Frenz, B. A. (1978). *The Enraf-Nonius CAD-4 SDP – a Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution. Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi, pp. 64–71. Delft Univ. Press.
Heaton, D. E., Jones, R. A., Kidd, K. B., Cowley, A. H. & Nunn, C. M. (1988). *Polyhedron*, **7**, 1901–1908.
Heuer, L., Sell, M., Schmutzler, R. & Schomburg, D. (1987). *Polyhedron*, **6**, 1295–1307.
Johnson, C. K. (1974). *ORTEPII*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.
Lee, K. E., Higa, K. T., Nissan, R. A. & Butcher, R. J. (1992). *Organometallics*, **11**, 2816–2821.
Palenik, G. J. & Donohue, J. (1962). *Acta Cryst.* **15**, 564–569.
Sanz, F. & Daly, J. J. (1971). *J. Chem. Soc. A*, pp. 1083–1086.
Weigand, W., Cordes, A. W. & Swepston, P. N. (1981). *Acta Cryst.* B**37**, 1631–1634.
Zanella, P., Rossetto, G., Brianese, N., Ossola, F., Porchia, M. & Williams, J. O. (1991). *Chem. Mater.* **3**, 225–242.

Acta Cryst. (1994). **C50**, 1247–1249

The 18-Crown-6 Potassium Salt of a Meissenheimer Anion, $[K(C_7H_3Cl_3N_3O_6)(C_{12}H_{24}O_6)]$

John C. Barnes, Jenifer Main and John D. Paton

Chemistry Department, University of Dundee, Dundee DD1 4HN, Scotland

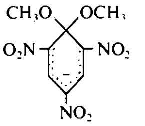
(*Received* 23 *December* 1993; *accepted* 22 *February* 1994)

Abstract

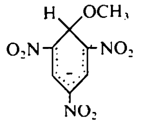
The title compound crystallizes as a centrosymmetric dimer, bis(μ-4-trichloromethyl-1,3,5-trinitro-2,5-cyclohexadien-1-ido)-$1\kappa^2O^1,O^{1'}$:$2\kappa O^3$;$1\kappa O^3$:$2\kappa^2O^1,O^{1'}$-bis-[(1,4,7,10,13,16-hexaoxacyclooctadecane-κ^6O)potassium], $[\{K(C_{12}H_{24}O_6)\}_2(\mu\text{-}C_7H_3Cl_3N_3O_6)_2]$, in which the coordination of the (18-crown-6)potassium ions is completed by a bidentate *para* nitro group from one anion and a monodentate *ortho* nitro group from the other. The CCl_3 group is axial and points away from the centre of inversion. The K^+ ion is 0.782 (2) Å out of the mean plane of the six crown O atoms.

Comment

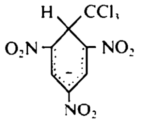
Meissenheimer (1902) presented the first chemical evidence for the molecular structures of the brightly coloured solutions formed by the interaction of aromatic nitro compounds with bases. There are recent reviews of the behaviour of these compounds in solution (Bunsel, Norris & Russell, 1968; Terrier, 1981) but very little has been published on their properties in the solid state and few structures have been determined. One reason is that the potassium salts of Meissenheimer anions such as (I) and (II) tend to give crystals of poor quality with only weak diffraction patterns. It was thought that better crystals might be obtained by the complexation of the K^+ ion with a crown ether. Reaction of the potassium salt of (I) with 18-crown-6 in ethyl acetate yielded 18-crown-6 potassium picrate (Barnes & Collard, 1988) as pale yellow crystals. The potassium salt of (II) (0.1 g, 0.30 mmol) reacted with 18-crown-6 (0.09 g, 0.3 mmol) in chloroform (4 ml) to give bright red crystals after slow evaporation at room temperature. These have been found to be the 18-crown-6 potassium complex of (III), a Meissenheimer anion in which the methoxy group has been replaced by CCl_3. (I) probably reacts similarly with chloroform but the poor quality orange crystals obtained gave an unsatisfactory weak data set from which no model could be obtained.



