

A diagram of the unit-cell packing is presented as Fig. 2. The molecules stack pairwise such that Au of one molecule sits approximately above (or below) the C(1)–N(1) triple bond. The closest approach of Au atoms is 3.695 (1) Å indicating no Au–Au bonding within this structure.

References

- BLODGETT, R. C., HEUER, M. A. & PIETRUSKO, R. G. (1984). *Semin. Arthritis Rheum.* **13**, 255–273.
- CORFIELD, P. W. R., DOEDENS, R. J. & IBERS, J. A. (1967). *Inorg. Chem.* **6**, 197–204.
- CORFIELD, P. W. R. & SHEARER, H. M. M. (1967). *Acta Cryst.* **23**, 156–162.
- ESPERAS, S. (1976). *Acta Chem. Scand. Ser. A*, **30**, 527–530.
- FORESTIER, J. B. (1929). *Soc. Med. Hop. Paris*, **53**, 323.
- International Tables for X-ray Crystallography* (1974). Vol. IV, p. 72. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- JONES, P. G. (1981). *Gold Bull.* **14**, 102–118.
- MCCLEVERTY, J. A. & DEMOTA, M. (1973). *J. Chem. Soc. Dalton Trans.* pp. 2571–2574.
- ROULET, R. & FAVEZ, R. (1975). *Chimia*, **29**, 346–348.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- SUTTON, B. M. (1983). In *Platinum, Gold and Other Metal Chemotherapeutic Agents*, edited by S. J. LIPPARD. *Am. Chem. Soc. Symp. Ser.* **209**, 355–369.
- SUTTON, B. M., MCGUSTY, E., WALZ, D. T. & DIMARTINO, M. J. (1972). *J. Med. Chem.* **15**, 1095–1098.

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Potassium Salt of 1,4-Dihydro-4,4-dimethoxy-5,7-dinitrobenzofurazan-3-oxide with Methanol:* a Meisenheimer Complex of 4,6-Dinitrobenzofuroxan

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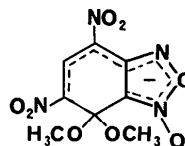
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Abstract. $C_8H_7N_4O_8 \cdot K^+ \cdot CH_3OH$, $M_r = 358.29$, triclinic, $P\bar{1}$, $a = 7.463$ (1), $b = 9.723$ (2), $c = 10.378$ (2) Å, $\alpha = 79.41$ (2), $\beta = 87.08$ (2), $\gamma = 72.21$ (2)°, $V = 704.8$ (2) Å³, $Z = 2$, $D_x = 1.69$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 4.87$ cm⁻¹, $F(000) = 368$, room temperature, $R = 0.069$ for 1325 reflections with $F_o^2 > 3\sigma(F_o^2)$. The geometry of the furoxan ring of the title compound is the same as previously observed in benzofuroxan and 4,6-dinitrobenzofuroxan. The distortion from planarity and the sequence of long and short bonds in the ring of the title compound, caused by the presence of the alkoxy groups, follow the same pattern observed in a related Meisenheimer complex of dinitrobenzofurazan.

Introduction. During previous studies of σ complexes of benzofuroxan, compound (I) was characterized in solution by NMR (Buncel, Chuaqui-Offermanns, Moir & Norris, 1979). However, the NMR assignment of the structure is equivocal as the molecule can rearrange, changing the position of the furoxan O atom. W. P. Norris isolated the Meisenheimer complex (I) as its K salt (Norris, Chafin, Spear & Read, 1984). To determine the position of the O in the solid state and to understand better the chemical reactivity of this molecule, we now report the crystal structure of the K

salt. (I) is compared with other benzofuroxans and benzofurazans.



