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FORMATION AND CRYSTAL AND MOLECULAR STRUCTURE OF THE CHARGE-TRANSFER COMPLEX, TRICARBONYLPHENANTHRENE-CHROMIUM-1,3,5-TRINITROBENZENE

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Summary

Arenetricarbonylchromium compounds form 1/1 charge-transfer adducts with 1,3,5-trinitrobenzene in solution, but only a few of these are stable in the crystalline form. The synthesis and structure of a 1/1 adduct of phenanthrenetricarbonylchromium with 1,3,5-trinitrobenzene is reported. The crystal structure has been determined by X-ray analysis. Space group $P\bar{1}$ with a 10.37, b 13.73, c 17.24 Å and $Z = 2$. In the solid state the phenanthrene and benzene rings are parallel to each other. The structure is composed of stacks of alternating donor and acceptor molecules. The distances from the carbon atoms of the phenanthrene molecule to the mean plane of the trinitrobenzene molecule average at 336 pm, the distances from the carbonyl oxygen atoms to the mean plane of trinitrobenzene average at 269 pm.

Spectroscopic [1–4], crystallographic [1,5] and some theoretical investigations [6] of 1/1 charge transfer complexes of arenetricarbonylchromium compounds with 1,3,5-trinitrobenzene have usually involved monocyclic arenetricarbonylchromium systems. We describe below the 1/1 donor–acceptor adduct formed from phenanthrenetricarbonylchromium (hereafter denoted by $\text{Cr}(\text{CO})_3\text{Phen}$) and 1,3,5-trinitrobenzene (hereafter denoted by TNB).

Preparative results

$\text{Cr}(\text{CO})_3\text{Phen}$ gave an intense colour when mixed with TNB in methylene chloride. Slow evaporation of an equimolar methylene chloride solution of the

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TABLE 1
INFRARED FREQUENCIES

Compound ^a	Bands (cm ⁻¹) ^b			
	$\nu(\text{CO})$ a	$\nu(\text{NO}_2)$ b	$\delta(\text{CH})$ c	$\delta(\text{CrCO})$ d
$\text{Cr}(\text{CO})_3\text{Phen} \cdot \text{TNB}$	1957s 1877s	1342s	811w	668m
$\text{Cr}(\text{CO})_3\text{Phen}$	1940s 1860s		806m	658m
TNB		1343s		

^a Phen = phenanthrene; TNB = 1,3,5-trinitrobenzene. ^b s, strong; m, medium and w, weak.

components yielded the crystalline 1/1 adduct $\text{Cr}(\text{CO})_3\text{PhenTNB}$. The IR bands of the TNB are not appreciably shifted on complex formation (column b, Table 1); this is in agreement with one previous observation [1] but in contrast to some others [7,8]. Frequency shifts are observed however for the $\text{Cr}(\text{CO})_3\text{Phen}$ bands (column a, c, d, Table 1). The symmetrical CO stretching mode (column a) is shifted towards higher frequency, as would be expected if charge is withdrawn from the metal by charge-transfer complex formation. The metal—CO bending vibration (column d) is also shifted to higher frequency and the same explanation may apply. The frequency shift of the symmetrical C—H bending vibration (column c) of the π -bound phenanthrene ring may be attributed to enhancement of this bending mode by the proximity of the TNB molecule.

X-ray investigation

The title compound crystallises in space group $P\bar{1}$, with a 10.37, b 13.73, c 17.24 Å, α 140.6, β 113.9, γ 93.12° and $Z = 2$ at $T -100^\circ\text{C}$. The crystal structure was determined by the heavy atom method *. ($R_1 = 0.044$ on 2630 independent significant reflections).

The configurations of the $\text{Cr}(\text{CO})_3\text{Phen}$ and TNB molecules as projected onto the plane of the bonded side ring of the phenanthrene ligand are depicted in Fig. 1 and 2, respectively. A perspective representation of the arrangement of molecules within the crystal is shown in Fig. 3. The final atomic coordinates together with their estimated standard deviations (esd) are given in Table 2, anisotropic temperature factors are presented in Table 5. Table 3 shows some short intermolecular separations.