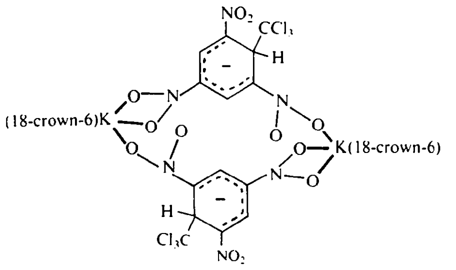
(I)



(II)



(III)



The structure of the title compound is dimeric about the centre of inversion at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ with the ring planes of the Meissenheimer anion approximately perpendicular to the *a* axis. The separation of these ring planes is 3.50 Å and the rings are arranged in a typical semi-overlapping arrangement associated with intermolecular π interactions (Prout & Kamenar, 1973) such that C(24$^{\rm i}$)—C(25$^{\rm i}$) lies perpendicularly below the ring diagonal C(23) to C(26) [symmetry code: (i) $1-x$, $1-y$, $1-z$]. The nominally single bonds to C(21) in the ring of the anion average 1.504 (4) Å, 10σ shorter than the exocyclic C(21)—C(27) bond. C(22)—C(23) and C(25)—C(26) average 1.354 (3) Å, 11σ shorter than C(23)—C(24) and C(24)—C(25). The tetrahedral C atom C(21) [C(26)—C(21)—C(22) 107.8 (2)°] is 0.389 (5) Å out of the mean plane through C(22), C(23), C(24), C(25) and C(26) with the H atom equatorial so that the CCl_3 group points axially towards the outside of the dimer. The normal to the mean plane of the three Cl atoms makes an angle of 14.8 (1)° to the normal to the mean plane through C(22), C(23), C(24), C(25) and C(26). The nitro groups are twisted out of the latter plane by 19.1 (2), 13.6 (2) and 18.4 (4)°, so that neither the loss of aromaticity nor the coordination to K^+ introduces deviation

Acta Crystallographica Section C
ISSN 0108-2701 © 1994

from the middle of the range of twist angles found for trinitrobenzenes in donor–acceptor complexes (Barnes & Golnazarians, 1987).

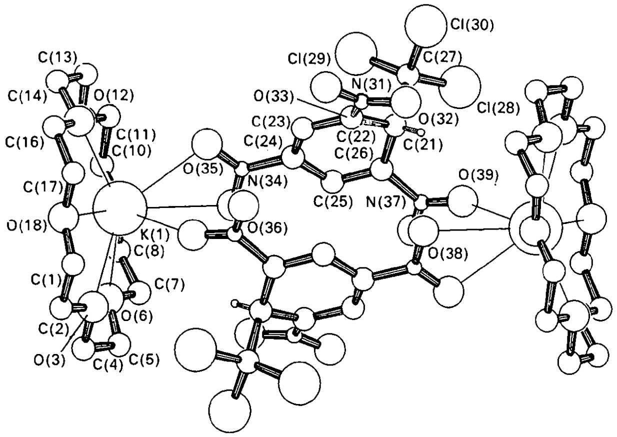


Fig. 1. The dimeric unit in the 18-crown-6 potassium complex of (III).

The K^+ ion is in a nine-coordinate piano-stool environment. The six O atoms from the crown occupy one side of the K^+ ion with the O atoms O(35) and O(36) from a bidentate nitro group *para* to the CCl_3 group of one anion and O(39^i) from a nitro group *ortho* to the CCl_3 group of a second anion on the other side. The K^+ ion is 0.782 (2) Å from the mean plane of the crown O atoms, slightly closer than in 18-crown-6 potassium picrate (Barnes & Collard, 1988) in which the K—O(crown) distances range from 2.862 to 2.989 Å compared with 2.800 (3) to 2.931 (4) Å in the present compound. The conformation of the crown is very similar in the two compounds; the average absolute O—C—C—O torsion angle and the average diametric O—K—O angle in the present compound are 62.7 (6) and 148.4 (1)°, respectively, while in 18-crown-6 potassium picrate the corresponding values are 65.8 and 144.5°, respectively.