(I)

Experimental. Suitable orange, euhedral crystals were obtained from methanol. Crystal for data collection approximately 0.10 × 0.20 × 0.32 mm. Prior to initiating the structure determination, it was determined that these crystals evolved at 377 K one molecule of CH₃OH per molecule of the Meisenheimer complex. Unit-cell parameters determined by a least-squares fit of 24 computer-centered reflections with 2θ values ranging from 6 to 24° (Mo $K\alpha$). 2103 intensity data for the octants $\bar{h}\bar{k}l$, $\bar{h}kl$, $h\bar{k}l$, hkl to 45° (2θ) (with values of $h = -9$ to $+9$, $k = -11$ to $+11$, and $l = 0$ to $+12$) were collected on a Nicolet R3 diffractometer with monochromatized Mo $K\alpha$ radiation using $2\theta/\theta$ scans and variable scan speeds from 2 to 10° (2θ) min⁻¹. Total time spent collecting backgrounds at each end of a scan was 50% of the scan time. Scan range from 1° < $K\alpha_1$ (2θ) to 1° > $K\alpha_2$ (2θ). Intensity data for three check reflections

* Current *Chemical Abstracts* name.

(211, 023, $\bar{2}\bar{1}\bar{1}$) collected every 45 reflections were constant throughout data collection. Structure solved using the default parameters for the direct-methods part of *SHELXTL* (Sheldrick, 1981). For the refinement the data were corrected for Lorentz and polarization effects but not for absorption or extinction and merged into a unique data set of 1842 intensities, 1325 with $F_o^2 > 3\sigma(F_o^2)$ (Lowe-Ma, 1984). Atomic scattering factors for C, N, O, K^+ were computed from numerical Hartree-Fock wavefunctions (Cromer & Mann, 1968). Atomic scattering factor for H taken from Stewart, Davidson & Simpson (1965). Refinement by least-squares minimization of $[w(F_o^2 - F_c^2)]^2$ using all F_o^2 data with $w = [1/\sigma(F_o^2)]^2$ where $\sigma(F_o^2)$ were based on counting statistics plus the term $0.02S$ ($S = \text{scan counts}$) (*XRAY76*; Stewart, 1976).^{*} Only K^+ and C(99), O(99) (solvent atoms) were refined as anisotropic atoms. Final $R(F^2) = \sum |F_o^2 - F_c^2| / \sum (F_o^2) = 0.096$, $wR(F^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2} = 0.14$ for all 1842 reflections; $R = (\sum k |F_o| - |F_c|) / (\sum k F_o) = 0.088$ for 1716 reflections with $|F_o|^2 > 0$ and $R = 0.069$ for 1325 reflections with $|F_o|^2 > 3\sigma(F_o^2)$. Goodness-of-fit = $[\sum w(kF_o)^2 - F_c^2]^{1/2} / (N_{REF} - N_{VAR})^{1/2} = 2.88$. During final least-squares cycle all $\Delta/\sigma < 0.1$. The final parameters from the $\Delta(F^2)$ refinement were used for the plots with *SHELXTL* (Sheldrick, 1981).

Discussion. The final positional and thermal parameters are given in Table 1.† Fig. 1 is a plot of the molecule with thermal ellipsoids indicating the numbering and showing the bond lengths and bond angles. H atoms are numbered by the C to which they are attached. O(99) and C(99) refer to the O and C atoms of the solvent molecule.

The assignment of the solvent atoms to C and O was based on the apparent electron density at each site, although a methyl group and a hydroxy group nominally have the same number of electrons. The choice for the solvent O was confirmed by contact distances of 2.76 and 2.87 Å between the solvent O atoms and the K^+ ion. Sums of the ionic radius for six-coordinate K and the van der Waals radius for O vary from 2.73 to 2.92 Å depending on the radii chosen (Jesson & Muettterties, 1969; Muller & Roy, 1974; Pauling, 1948). The coordination and distances about the K^+ ion are shown in Fig. 2. The contact distances suggest that the K^+ ion is seven-coordinate in this structure.