The molecular structure of $\text{Cr}(\text{CO})_3\text{PhenTNB}$ is closely related to that of other charge-transfer complexes, e.g. anisole tricarbonylchromium TNB [5] and aromatic molecules e.g. azulene-TNB [9], anthracene-TNB [10], with the donor—acceptor interaction involving the π -electrons of the aromatic ring. The aromatic donor—acceptor interactions are greatest when the rings are parallel and the ring centres are situated directly above each other. Small deviations

* Diffractometer: Syntex P-3, ω -scan, $\Delta\omega$ 1°, $1 \leq \omega \leq 29.3^\circ \text{ min}^{-1}$, $2 \leq 2\theta \leq 40^\circ$, λ -Mo 71.069 pm, Graphite monochromator. Structure solving system: Syntex-EXTL.

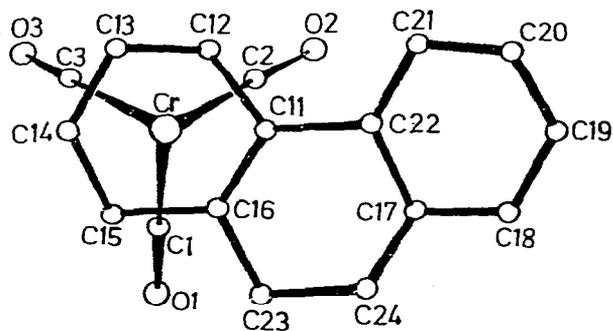


Fig. 1. Tricarboxylphenanthrenechromium fragment.

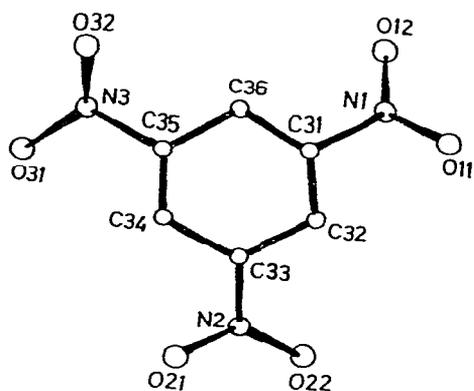


Fig. 2. Trinitrobenzene fragment.

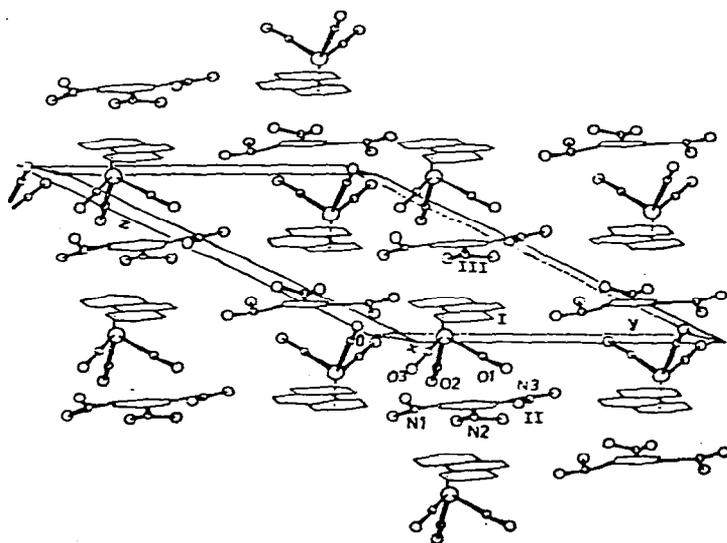


Fig. 3. General view of the arrangements of molecules. The symmetry labels have the following meaning: I, x, y, z ; II, $1-x, 1-y, -z$; III, $1-x, 2-y, 1-z$.

TABLE 2

FRACTIONAL ATOMIC COORDINATES (esd values in parentheses, atoms labeled as in Fig. 1 and 2)

