

Table 3. Bond angles (°) (the standard deviation in the last digit is given in parentheses)

Sb(1)—O(3)—Sb(2) 140.0 (3)			
Left side Fig. 1		Right side Fig. 1	
O(1)—Sb(1)—O(3)	176.6 (3)	O(3)—Sb(2)—O(2)	178.2 (3)
C(1)—O(1)—Sb(1)	135.1 (7)	Sb(2)—O(2)—C(6)	136.7 (7)
O(1)—C(1)—C(5)	120 (1)	O(2)—C(6)—C(9)	118 (1)
O(1)—C(1)—C(2)	123 (1)	O(2)—C(6)—C(7)	128 (1)
C(2)—C(1)—C(5)	117 (1)	C(7)—C(6)—C(9)	114 (1)
C(1)—C(2)—C(3)	123 (1)	C(6)—C(7)—C(8)	124 (1)
C(1)—C(2)—C(4)	120 (1)	C(6)—C(7)—C(10)	116 (1)
C(3)—C(2)—C(4)	117 (1)	C(8)—C(7)—C(10)	120 (1)
C(2)—C(3)—N(1)	179 (1)	C(7)—C(8)—N(4)	171 (2)
C(2)—C(4)—N(2)	179 (1)	C(7)—C(10)—N(6)	176 (2)
C(1)—C(5)—N(3)	178 (2)	C(6)—C(9)—N(5)	170 (2)
C(11)—Sb(1)—O(1)	84.3 (4)	C(29)—Sb(2)—O(2)	78.8 (4)
C(17)—Sb(1)—O(1)	81.1 (4)	C(35)—Sb(2)—O(2)	84.6 (4)
C(23)—Sb(1)—O(1)	85.8 (4)	C(41)—Sb(2)—O(2)	88.0 (4)

bridging O atom by an average of 6.2°. The angles around the O atoms are normal: Sb(1)—O(3)—Sb(2), 140.0°; C(1)—O(1)—Sb(1), 135.1°; Sb(2)—O(2)—

C(6), 136.7°. This structure sheds no light on the (TCNE.TPP)₂ structure, since the bonding between groups is through O atoms that are not present in the other adduct.

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Structure of the Potassium Methoxide Adduct of *s*-Trinitrobenzene, a Meisenheimer Complex

BY RICCARDO DESTRO, TULLIO PILATI AND MASSIMO SIMONETTA

Istituto di Chimica Fisica e Centro CNR, Università, Via Golgi 19, 20133 Milano, Italy

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Abstract. K(C₇H₆N₃O₇)·½H₂O, C₇H₆KN₃O₇·½H₂O, *M*_r = 292.3, monoclinic, *C*2/*c*, *a* = 12.411 (2), *b* = 9.051 (2), *c* = 19.565 (3) Å, β = 101.50 (2)°, *Z* = 8, *D*_x = 1.803 Mg m⁻³ (not measured). Data were collected on a computer-controlled four-circle diffractometer (Mo *K*α radiation, λ = 0.71069 Å, graphite monochromator), *F*(000) = 1192, μ(Mo *K*α) = 0.390 mm⁻¹. Final *R* = 0.045 for 2999 observed (*I* > 0) reflexions, 0.049 including unobserved. The methoxy group is covalently bound to the ring of *s*-trinitrobenzene at a C atom which attains tetrahedral (*sp*³) configuration. To relieve overcrowding between OCH₃ and the two neighbouring nitro groups, the anion assumes a butterfly shape.

Introduction. Meisenheimer complexes, the covalently-bound addition products resulting from reactions of aromatic nitro compounds with bases or other nucleo-

philic species, have been extensively studied by spectroscopic methods (for a review see Crampton, 1969). The molecular geometry of some of them has also been elucidated by X-ray diffraction. To our knowledge, the X-ray structure determinations so far reported concern only dialkoxy adducts, *i.e.* complexes derived from addition of an alkoxide ion to a benzene ring at a position which already carries an alkoxy group. They include: 1,1'-diethoxy-2,4,6-trinitrobenzene potassium or caesium (KDETNB; Destro, Gramaccioli & Simonetta, 1968); 1,1'-dimethoxy-2,4,6-trinitrobenzene potassium dihydrate (KDMTNB; Ueda, Sakabe, Tanaka & Furusaki, 1968); and 4,4'-dimethoxy-5,7-dinitrobenzofurazan (KDMDNBF; Messmer & Palenik, 1971). The present work is the first crystallographic study of an unsymmetrically substituted complex, obtained by addition of a methoxide ion to *s*-trinitrobenzene. Methanolic solutions of the adduct have been