^{*} Note that this version as supplied could not contribute all, negative and positive, F_o^2 to the binary data file and, hence, could not correctly contribute all F_o^2 to the matrix during refinement (see Lowe-Ma, 1984).

† Lists of structure factors, bond lengths and angles, anisotropic temperature factors, and a stereoscopic packing plot have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42454 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic positional (fractional coordinates) and thermal parameters with estimated standard deviations in parentheses

	x	y	z	$U^*(\text{Å}^2)$
C(1)	0.8628 (7)	0.2859 (6)	0.2605 (5)	0.0291 (13)
C(2)	0.6778 (7)	0.3278 (6)	0.1890 (6)	0.0296 (13)
C(3)	0.6560 (8)	0.3010 (6)	0.0655 (6)	0.0338 (15)
C(4)	0.8043 (8)	0.2369 (6)	-0.0093 (6)	0.0327 (14)
C(5)	0.9896 (7)	0.1875 (6)	0.0432 (6)	0.0310 (14)
C(6)	1.0117 (7)	0.2079 (6)	0.1715 (5)	0.0292 (14)
C(7)	0.9041 (10)	0.5220 (8)	0.1859 (7)	0.0408 (16)
C(8)	0.8118 (11)	0.0679 (8)	0.3861 (8)	0.0490 (18)
H(3)	0.507 (6)	0.338 (5)	0.036 (4)	0.018 (12)
H(7A)	0.928 (8)	0.599 (7)	0.218 (6)	0.062 (20)
H(7B)	0.788 (9)	0.560 (6)	0.150 (6)	0.056 (18)
H(7C)	0.988 (11)	0.489 (9)	0.114 (8)	0.104 (27)
H(8A)	0.815 (9)	0.018 (8)	0.481 (8)	0.090 (24)
H(8B)	0.872 (8)	0.004 (6)	0.330 (6)	0.054 (18)
H(8C)	0.688 (8)	0.088 (6)	0.354 (6)	0.053 (18)
N(1)	1.1544 (7)	0.1218 (6)	-0.0057 (5)	0.0499 (14)
N(2)	1.1925 (6)	0.1525 (5)	0.2033 (5)	0.0378 (13)
N(3)	0.7685 (7)	0.2244 (6)	-0.1388 (5)	0.0468 (14)
N(4)	0.1514 (6)	0.3982 (5)	0.2547 (5)	0.0372 (13)
O(1)	1.2889 (6)	0.0973 (5)	0.0917 (4)	0.0516 (12)
O(2)	1.2859 (6)	0.1388 (5)	0.3017 (4)	0.0484 (12)
O(3)	0.6069 (6)	0.2640 (5)	-0.1803 (5)	0.0627 (14)
O(4)	0.9074 (6)	0.1766 (5)	-0.2070 (5)	0.0622 (14)
O(5)	0.5299 (5)	0.4270 (4)	0.3646 (4)	0.0465 (11)
O(6)	0.3583 (6)	0.4368 (4)	0.2002 (4)	0.0511 (12)
O(7)	0.9097 (5)	0.4054 (4)	0.2934 (4)	0.0332 (10)
O(8)	0.8695 (5)	0.1956 (4)	0.3854 (4)	0.0368 (10)
K^+	0.8018 (2)	0.3901 (2)	0.5600 (1)	0.039†
O(99)	0.1849 (5)	0.3143 (5)	0.5176 (4)	0.053†
C(99)	0.3488 (9)	0.2281 (7)	0.5994 (7)	0.081†

^{*} U for the expression $\exp[-8\pi^2 U(\sin\theta/\lambda)^2]$.

† $U_{eq} = \frac{1}{3} \sum_i \text{diagonalized } U_{ii}$.