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> (Å ²)
Cr	0.1726(1)	0.2784(1)	0.0888(1)	
O(1)	0.1871(4)	0.2823(4)	-0.0794(3)	
O(2)	-0.2272(3)	-0.0694(4)	-0.2296(3)	
O(3)	0.2426(4)	-0.0122(4)	-0.0775(4)	
C(1)	0.1801(4)	0.2797(5)	-0.0154(4)	2.43(6)
C(2)	-0.0728(5)	0.0640(5)	-0.1072(4)	2.53(6)
C(3)	0.2182(4)	0.1031(5)	-0.0097(4)	2.68(7)
C(11)	0.1071(4)	0.4619(4)	0.2440(4)	2.16(6)
C(12)	0.1408(4)	0.3681(5)	0.2514(4)	2.51(6)
C(13)	0.3040(4)	0.3978(5)	0.3096(4)	2.81(7)
C(14)	0.4372(4)	0.5161(5)	0.3573(4)	2.81(6)
C(15)	0.4047(4)	0.6018(5)	0.3438(4)	2.62(6)
C(16)	0.2411(4)	0.5786(5)	0.2891(4)	2.29(6)
C(17)	-0.0802(5)	0.5397(5)	0.1867(4)	2.61(6)
C(18)	-0.2323(5)	0.5333(5)	0.1476(5)	3.27(7)
C(19)	-0.3563(5)	0.4390(6)	0.1195(5)	3.60(8)
C(20)	-0.3322(5)	0.3483(6)	0.1285(5)	3.55(8)
C(21)	-0.1858(5)	0.3490(5)	0.1638(4)	2.78(7)
C(22)	-0.0576(4)	0.4447(5)	0.1935(4)	2.40(6)
C(23)	0.2071(5)	0.6662(5)	0.2741(4)	2.81(9)
C(24)	0.0548(5)	0.6461(5)	0.2244(4)	2.91(7)
C(31)	0.7183(4)	1.1830(5)	0.3497(4)	
C(32)	0.8755(4)	1.2053(5)	0.3953(4)	
C(33)	0.9042(4)	1.1133(5)	0.4018(4)	
C(34)	0.7856(4)	1.0050(5)	0.3666(4)	
C(35)	0.6307(4)	0.9877(5)	0.3212(4)	
C(36)	0.5921(4)	1.0750(5)	0.3114(4)	
N(1)	0.6821(4)	1.2796(4)	0.3422(4)	
O(11)	0.8045(4)	1.3985(5)	0.4011(4)	
O(12)	0.5346(4)	1.2382(5)	0.2811(5)	
N(2)	1.0707(4)	1.1327(4)	0.4493(3)	
O(21)	1.1025(3)	1.0656(4)	0.4695(3)	
O(22)	1.1650(3)	1.2128(4)	0.4636(3)	
N(3)	0.5001(4)	0.8732(4)	0.2830(4)	
O(31)	0.5181(4)	0.7693(4)	0.2629(4)	
O(32)	0.3822(4)	0.8890(5)	0.2735(4)	

from parallelism occurs in some complexes; thus for example in azulene-TNB the molecules are inclined at an angle of 2°, in anthracene-TNB the deviation is 8°, and anisole-tricarbonylchromium TNB the two aromatic planes are inclined to each other at 3°. In the present adduct, the planes of the phenanthrene ligand and the benzene ring of TNB are almost parallel (1.5°).

The perpendicular distance from the carbon atoms of the phenanthrene ligand to the mean plane of the TNB molecule range from 3.17 to 3.47 Å with an average of 3.36 Å. In aromatic donor-acceptor complexes the separations are shorter (perylene-fluoranyl, 3.23 Å; anthracene-TNB, 3.28 Å). The increase in the separation suggests a weakening of aromatic charge-transfer interaction in Cr(CO)₃Phen. TNB with respect to the adducts of free arenes. This can reasonably be ascribed to the strong electron-withdrawing capacity of the tricarbonylchromium group which leads to a decrease in the electron donor ability of the phenanthrene ligand. The distances from the carbonyl oxygen atoms to

TABLE 3

(A) INTERATOMIC DISTANCES (Å) AND BOND ANGLES $^{\circ}$ (degree) (esd values in parentheses)

