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Hexamethylbenzene–Tetracyanoethylene (1:1) Complex

By Masao Saheki, Haruka Yamada, Hiroshi Yoshioka and Kazumi Nakatsu
Faculty of Science, Kwansei Gakuin University, Uegahara Nishinomiya, Hyogo 662, *Japan*

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Abstract. Hexamethylbenzene(HMB)–tetracyanoethylene(TCNE), $C_{12}H_{18}.C_6N_4$, triclinic, $P\bar{1}$, $a=8{\cdot}868$ (5), $b=8{\cdot}820$ (4), $c=6{\cdot}705$ (4) Å, $\alpha=77{\cdot}56$ (6), $\beta=113{\cdot}18$ (6), $\gamma=119{\cdot}21$ (3)°, $Z=1$, $D_x=1{\cdot}146$ g cm^{-3}. Centrosymmetric planar component molecules are stacked alternately in columns parallel to **c**. Both molecular planes are perpendicular to **c**, the interplanar separation being 3·35 Å. The TCNE residues are disordered in two perpendicular orientations about the plane normal with relative occupancies of 3:1.

Introduction. The needle-shaped purple black crystals elongated along **c** were obtained by evaporating the solvent from an ether solution containing equimolar amounts of HMB and TCNE. The unstable specimen with approximate dimensions $1{\cdot}0\times0{\cdot}2\times0{\cdot}1$ mm was sealed in a thin-walled capillary tube and used for the intensity measurement. The intensities of unique reflexions out to $2\theta=50°$ were measured on an automatic four-circle diffractometer using Zr-filtered Mo $K\alpha$ radiation in the $\omega-2\theta$ scan mode. 1394 reflexions were measured, and of those 684 reflexions with $|F_o|>3\sigma(F)$ were considered observed and were used in the structure analysis.

The structure was solved by the Patterson method. A difference Fourier map revealed a partially disordered TCNE(*B*), which is almost perpendicular to the higher weight TCNE(*A*) with the common normal. The structure was refined by the block-diagonal least-squares method with several different relative occupancies for the TCNE's; the cyano C atoms were assumed to be at the same positions in both the TCNE's. Reasonable bond lengths and the minimum *R* value were obtained when the occupancy factors of 0·75 and 0·25 were assigned to TCNE(*A*) and (*B*) residues, respectively. On the other hand, the HMB residue was definitely ordered, but the H atoms could not be found, probably because of rotational motion of the methyl groups. Subsequent refinement with anisotropic thermal parameters converged to a final conventional *R* value of 0·104. Unit weight was given to all the reflexions. All the numerical calculations were carried out on a FACOM 270–20 computer of this university with programs written in our laboratory. Figs. 1 and 2 were drawn with the aid of the program *DEAM* (A. Takenaka, private communication). The final atomic parameters are listed in Table 1.*

Discussion. HMB and TCNE form (1:1) and (2:1) charge-transfer complexes in the crystalline state. Infrared spectra of the complexes (Moszyńska & Tramer, 1967; Hall & Devlin, 1967; Saheki & Yamada, 1976) showed new bands which appeared on the complex formation. To provide a structural basis for the spectroscopic studies we undertook an X-ray structure analysis of the (1:1) complex.

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* The table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31449 (6 pp.). Copies may be obtained from the authors or through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Fractional atomic coordinates* ($\times10^3$) *and thermal parameters* ($\times10^3$ Å^2)