reported (Gold & Rochester, 1964) to be unstable and eventually produce 3,5-dinitroanisole and nitrite. For the complex (hereinafter KMTNB), Foster (1959) has suggested a mode of interaction analogous to that of the adducts of picryl ethers with alkoxides, and NMR measurements (Crampton & Gold, 1964; Foster & Fyfe, 1965) have supported this formulation. To obtain a detailed description of the deformations occurring in the trinitrobenzene system we have undertaken this investigation.

Red-brown prismatic crystals, kindly supplied by Professor Foster, rapidly deteriorate if exposed to air and/or moisture. The crystal used for data collection was ground to a sphere of approximate diameter 0.4 mm and sealed in a Lindemann-glass capillary. Cell dimensions were obtained by a least-squares fit to the $\sin^2 \theta$ values of 30 *hkl* reflexions measured on a diffractometer. Systematic absences *hkl*, $h + k \neq 2n$ and $h0l$, $l \neq 2n$ indicated the space groups *C2* or *C2/c*; intensity statistics and the successful structure determination confirm *C2/c*. Intensity data were collected to a maximum 2θ value of 60° (Mo $K\alpha$ radiation, $\lambda = 0.71069 \text{ \AA}$, graphite monochromator), using a variable rate θ - 2θ scan technique. Background measurements were taken at both ends of the scan range, each for a time equal to one-half of the scan time. Two standard reflexions were checked after every 40 intensity measurements. They showed a steady drop in intensity which reached 5% at the end of the data collection. 3156 unique reflexions were measured, of which 2999 having scan count greater than background were treated as observed. Each reflexion was assigned a variance of $\sigma^2(I) = \sigma^2(I)_{c.s.} + (0.03S)^2$, where *S* is the scan count. The intensities and their standard deviations were corrected for Lorentz, polarization and linear decay effects but not for absorption.

The structure was solved by *MULTAN* (Germain, Main & Woolfson, 1971). All non-hydrogen atoms were derived from the *E* map corresponding to the solution with the highest combined figure of merit. A relatively small peak, lying on a twofold axis and initially considered as spurious, does actually correspond to a water O atom. This finding agrees with the remark of Foster & Fyfe (1965), who indicated that crystals may include some water of crystallization, depending on the mode of preparation. The positions of all H atoms were obtained from difference syntheses. Refinement was by full-matrix least-squares minimization of the quantity $\sum w(|F_o| - k|F_c|)^2$, with weights $w = 4F_o^2/\sigma^2(F_o^2)$. Final cycles included 196 parameters in a single matrix: coordinates and anisotropic temperature coefficients b_{ij} for the heavy atoms, coordinates and isotropic *B* values for the H atoms, and a scale factor. The final *R* is 0.045 for the 2999 observed reflexions (0.049 including unobserved), the weighted *R* $\{R_w = [\sum w(\Delta F)^2/\sum wF_o^2]^{1/2}\}$ is 0.046, and the goodness-of-fit, based on 2999 observations and

Table 1. *Positional parameters for heavy atoms* ($\times 10^5$) *and for hydrogen atoms* ($\times 10^3$)