Experimental

Crystal data

$[K(C_7H_3Cl_3N_3O_6)$-
$(C_{12}H_{24}O_6)]$
$M_r = 634.89$
Triclinic
$P\overline{1}$
$a = 11.676$ (3) Å
$b = 11.845$ (3) Å
$c = 13.110$ (4) Å
$\alpha = 72.59$ (3)°
$\beta = 61.72$ (3)°
$\gamma = 63.44$ (2)°
$V = 1419.4$ (7) Å^3
$Z = 2$
$D_x = 1.485$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 7$–14°
$\mu = 0.531$ mm^{-1}
$T = 293$ (2) K
Plate
0.46 × 0.41 × 0.10 mm
Dark red

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
5581 measured reflections
4369 independent reflections
1975 observed reflections
$[I > 2\sigma(I)]$

$R_{\text{int}} = 0.037$
$\theta_{\max} = 23.97°$
$h = -11 \rightarrow 12$
$k = -12 \rightarrow 12$
$l = 0 \rightarrow 14$
3 standard reflections
frequency: 60 min
intensity variation: insignificant

Refinement

Refinement on F^2
$R(F) = 0.0360$
$wR(F^2) = 0.0930$
$S = 0.332$
4369 reflections
350 parameters
U refined for groups of H atoms, position and U refined for H(21)
Calculated weights
$w = 1/[\sigma^2(F_o^2) + (0.1000P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.284$ e Å^{-3}
$\Delta\rho_{\min} = -0.192$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
K(1)	0.28449 (7)	0.82025 (5)	0.83588 (5)	0.0591 (2)
C(1)	0.0000 (5)	0.7110 (4)	1.0517 (4)	0.0917 (14)
C(2)	−0.0842 (5)	0.8379 (4)	1.0103 (4)	0.0943 (14)
O(3)	−0.0059 (3)	0.8779 (2)	0.8971 (2)	0.0791 (7)
C(4)	−0.0818 (4)	0.9966 (4)	0.8541 (4)	0.0855 (12)
C(5)	0.0087 (5)	1.0336 (4)	0.7335 (4)	0.0892 (13)
O(6)	0.1176 (3)	1.0487 (3)	0.7383 (2)	0.0826 (8)
C(7)	0.2080 (6)	1.0879 (5)	0.6297 (4)	0.105 (2)
C(8)	0.3042 (7)	1.1228 (5)	0.6434 (4)	0.120 (2)
O(9)	0.3814 (4)	1.0200 (3)	0.6969 (3)	0.1036 (10)
C(10)	0.4728 (5)	1.0470 (5)	0.7167 (5)	0.122 (2)
C(11)	0.5601 (6)	0.9321 (6)	0.7637 (6)	0.152 (3)
O(12)	0.4791 (3)	0.8829 (4)	0.8702 (4)	0.1211 (13)
C(13)	0.5608 (6)	0.7661 (7)	0.9211 (6)	0.148 (3)
C(14)	0.4713 (6)	0.7199 (6)	1.0287 (5)	0.135 (2)
O(15)	0.3860 (4)	0.6841 (3)	1.0096 (3)	0.1075 (11)
C(16)	0.3008 (6)	0.6322 (4)	1.1141 (4)	0.112 (2)
C(17)	0.2022 (6)	0.6085 (4)	1.0911 (4)	0.111 (2)
O(18)	0.1131 (3)	0.7227 (2)	1.0557 (2)	0.0866 (9)
C(21)	0.8048 (3)	0.3433 (3)	0.3977 (2)	0.0467 (7)
C(22)	0.7368 (3)	0.3200 (2)	0.5282 (2)	0.0479 (7)
C(23)	0.6594 (3)	0.4149 (3)	0.5972 (3)	0.0533 (8)
C(24)	0.6181 (3)	0.5411 (3)	0.5480 (3)	0.0523 (8)
C(25)	0.6368 (3)	0.5672 (3)	0.4308 (3)	0.0537 (8)
C(26)	0.7181 (3)	0.4731 (3)	0.3602 (2)	0.0500 (7)
C(27)	0.9583 (3)	0.3298 (3)	0.3573 (2)	0.0548 (8)
Cl(28)	1.03642 (9)	0.35858 (9)	0.20224 (7)	0.0729 (3)
Cl(29)	0.97058 (11)	0.43940 (10)	0.41512 (10)	0.0850 (3)
Cl(30)	1.05768 (8)	0.17412 (8)	0.39945 (8)	0.0748 (3)
N(31)	0.7441 (3)	0.1937 (2)	0.5819 (2)	0.0573 (7)
O(32)	0.7869 (3)	0.1112 (2)	0.5201 (2)	0.0716 (7)
O(33)	0.7073 (3)	0.1701 (2)	0.6887 (2)	0.0760 (7)
N(34)	0.5345 (3)	0.6387 (2)	0.6214 (2)	0.0670 (8)
O(35)	0.5278 (3)	0.6159 (2)	0.7228 (2)	0.0859 (8)
O(36)	0.4670 (3)	0.7445 (2)	0.5847 (2)	0.0850 (9)
N(37)	0.7122 (3)	0.4951 (3)	0.2489 (2)	0.0665 (8)
O(38)	0.6676 (3)	0.6039 (3)	0.2070 (2)	0.0976 (10)
O(39)	0.7513 (3)	0.4018 (3)	0.2001 (2)	0.0801 (8)