C(1) —Cr	1.844(8)	C(17)—C(18)	1.407(9)	C(1)—Cr—C(2)	89.21
C(2) —Cr	1.843(5)	C(17)—C(22)	1.421(13)	C(1)—Cr—C(3)	87.77
C(3) —Cr	1.832(7)	C(18)—C(19)	1.381(12)	C(2)—Cr—C(3)	88.13
C(1) —O(1)	1.161(10)	C(19)—C(20)	1.393(15)	O(1)—C(1)—Cr	179.18
C(2) —O(2)	1.156(6)	C(20)—C(21)	1.383(10)	O(2)—C(2)—Cr	179.46
C(3) —O(3)	1.167(9)	C(21)—C(22)	1.405(11)	O(3)—C(3)—Cr	177.73
C(11)—Cr	2.282(5)	C(22)—C(11)	1.471(8)		
C(12)—Cr	2.223(6)	C(31)—C(32)	1.379(8)		
C(13)—Cr	2.223(7)	C(32)—C(33)	1.390(12)		
C(14)—Cr	2.232(4)	C(33)—C(34)	1.376(11)		
C(15)—Cr	2.220(5)	C(34)—C(35)	1.379(8)		
C(16)—Cr	2.262(6)	C(35)—C(36)	1.392(12)		
C(11)—C(12)	1.436(12)	C(31)—C(36)	1.392(10)		
C(12)—C(13)	1.397(9)	C(31)—N(1)	1.482(12)		
C(13)—C(14)	1.412(11)	C(33)—N(2)	1.479(8)		
C(14)—C(15)	1.399(13)	C(35)—N(3)	1.478(10)		
C(15)—C(16)	1.431(8)	N(1) —O(11)	1.214(10)		
C(11)—C(16)	1.435(10)	N(1) —O(12)	1.202(8)		
C(11)—C(22)	1.471(8)	N(2) —O(21)	1.230(11)		
C(16)—C(23)	1.447(13)	N(2) —O(22)	1.223(9)		
C(23)—C(24)	1.339(9)	N(3) —O(31)	1.228(11)		
C(24)—C(17)	1.444(11)	N(3) —O(32)	1.220(8)		

$^{\circ}$ The remaining bond angles are close to their standard values, and are mentioned in the text where appropriate.

the mean plane of the TNB molecule range from 2.55 to 2.88 Å (average 2.69 Å). Thus it can be concluded that the electron donation by Cr(CO)₃Phen in the charge-transfer complex involves both the aromatic ring and tricarbonyl-chromium group. Enhanced donation from the carbonyl groups as evidenced by the short distances is in conflict with the usual assumptions, but there is an analogy in formation of the Lewis acid—metal carbonyl adducts at the CO ligand [11,12].

Of the three carbonyl groups, C(1)—O(1) is involved in the minimum separations with the TNB molecule. The distances of C(1) and O(1) are especially short with the atoms N(2), O(21), O(22), C(32), C(33) (C(1)—N(2), 3.46; O(1)—N(2), 2.94; C(1)—C(33), 3.67; O(1)—C(33), 3.13 Å). The phenanthrene ligand makes short contacts to the TNB molecule with all its carbon atoms, the shortest distances being: C(12)—N(1), 3.48; C(18)—N(2), 3.56; C(23)—N(3), 3.46;

TABLE 4

INTERMOLECULAR DISTANCES (Å) $^{\circ}$ (≤ 3.5 Å)

C(1) —N(2) ^{II}	3.46	O(2) —O(22) ^{II}	3.24
C(1) —O(22) ^{II}	3.52	O(3) —C(32) ^{II}	3.20
O(1) —C(33) ^{II}	3.13	C(11)—C(31) ^{III}	3.48
O(1) —C(34) ^{II}	3.35	C(11)—C(36) ^{III}	3.47
O(1) —N(2) ^{II}	2.94	C(12)—N(1) ^{III}	3.48
O(1) —O(21) ^{II}	3.08	C(16)—C(36) ^{III}	3.44
O(1) —O(22) ^{II}	3.39	C(17)—C(34) ^{III}	3.49
C(22)—O(22) ^{II}	3.45	C(21)—C(32) ^{III}	3.43

$^{\circ}$ II and III indicates the symmetry operations as depicted in Fig. 3.