	x	y	z
K	66952 (3)	46269 (5)	25593 (2)
C(1)	50415 (11)	21222 (16)	37155 (7)
C(2)	42520 (11)	20528 (15)	41987 (7)
C(3)	45438 (12)	19373 (16)	49036 (7)
C(4)	56472 (12)	16570 (16)	52098 (7)
C(5)	64121 (11)	13347 (16)	47892 (8)
C(6)	61101 (11)	14837 (16)	40893 (8)
C(7)	54591 (15)	46797 (19)	40235 (10)
N(1)	31051 (10)	21527 (15)	38877 (7)
N(2)	59514 (12)	14813 (14)	59388 (7)
N(3)	68584 (11)	9968 (16)	36628 (7)
O(1)	51737 (8)	36230 (12)	34740 (6)
O(2)	28462 (9)	22842 (14)	32438 (6)
O(3)	24208 (10)	20622 (18)	42561 (7)
O(4)	52347 (12)	16159 (16)	62979 (6)
O(5)	69232 (11)	11716 (15)	62040 (6)
O(6)	77611 (10)	4876 (15)	39361 (8)
O(7)	65769 (12)	11300 (20)	30256 (7)
O(W)	50000 (0)	67191 (24)	25000 (0)
H(1)	479 (1)	158 (2)	330 (1)
H(3)	403 (2)	194 (2)	516 (1)
H(5)	713 (2)	96 (2)	497 (1)
H(71)	558 (2)	564 (2)	384 (1)
H(72)	486 (2)	481 (2)	428 (1)
H(73)	614 (2)	440 (3)	432 (2)
H(W)	496 (3)	722 (3)	279 (2)

196 parameters, is 1.57. Atomic form factors for K, C, N and O were from Cromer & Waber (1965), and for H from Stewart, Davidson & Simpson (1965). Final positional parameters are listed in Table 1.*

Discussion. Fig. 1 shows the numbering scheme and the geometry of the anion. The C(1)–H(1) distance is 0.94 (2) Å and the O(1)–C(1)–H(1) angle is $104 (1)^\circ$. All other bond distances and angles involving H atoms are in the usual range. As expected, the methoxy group is covalently bound to the ring at a C atom which therefore changes its hybridization from sp^2 to sp^3 .

The deformations in the benzene ring, *viz* the lengthening of C(1)–C(α) bonds, the narrowing of the C(6)–C(1)–C(2) angle, and the shortening of the C(2)–C(3) and C(5)–C(6) bonds are similar to those found in other Meisenheimer complexes (see Table 2). The only significant differences between the corresponding geometrical parameters are in the C(4)–N(2) and C(1)–O(1) bond lengths, which are longer in KMTNB by over 0.02 and 0.03 Å, respectively. The explanation of the differences may be partly electronic and partly steric in origin. In fact, the molecular

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34056 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

conformation of KMTNB is distinctly different from those of the previously studied dialkoxy adducts. In the latter compounds, the system formed by the ring and the nitro groups is substantially planar, in agreement with the model based on theoretical arguments for the least-strained structures. Small deviations from such a model, that is slight rotations of the nitro groups (up to 15° in KDMDNBF) and non-strict planarity of the ring [maximum deviation 0.03 Å for C(2) in KDMTNB], could be ascribed to packing effects.

Table 2. Comparison of some geometrical parameters of KMTNB with those found in other Meisenheimer complexes

The average values of all the chemically equivalent bond lengths (Å) and angles ($^\circ$) in the molecules are reported.

	KMTNB ^a	KDMTNB ^b	KDETNB ^c	KDMDNBF ^d
C(1)—C(2)	1.495	1.496	1.514	1.500
C(2)—C(3)	1.355	1.355	1.347	1.368
C(3)—C(4)	1.405	1.394	1.407	1.398
C(1)—O(1)	1.458	1.425	1.417	1.415
C(2)—N(1)	1.436	1.443	1.449	1.436
N(1)—O(2,3)	1.232	1.227	1.226	1.229
C(4)—N(2)	1.410	1.387	1.390	1.389
N(2)—O(3,4)	1.246	1.247	1.246	1.248
R—C(1)—R'	104	100.1	100.9	100.8
C(2)—C(1)—C(6)	107.7	108.8	107.8	107.1
C(1)—C(2)—C(3)	124.8	125.5	125.8	126.2
C(2)—C(3)—C(4)	119.2	119.0	120.2	123.0
C(3)—C(4)—C(5)	120.2	122.0	119.9	118.5

(a) This structure, $R = -OCH_3$, $R' = H$. (b) Ueda *et al.* (1968), $R = R' = -OCH_3$. (c) Destro *et al.* (1968), $R = R' = -OC_2H_5$, two molecules in the asymmetric unit. (d) Messmer & Palenik (1971), $R = R' = -OCH_3$, two molecules in the asymmetric unit.