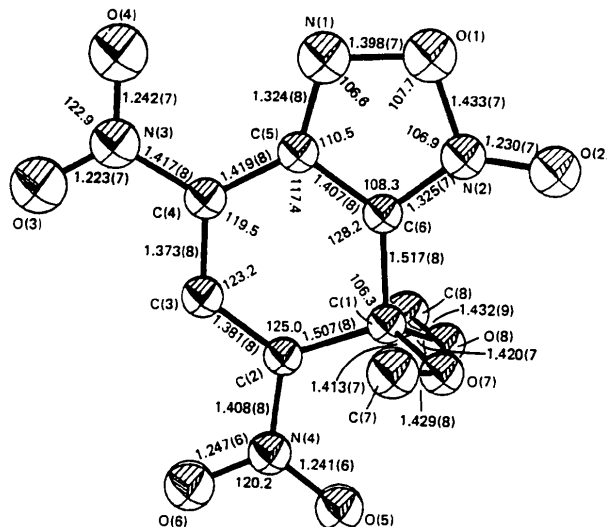


Fig. 1. Bond lengths (Å), bond angles ($^\circ$), and 50% probability thermal ellipsoids for molecule (I). Estimated standard deviations of the last digit for the bond lengths are given in parentheses. The estimated standard deviations on the bond angles are 0.4–0.6 $^\circ$.

H atoms of the solvent molecule CH_3OH were searched for on Fourier synthesis (electron density) and difference Fourier maps. Although the maps indicated slight positive electron density at approximately reasonable positions, these 'hydrogens' were not sufficiently resolved from background 'noise' to be well behaved during least-squares refinement. H atoms for the solvent molecule were not included in the final refinement cycles. A contact distance of 2.99 (3) Å between O(99) and O(2) suggests the presence of hydrogen bonding. Two of the H atoms of the methoxy groups had large thermal parameters and the geometry of all of the H atoms of the methoxy groups was less than ideal, but their parameters converged during least-squares refinement. There does not appear to be disorder in the methyl groups.

The highest peaks and lowest troughs on the final difference Fourier map were $+0.7$ to $-0.6 e \text{ \AA}^{-3}$. The seven largest difference peaks of $+0.5$ to $+0.7 e \text{ \AA}^{-3}$ were all associated with nitro-group O atoms O(3), O(4), O(5), and O(6). Although no other disorder was observed in the rest of the molecule, the difference Fourier peaks about the nitro-group O atoms suggest slight O displacements. The refined thermal parameters for O(3), O(4), O(5), O(6) are not unusually large.

A comparison of (I) with the closely related compounds benzofuroxan (II) (Britton & Olson, 1979), 4,6-dinitrobenzofuroxan (III) (Prout, Hodder & Viterbo, 1972) and Meisenheimer complex (IV) (Messmer & Palenik, 1971) shows many similarities. The furoxan rings of (I) and (III) are similar, except for slight shortening of the C(5)—N(1), C(6)—N(2) bonds in (I) relative to the same bonds in (III) and minor bond-angle deviations. The geometries of the furoxan rings of (I) and (II) are the same within the e.s.d.'s. This