Table 2. *Selected geometric parameters* (Å, °)

K(1)—O(15)	2.800 (3)	C(23)—C(24)	1.399 (4)
K(1)—O(9)	2.839 (3)	C(24)—C(25)	1.400 (4)
K(1)—O(35)	2.852 (3)	C(24)—N(34)	1.408 (4)
K(1)—O(18)	2.873 (3)	C(25)—C(26)	1.356 (4)
K(1)—O(3)	2.878 (3)	C(26)—N(37)	1.433 (4)
K(1)—O(6)	2.887 (3)	C(27)—Cl(30)	1.771 (3)
K(1)—O(12)	2.931 (4)	C(27)—Cl(29)	1.772 (3)
K(1)—O(39^{i})	3.038 (3)	C(27)—Cl(28)	1.785 (3)
K(1)—O(36)	3.098 (3)	N(31)—O(32)	1.231 (4)
K(1)—N(34)	3.359 (3)	N(31)—O(33)	1.236 (4)
C(21)—C(26)	1.503 (4)	N(34)—O(36)	1.241 (4)
C(21)—C(22)	1.504 (4)	N(34)—O(35)	1.246 (4)
C(21)—C(27)	1.553 (5)	N(37)—O(38)	1.217 (4)
C(22)—C(23)	1.351 (4)	N(37)—O(39)	1.239 (4)
C(22)—N(31)	1.432 (4)		
O(15)—K(1)—O(35)	76.52 (10)	O(18)—K(1)—O(36)	138.03 (8)
O(9)—K(1)—O(35)	97.14 (10)	O(3)—K(1)—O(36)	111.44 (9)
O(35)—K(1)—O(18)	109.63 (9)	O(6)—K(1)—O(36)	87.32 (8)
O(35)—K(1)—O(3)	130.79 (9)	O(12)—K(1)—O(36)	99.20 (11)
O(15)—K(1)—O(6)	151.55 (9)	C(26)—C(21)—C(22)	107.8 (2)
O(35)—K(1)—O(6)	129.81 (9)	C(26)—C(21)—C(27)	112.1 (3)
O(35)—K(1)—O(12)	84.29 (10)	C(22)—C(21)—C(27)	110.9 (3)
O(3)—K(1)—O(12)	144.33 (10)	C(22)—C(23)—C(24)	119.9 (3)
O(15)—K(1)—O(39^{i})	94.74 (10)	C(23)—C(24)—C(25)	119.6 (3)
O(9)—K(1)—O(39^{i})	137.93 (9)	C(26)—C(25)—C(24)	119.9 (3)
O(35)—K(1)—O(39^{i})	61.34 (9)	C(25)—C(26)—C(21)	122.7 (3)
O(18)—K(1)—O(39^{i})	70.89 (8)	C(21)—C(27)—Cl(30)	110.5 (2)
O(3)—K(1)—O(39^{i})	70.14 (8)	C(21)—C(27)—Cl(29)	112.3 (2)
O(6)—K(1)—O(39^{i})	107.25 (8)	C(21)—C(27)—Cl(28)	110.1 (2)
O(12)—K(1)—O(39^{i})	141.63 (10)	O(32)—N(31)—O(33)	121.6 (3)
O(15)—K(1)—O(36)	118.29 (10)	O(36)—N(34)—O(35)	121.4 (3)
O(9)—K(1)—O(36)	72.52 (9)	O(38)—N(37)—O(39)	122.8 (3)
O(35)—K(1)—O(36)	42.51 (8)		