TABLE 5
 ANISOTROPIC TEMPERATURE FACTORS ^a

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr(1)	1.61	1.79	1.89	1.00	1.15	1.58
O(1)	4.03	3.28	3.24	3.27	2.68	2.89
O(2)	2.03	3.12	2.85	0.92	1.25	2.35
O(3)	5.12	4.20	4.86	3.68	3.96	4.05
C(31)	2.62	2.20	2.20	1.61	1.75	1.96
C(32)	2.20	2.16	2.08	1.18	1.48	1.82
C(33)	2.14	2.30	1.91	1.45	1.42	1.77
C(34)	2.83	2.27	2.08	1.57	1.65	1.90
C(35)	2.53	2.20	2.12	1.22	1.58	1.84
C(36)	2.18	2.37	2.10	1.37	1.48	1.89
N(1)	3.21	3.45	3.70	2.33	2.52	3.27
O(11)	4.71	6.12	8.86	3.66	4.76	7.04
O(12)	4.24	7.68	8.56	4.50	4.60	7.72
N(2)	2.40	2.76	2.44	1.60	1.61	2.13
O(21)	3.80	4.31	3.85	3.05	2.57	3.67
O(22)	3.07	5.02	5.25	2.76	3.17	4.53
N(3)	2.97	3.29	3.27	1.59	2.04	2.91
O(31)	4.21	4.77	5.97	2.51	3.26	5.02
O(32)	4.41	6.04	7.21	3.52	4.56	6.07

^a The temperature factor is defined by $T = \exp[-\frac{1}{3}(h^2a^{*2}B_{11} + \dots + 2hka^*b^*B_{12} + \dots)] B$ in \AA^2 .

C(16)—C(36); 3.44; C(21)—C(32), 3.43 \AA .

The structure of the $\text{Cr}(\text{CO})_3\text{Phen}$ part of the adduct is very similar to that of free $\text{Cr}(\text{CO})_3\text{Phen}$ [13]. The tricarbonylchromium fragment has an approximate C_{3v} symmetry. The carbonyl groups are almost linear and roughly perpendicular to each other though not to the same extent as in free $\text{Cr}(\text{CO})_3\text{Phen}$ (Table 2). The Cr—C—O moieties are linear [14].

The chromium atom is attached to an outside ring of the phenanthrene ligand. The dihedral angle between the plane of the phenanthrene nucleus and that defined by carbonyl C (or O) atoms is 4.2° (for free $\text{Cr}(\text{CO})_3\text{Phen}$, the value is 5°). The bonded outside ring of the phenanthrene ligand is inclined to this plane defined by carbonyl C (or O) atoms by only 1.1° . The angle between the plane of the bonded side ring and the mean plane through the non-bonded part is 4.7° (for free $\text{Cr}(\text{CO})_3\text{Phen}$, the value is 3.8°).

The mean C—C bond lengths in the bonded side ring and the non-bonded side ring of the phenanthrene ligand are 1.418 and 1.398 \AA . The difference in the bond lengths is similar but not exactly the same as that in free $\text{Cr}(\text{CO})_3\text{Phen}$. The mean C—C bond length in the centre ring of the phenanthrene ligand is 1.426 \AA . The C(17)—C(24) bond length which is shorter in $\text{Cr}(\text{CO})_3\text{Phen}$, has increased to 1.444 \AA (Table 2). The bond angles C(12) C(11) C(22) and C(11) C(22) C(21) are equal to 122.95 and 121.75° , respectively.

In the benzene ring of the TNB molecule the valency angles at the carbon atoms bearing the nitro groups are appreciably larger (average value 123.17°) than those at the carbon atoms bearing hydrogen atoms (average value 116.83°). This effect occurs also in other aromatic nitro compounds.

The reason may lie in the strong electron-withdrawing power of the nitro group [5]. The angles between the benzene ring plane of the TNB molecule and

the mean planes of the individual nitro groups are 10.5° (with O(11) N(1) O(12)), 6.8° (with O(21) N(2) O(22)) and 12.6° (with O(31) N(3) O(32)).

Experimental

The $\text{Cr}(\text{CO})_3\text{Phen}$ complex (0.29 g, 1.00 mmol) is ground with TNB (0.21 g, 1.00 mmol), 3 ml of methylene chloride is added, and the solution filtered through a small layer of silica gel. On slow evaporation of the dark red solution the adduct separates as dark red crystals. These are filtered off, washed with a little methylene chloride, and dried under vacuum. Yield 63%. The adduct is stable in air but the solution must be handled under dry nitrogen. M.p. $93-94^\circ\text{C}$. Found: C, 52.20; H, 2.47; N, 7.77; Cr, 9.40. $\text{C}_{23}\text{H}_{13}\text{CrN}_3\text{O}_6$, calcd.: C, 52.37; H, 2.47; N, 7.97 and Cr, 9.87%.

Infrared spectra were determined as K Br discs on a Perkin-Elmer Model 621 spectrometer.

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