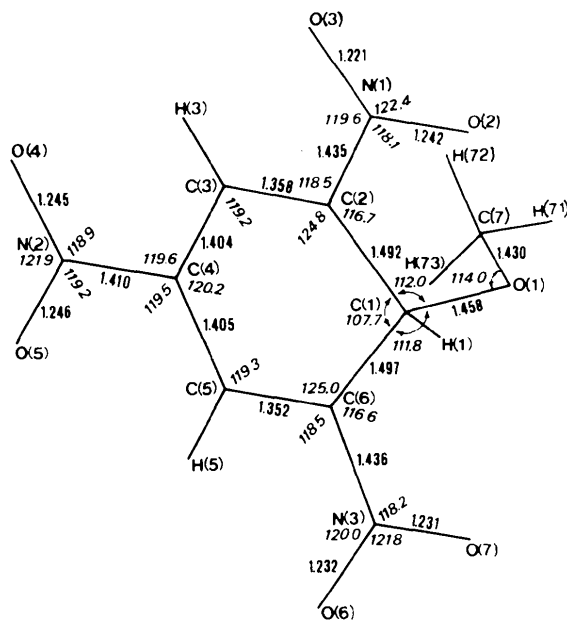


Fig. 1. Bond distances and angles involving heavy atoms. Standard deviations are in the ranges 0.0016–0.0024 Å and 0.10–0.15 $^\circ$.

By contrast, the most evident feature of KMTNB is the boat-like conformation of the ring (see Fig. 2), arising from the relatively large displacements of atoms C(1) and C(4) from the plane defined by the other four C atoms (plane A of Table 3). The alterations introduced into the ring system by the displacement of atom C(1) are such as to maintain approximate planarity of the bonding about the C(2) and C(6) atoms (see Table 3 and Fig. 2); consequently, the anion as a whole assumes a butterfly shape. This arrangement drastically reduces the interactions between the methoxy group and the two flanking nitro groups, the O(1)···O(2) and O(1)···O(7) contacts being 3.082 and 3.083 Å, respectively. (In dialkoxy complexes the corresponding distances are around 2.80 Å.) As inferred from Fig. 2,

Table 3. Deviations (Å) from least-squares planes

The equations are referred to the monoclinic axes and fractional coordinates. Atoms marked with an asterisk were omitted from the least-squares calculations; the remaining atoms were given equal weights.

	Plane A	Plane B	Plane C	Plane D			
	Δ	Δ	Δ	Δ			
C(1)*	-0.253	C(1)	0.013	C(1)	-0.009	C(1)	0.000
C(2)	0.006	C(2)	0.006	C(4)*	0.145	O(1)	0.000
C(3)	-0.007	C(3)	-0.017	C(5)	0.007	H(1)	0.000
C(4)*	-0.083	C(4)*	0.162	C(6)	0.001	C(7)*	0.124
C(5)	0.007	N(1)	-0.009	N(3)	0.007	C(4)*	-0.080
C(6)	-0.007	O(2)	-0.011	O(6)	-0.012	N(2)*	-0.120
N(1)*	0.253	O(3)	0.021	O(7)	0.007		
N(2)*	-0.047						
N(3)*	0.232						

$$\text{Plane A: } 2.7923x + 8.7961y + 0.4673z = 3.1953$$

$$\text{Plane B: } 0.1829x + 9.0103y + 1.7369z = 2.6631$$

$$\text{Plane C: } 5.0168x + 8.2626y - 0.4858z = 4.0937$$

$$\text{Plane D: } 12.1218x - 1.8654y - 4.9568z = 3.8737$$

Dihedral angles ($^\circ$): $A \wedge B$ 12.2, $A \wedge C$ 10.9, $A \wedge D$ 89.1, $B \wedge C$ 23.1.