suggests that the two methoxy groups at C(1) have not greatly influenced the bonding of the furoxan ring in (I) relative to (II) and (III). The six-membered rings of (I) and (IV) are also very similar. Some of the bond lengths and angles vary by slightly more than the e.s.d.'s, but the *pattern* of long and short bond lengths and angles is the same. As observed in (IV) and other Meisenheimer complexes (Ueda, Sakabe, Tanaka & Furusaki, 1968; Destro, Gramaccioli & Simonetta, 1968; Destro, Pilati & Simonetta, 1979), the bond lengths and angles about the C atom to which the alkoxy groups are attached suggest that the C has approximately sp^3 hybridization. In one of the two crystallographically independent molecules of (IV), molecule *A*, the C atom with the alkoxy groups was bent out of the plane of the molecule by 0.059 Å. However, the other independent molecule, *B*, of (IV) was planar. As one of the ring C atoms is sp^3 -hybridized should not the unexpected planarity of molecule *B* be considered as being due to packing effects rather than ascribing the expected non-planarity of molecule *A* to packing effects? Even smaller differences in planarity were observed between the two independent anions of the diethoxide complex of *s*-trinitrobenzene (Destro, Gramaccioli & Simonetta, 1968). A much larger and more significant distortion was observed in the monomethoxide complex of *s*-trinitrobenzene, KMTNB (Destro, Pilati & Simonetta, 1979). Least-squares-planes calculations (*SHELXTL*, Sheldrick, 1981) of molecule (I) were performed with and without the nitro-group O atoms and C(1) (see Table 2). These indicate that the deviation of C(1) from the planarity of the rest of the molecule is of about the same magnitude, 0.067 Å, as observed in molecule *A* of (IV) (0.059 Å) and not as extreme as the distortions from planarity observed in KMTNB. The ring system of (I) could still be considered as approximately planar even though C(1) has sp^3 hybridization. In molecule (I) the nitro groups exhibit slight rotations away from the average plane of the two rings of 3.9 and 6.0°. Again, these are very similar to, though slightly less than, the nitro-group rotations observed in (III). The angles of the planes of the methoxy groups to the molecular plane in (I) are 89.0 and 94.4°. The angle between the 'benzene' ring including C(1) and the furoxan ring is 1.9°.

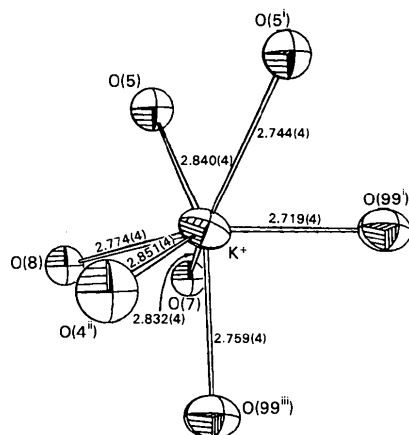
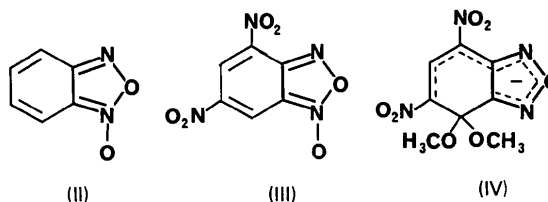


Fig. 2. Contact distances less than 3.0 Å about the K^+ ion. Atoms O(5ⁱ), O(99ⁱ), O(4ⁱⁱ), and O(99ⁱⁱⁱ) are symmetry-related to O(5), O(99), and O(4) in Table 1. Symmetry transforms: (i) $-x, -y, -z$; (ii) $x, y, 1+z$; (iii) $1+x, y, z$.



The author thanks Dr W. P. Norris, Chemistry Division, Naval Weapons Center, for crystals of the title compound.

Table 2. Deviations (Å) from least-squares planes

	Plane (1)	Plane (2)	Plane (3)
C(1)	0.0512	0.0670*	0.0851*
C(2)	-0.0017	0.0289	0.0356*
C(3)	-0.0647	-0.0273	-0.0373*
C(4)	-0.0346	-0.0033	-0.0214*
C(5)	-0.0104	0.0069	-0.0024
C(6)	-0.0134	-0.0031	0.0046
N(1)	0.0042	0.0133	-0.0006
N(2)	-0.0160	-0.0185	-0.0049
N(3)	-0.0010	0.0382*	0.0030*
N(4)	-0.0002	0.0378*	0.0514*
O(1)	0.0068	0.0032	0.0033
O(2)	-0.0457	-0.0583*	-0.0310*
O(3)	-0.0617	-0.0105*	-0.0529*
O(4)	0.1327	0.1661*	0.1240*
O(5)	0.0850	0.1172*	0.1457*
O(6)	-0.0302	0.0200*	0.0248*

Plane (1): $3.076(15)X + 8.953(51)Y - 1.974(70)Z = 4.6485(137)$

Plane (2): $3.012(8)X + 8.950(36)Y - 2.017(64)Z = 4.5650(79)$

Plane (3): $3.036(5)X + 8.990(39)Y - 1.895(48)Z = 4.6106(61)$

* Deviations for atoms which did *not* contribute to the best-plane calculation.