$T=\exp\,[-2\pi^2(a^{*2}h^2U_{11}+b^{*2}k^2U_{22}+c^{*2}l^2U_{33}+2a^*b^*hkU_{12}+2b^*c^*klU_{23}+2a^*c^*hlU_{13})]$. The e.s.d.'s of the least significant digit are given in parentheses.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
C(1)	614 (1)	678 (1)	7 (1)	61 (6)	38 (5)	45 (5)	12 (5)	−6 (4)	21 (4)
C(2)	691 (1)	563 (1)	81 (1)	36 (5)	67 (6)	45 (5)	22 (5)	−5 (4)	13 (4)
C(3)	577 (1)	384 (1)	74 (1)	70 (6)	55 (6)	39 (5)	41 (5)	5 (4)	18 (4)
C(4)	738 (2)	878 (1)	15 (2)	98 (9)	33 (6)	120 (10)	0 (6)	−5 (6)	50 (8)
C(5)	901 (1)	633 (2)	172 (2)	32 (6)	140 (11)	92 (9)	26 (7)	−19 (8)	13 (6)
C(6)	661 (2)	253 (2)	156 (2)	117 (10)	100 (9)	88 (8)	95 (8)	21 (7)	34 (7)
TC(1)	459 (2)	416 (2)	503 (2)	57 (9)	76 (9)	54 (8)	28 (8)	−4 (8)	18 (7)
TC(2)	565 (2)	317 (1)	588 (2)	83 (8)	80 (8)	62 (7)	47 (7)	10 (5)	28 (6)
TC(3)	253 (1)	327 (1)	421 (2)	63 (7)	89 (8)	64 (7)	34 (6)	−11 (6)	16 (5)
TN(1)	639 (2)	235 (2)	649 (2)	75 (9)	85 (9)	90 (9)	44 (8)	4 (7)	25 (7)
TN(2)	103 (2)	259 (2)	358 (2)	58 (8)	96 (10)	95 (10)	26 (7)	−14 (8)	16 (7)
TDC(1)†	417 (5)	497 (5)	460 (6)	59 (26)	61 (24)	66 (26)	8 (23)	−11 (20)	46 (23)
TDN(1)†	565 (4)	183 (3)	625 (4)	29 (15)	36 (16)	56 (18)	0 (13)	−2 (13)	8 (13)
TDN(2)†	114 (4)	201 (4).	392 (5)	54 (20)	34 (18)	66 (21)	6 (15)	−11 (14)	3 (16)

† TDC and TDN refer to the atoms in the lower weight TCNE(*B*)'s (see Fig. 3).

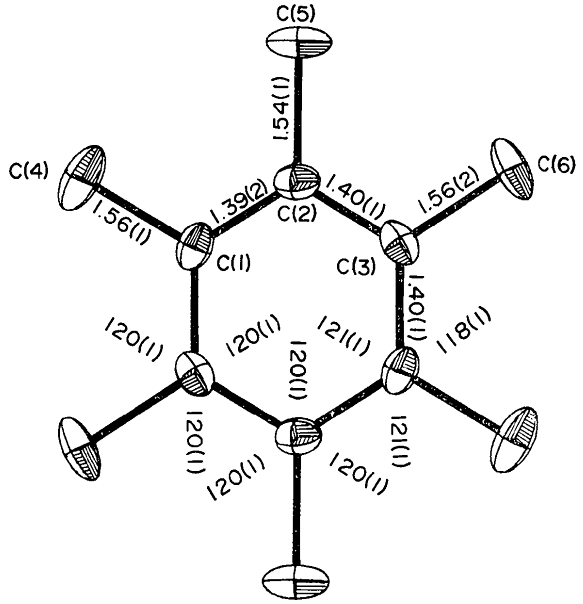

Fig. 1. Bond lengths and angles of HMB.

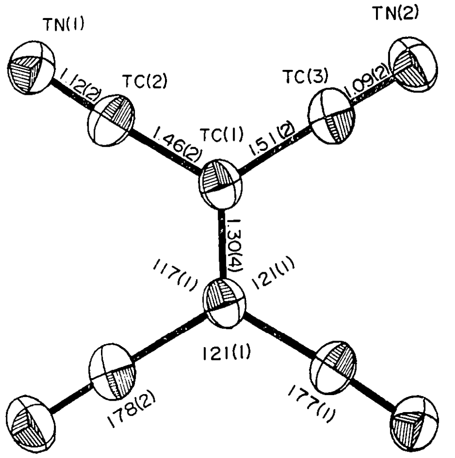

Fig. 2. Bond lengths and angles of higher weight TCNE (*A*).