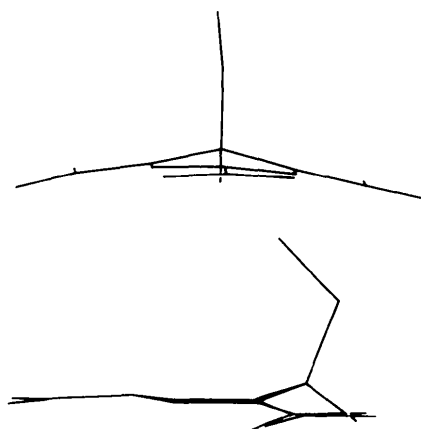


Fig. 2. Two views of KMTNB along the principal moments of inertia of the anion.

in the observed conformation of KMTNB the 14 π -electron system undergoes only slight deformations. Evidently, the alternative way of relieving steric strain, that is an extensive rotation of the nitro groups with respect to the planar ring, is energetically less favoured, since it would imply a greater decrease in conjugation between the NO₂ groups and the ring.

The displacement of C(4) from plane *A* can be blamed mainly on packing effects. Indeed, the shortest heavy-atom contact within pairs of anions related to one another by centres of symmetry is C(3)···C'(4), 3.266 (2) Å. If the atom C(4) lay on plane *A*, this intermolecular distance would become even more critical, falling below 3.2 Å.

The water molecules are hydrogen bonded to the nitro groups in position 4. The distance O(*W*)···O(4) (at 1 - *x*, 1 - *y*, 1 - *z*) is 2.857 (2) Å, and the O-H···O angle is close to linear [172 (2)°]. The metal ions coordinate eight O atoms in an irregular polyhedron. Metal-oxygen distances lie in the range 2.765–2.990 Å.

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Bis[bromo(diethylenetriamine)platinum(II)] Tetrabromoplatinate(II)

BY R. MELANSON AND F. D. ROCHON

Département de Chimie, Université du Québec à Montréal, CP 8888, Montréal H3C 3P8, Canada

AND J. HUBERT

Département de Chimie, Université de Montréal, CP 6210 Montréal H3C 3V1, Canada

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Abstract. $2[\text{C}_4\text{H}_{13}\text{BrN}_3\text{Pt}]^+ \cdot [\text{Br}_4\text{Pt}]^{2-}$, $[\text{PtBr}(\text{C}_4\text{H}_{13}\text{N}_3)_2][\text{PtBr}_4]$, $M_r = 1271.1$, orthorhombic, $Pna2_1$, $a = 19.720$ (13), $b = 12.638$ (13), $c = 9.416$ (7) Å, $Z = 4$, $V = 2346$ (3) Å³, $D_x = 3.597$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 29.586$ mm⁻¹, $T = 295$ K. The refinement of the positional and thermal parameters, carried out by full-matrix least-squares calculations, converged to $R = 0.048$ and $R_w = 0.054$. The coordination around the platinum atoms is planar. The crystal structure is stabilized by hydrogen bonding.

Introduction. The complex salt $[\text{Pt}(\text{dien})\text{Br}]_2[\text{PtBr}_4]$ (dien = diethylenetriamine) was prepared by the following method. K₂PtCl₄ and an excess of HBr were mixed together in water overnight. The solution was then evaporated to dryness. The residue (K₂PtBr₄) was mixed with $[\text{Pt}(\text{dien})\text{Br}]\text{Br}$ in aqueous solution and

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crystals of $[\text{Pt}(\text{dien})\text{Br}]_2[\text{PtBr}_4]$ were obtained upon evaporation. A set of precession photographs indicated either space group $Pna2_1$ or $Pnam$.

The intensity data were collected from a crystal measuring 0.09 × 0.15 × 0.40 mm, elongated along the *c* axis, on a Syntex P1 diffractometer using graphite-monochromatized Mo *K* α radiation. The data were collected by the $2\theta/\theta$ scan technique (ω scan at half the speed of 2θ), in the region of $2\theta < 50^\circ$ at a variable speed (24 to 1° min⁻¹). Most reflexions were measured at a speed of 1° min⁻¹. The background-time to scan-time ratio was 0.40. The reflexions for which the intensity was less than $3\sigma(I)$ were considered as unobserved. The standard deviation $\sigma(I)$ was calculated as already described (Melanson, Hubert & Rochon, 1975). By this criteria, 1314 out of the 2155 measured reflexions were considered as observed. An absorption correction based on the equations of the

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