References

- BRITTON, D. & OLSON, J. M. (1979). *Acta Cryst.* **B35**, 3076–3078.
- BUNCEL, E., CHUAQUI-OFFERMANN, N., MOIR, R. Y. & NORRIS, A. R. (1979). *Can. J. Chem.* **57**, 494–499.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- DESTRO, R., GRAMACCIOLI, C. M. & SIMONETTA, M. (1968). *Acta Cryst.* **B24**, 1369–1386.
- DESTRO, R., PILATI, T. & SIMONETTA, M. (1979). *Acta Cryst.* **B35**, 733–736.
- JESSON, J. P. & MUETTERTIES, E. L. (1969). *Chemist's Guide; Basic Chemical and Physical Data*, p. 5. New York: Marcel Dekker.
- LOWE-MA, C. K. (1984). Modifications to the XRAY76 system of computer programs. Naval Weapons Center Tech. Memorand. 5305 (unclassified). Magnetic-tape program and Lorentz and polarization corrections were taken from the CRYM crystallographic computing system (Dr R. E. Marsh, California Institute of Technology).
- MESSMER, G. G. & PALENIK, G. J. (1971). *Acta Cryst.* **B27**, 314–321.
- MULLER, O. & ROY, R. (1974). *The Major Ternary Structural Families. Vol. 4. Crystal Chemistry of Non-Metallic Materials*, p. 6. New York: Springer-Verlag.
- NORRIS, W. P., CHAFIN, A., SPEAR, R. J. & READ, R. W. (1984). *Heterocycles*, **22**(2), 271–274.
- PAULING, L. (1948). *The Nature of the Chemical Bond*, p. 189. New York: Cornell Univ. Press.
- PROUT, C. K., HODDER, O. J. R. & VITERBO, D. (1972). *Acta Cryst.* **B28**, 1523–1526.
- SHELDRIK, G. M. (1981). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*. Univ. of Göttingen. [Nicolet XRD version 3.0A.]
- STEWART, J. M. (1976). Editor. The XRAY76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- UEDA, H., SAKABE, N., TANAKA, J. & FURUSAKI, A. (1968). *Bull. Chem. Soc. Jpn.* **41**, 2866–2871.

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Structure of 4-*tert*-Butyl-2,6-dimethylacetophenone–Iron(III) Chloride (1/1)

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Abstract. $C_{14}H_{20}O.FeCl_3$, $M_r = 366.52$, triclinic, $P\bar{1}$, $a = 9.309(1)$, $b = 9.387(1)$, $c = 10.159(2)$ Å, $\alpha = 89.03(2)$, $\beta = 91.39(2)$, $\gamma = 95.19(1)^\circ$, $V = 883.7$ Å³, $Z = 2$, $D_x = 1.32$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 1.314$ mm⁻¹, $F(000) = 378$, $T = 210(2)$ K, $R = 0.034$ for 2360 observed reflections. The Fe^{III} atom is tetrahedrally coordinated by three Cl atoms [average Fe–Cl bond length 2.164(1) Å] and the O atom [Fe–O bond length 1.958(2) Å]. Another symmetry-

related Cl atom is at 3.845(1) Å from Fe. The acetyl group is rotated 43.7(5)° out of the aromatic ring plane. The *tert*-butyl group adopts a position deviating ~30° from the energetically most favourable position, in which a C–C bond of the *tert*-butyl group lies in the aromatic ring plane. The packing in the crystal is mainly governed by a weak Fe...Cl contact and by van der Waals interactions between the aromatic ring and the *tert*-butyl groups from neighbouring molecules.