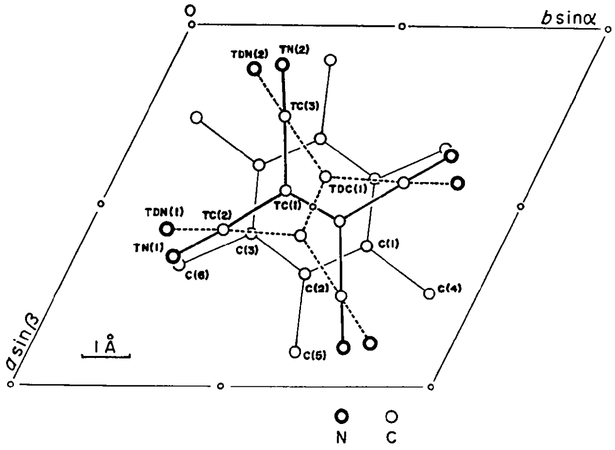

Fig. 3. Crystal structure viewed along **c**. TCNE (*A*) is shown by solid lines, TCNE (*B*) by broken lines.

The structures of the component molecules are shown in Figs. 1 and 2. Each residue is planar, the root-mean-square deviations being 0·01, 0·01 and 0·02 Å for the HMB, higher weight TCNE(*A*) and lower weight TCNE(*B*) residues, respectively. The dimensions of the HMB residue are normal and may be compared with those of the free HMB (Brockway & Robertson, 1939) and of the HMB's in the complexes with chloranil (Harding & Wallwork, 1955; Jones & Marsh, 1962) and 1,2,4,5-tetracyanobenzene (Niimura, Ohashi & Saito, 1968). On the other hand, in the TCNE(*A*) residue the bond distances and angles are somewhat different from the average values found in the free (Bekoe & Trueblood, 1960; Little, Pautler & Coppens, 1971) and complexed TCNE's (Williams & Wallwork, 1967; Ikemoto & Kuroda, 1968; Ikemoto, Yakushi & Kuroda, 1970; Bernstein & Trueblood, 1971); the discrepancies are, however, not fully significant owing to the rather large e.s.d.'s. The TCNE(*B*) residue will not be discussed because of the imprecise determination.

The crystal structure viewed along **c** is shown in Fig. 3. The component molecules occupy the centres of symmetry at $(\frac{1}{2},\frac{1}{2},0)$ and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, and are stacked on top of each other to form a column along **c**. The molecular planes are parallel to each other (the dihedral angle between the planes of HMB and TCNE(*A*) residues is 0·4°) and perpendicular to **c**. The interplanar separation is 3·35 Å, which is less than the normal van der Waals separation but somewhat larger than the separations found in aromatic molecule–TCNE complexes: 3·30 Å in naphthalene–TCNE (Williams & Wallwork, 1967), 3·323 Å in pyrene–TCNE (Ikemoto & Kuroda, 1968), 3·186 Å in perylene–TCNE (Ikemoto, Yakushi & Kuroda, 1970) and 3·20 Å in [3,3]-paracyclophane–TCNE (Bernstein & Trueblood, 1971). The present large separation would be due to the rotating bulky methyl groups. The columns are assembled in a closest packing manner with the usual van der Waals contacts between them. Thus the arrangement of donor and acceptor molecules in the present crystal corresponds rather to the type *C* than to the type *A* in Prout & Wright's (1968) classification of π–π complexes.

