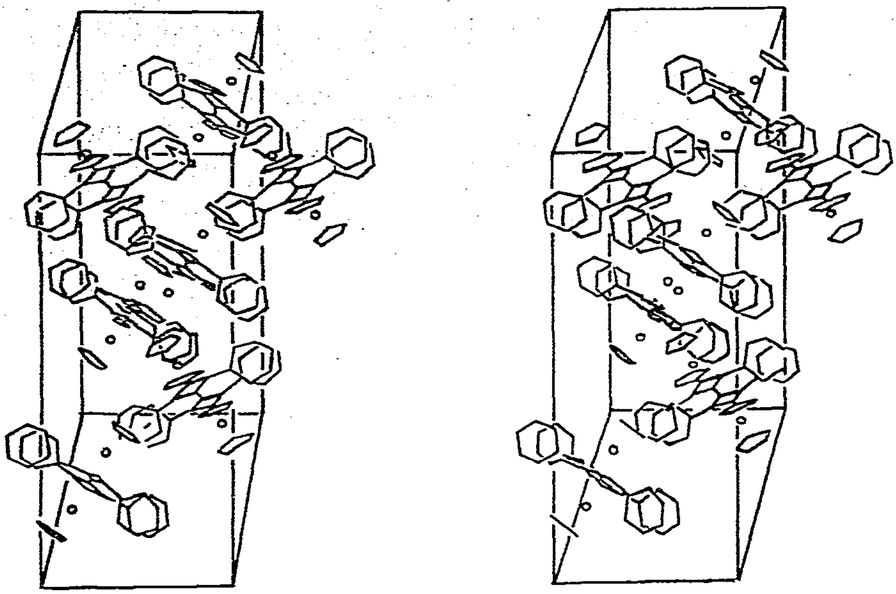

Fig. 6. Stereoview of molecular packing in the unit cell of compound III.

in particular C(10)—C(11) in compound I and C(16)—C(17) in both compound I and III. Interestingly the bond angle subtented at the CS atoms lie roughly halfway in between those expected for C—S—C and C—C—C in thiophene [20]. The phenyl rings in both complexes exhibited both shorter and longer bonds than expected. For example in compound I, C(23)—C(24) is very short while C(19)—C(24) is uncommonly long. However, the average bond distances and angles are very close to those ideally expected for a phenyl group. The disorder in compound III is not as severe as for compound I but still quite evident. The bond distances and thermal parameters show the same trends as for compound I.

Packing diagrams for the two crystals are shown in Figs. 5 and 6. There are no contacts less than 3.3 Å indicating no unusual intermolecular attractions.

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