The perpendicular arrangement of TCNE(*A*) and (*B*) residues closely resembles that found in [3,3]paracyclophane–TCNE (Bernstein & Trueblood, 1971). The jumping motion between the sites of TCNE(*A*) and (*B*) residues about the plane normal is prohibited because of steric hindrance between the columns. The orientation of the TCNE(*A*) residue with respect to the HMB residue is very similar to that of the TCNE with the benzene ring in naphthalene–, pyrene–, perylene–, [3,3]paracyclophane–TCNE complexes, and deviates only 9° from that obtained on the basis of energy calculations by Kuroda, Amano, Ikemoto & Akamatu (1967) for naphthalene–, and pyrene–TCNE complexes, and by Herndon & Feuer (1968) for 1,3,5- and 1,2,3-trimethylbenzene–TCNE complexes. No calculation of the charge-transfer interaction for the present complex has been carried out.

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N-Methylaminoethanolatobis(ethylenediamine)cobalt(III) Perchlorate Monohydrate

BY H. MIYAMAE, T. NISHIDA,* K. OGINO,† S. SATO AND Y. SAITO

The Institute for Solid State Physics, The University of Tokyo, Roppongi-7, Minato-ku, Tokyo 106, Japan

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Abstract. Rac-[Co(*N*-Me-eta) (en)$_2$] (ClO$_4$)$_3$.H$_2$O, triclinic, $P\bar{1}$, $a=9{\cdot}091$ (3), $b=13{\cdot}689$ (3), $c=8{\cdot}665$ (3) Å, $\alpha=96{\cdot}34$ (3), $\beta=125{\cdot}52$ (2), $\gamma=76{\cdot}72$ (3)°, $Z=2$, $D_m=1{\cdot}75$, $D_x=1{\cdot}75$ g cm^{-3}. The cobalt atom is surrounded nearly octahedrally by five nitrogen atoms and an oxygen atom. Average Co–N distance is 1·976 (4) Å and Co–O is 1·879 (4) Å. The Co–N–C(methyl) angle of 121·4 (4)° is largely deviated from the normal tetrahedral angle owing to the repulsion between the methyl carbon atom and the amino nitrogen atoms.

Introduction. Red-purple platy crystals were grown from an aqueous solution. Intensities and cell dimensions were measured on a Rigaku automated four-circle diffractometer with a crystal of dimensions $0{\cdot}1\times0{\cdot}3\times0{\cdot}3$ mm. Data were collected by the ω–2θ scan technique to a maximum 2θ value of 55° with Mo $K\alpha$ radiation ($\lambda=0{\cdot}7107$ Å) monochromated by a graphite plate. 5223 reflexions were measured of which 3663 ($|F|>3\sigma$) were classified as 'observed'. The intensities were corrected for Lorentz–polarization factors. No correction was made for absorption [μ(Mo $K\alpha$)$=13{\cdot}5$ cm^{-1}]. All the positions of non-hydrogen atoms were located by routine Patterson and Fourier syntheses assuming space group $P\bar{1}$. Refinement of the structure was carried out by block-diagonal least-squares techniques. Positional parameters of the non-hydrogen atoms were refined with anisotropic thermal factors. The structure converged at $R=0{\cdot}073$. A difference synthesis gave the positions of all the hydrogen atoms: during further refinement the atomic parameters of the hydrogen atoms were allowed to vary by assuming isotropic thermal motion. The final discrepancy index (3663 reflexions) became 0·054. A final difference map showed no peaks greater than 0·6 e Å^{-3}. The atomic scattering factors for non-hydrogen atoms were those listed in *International Tables for X-ray Crystallography* (1962). For hydrogen atoms the values given by Stewart, Davidson & Simpson (1965) were used. Atomic coordinates and thermal parameters are listed in Table 1.‡

The bond lengths and angles are listed in Tables 2 and 3. A projection of the structure along the *a* axis is shown in Fig. 1, together with the labelling of the atoms. Table 2 lists the interatomic distances and

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[*] Department of Chemistry, Faculty of Science, Tohoku University, Aramaki, Sendai 980, Japan.

[†] College of Medical Sciences, Tohoku University, Seiryo-machi, Sendai 980, Japan.

[‡] A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31468 (22 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.