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Data collection, cell refinement and data reduction: *CAD*-4 *Software* (Enraf–Nonius, 1989). The structure was solved using the direct methods routine *TREF* in *SHELXS*86 (Sheldrick, 1990), which located the K^+ ion, most of the 18-crown-6 molecule and part of the anion, and gave three unexpected strong peaks which were eventually interpreted as the Cl atoms of the CCl_3 group. Routine least-squares refinement and difference syntheses carried out using *SHELX*76 (Sheldrick, 1976), with *SHELXL* (Sheldrick, 1994) used for the last cycles, completed the structure. Molecular graphics were prepared using *PLUTON*92 (Spek, 1992).

We wish to thank Professor R. Foster and Dr J. A. Chudek (Dundee University) for suggesting the problem, providing a sample of (II) and valuable discussions of the results, and Drs C. K. Prout and D. J. Watkin, Oxford University, for the opportunity to use the diffractometer.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: LI1100). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Barnes, J. C. & Collard, J. (1988). *Acta Cryst.* C**44**, 565–566.

Barnes, J. C. & Golnazarians, W. (1987). *Acta Cryst.* C**43**, 549–552.

Bunsel, E., Norris, A. R. & Russell, K. E. (1968). *Q. Rev.* **22**, 123–146.

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Meissenheimer, J. (1902). *Ann. Chem.* **322**, 205–214.

Prout, C. K. & Kamenar, B. (1973). In *Molecular Complexes*, Vol. 1, edited by R. Foster. London: Elek.

Sheldrick, G. M. (1976). *SHELX*76. *Program for Crystal Structure Determination*. Univ. of Cambridge, England.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1994). *J. Appl. Cryst.* In preparation.

Spek, A. L. (1992). *PLUTON*92. *Molecular Graphics Program*. Univ. of Utrecht, The Netherlands.

Terrier, F. (1982). *Chem. Rev.* **82**, 77–152.

Acta Cryst. (1994). C**50**, 1249–1252

(Nitrato-κO)(triphenylphosphine-κP){3,6,9-trithiabicyclo[9.4.0]pentadeca-1(11),12,14-triene-$\kappa^3 S^{3,6,9}$}mercury(II) Nitrate Hydrate Hemiethanol Solvate

RAIKKO KIVEKÄS*

Department of Chemistry, P.O. Box 6,
FIN-00014 University of Helsinki, Finland

REIJO SILLANPÄÄ

Department of Chemistry, University of Turku,
FIN-20500 Turku, Finland

LLUIS ESCRICHE, MARÍA-PILAR ALMAJANO,
FRANCESC TEIXIDOR AND JAUME CASABÓ

Departament de Química, Universitat Autònoma de
Barcelona and Institut de Ciència dels Materials
(CSIC), Campus de Bellaterra, 08193 Bellaterra,
Barcelona, Spain

(*Received* 17 *August* 1993; *accepted* 13 *January* 1994)

Abstract

In the title compound, $[Hg(NO_3)(C_{12}H_{16}S_3)(C_{18}H_{15}P)][NO_3].H_2O.0.5C_2H_6O$, the coordination sphere of the Hg^{2+} ion is a distorted trigonal bipyramid defined by the three S atoms of the trithiamacrocycle, the P atom of the triphenylphosphine group and an O atom of one nitrate group.

Comment

Among crown thioethers, 1,4,7-trithianonane (9S3) is unique in the unusual electronic and redox behaviour of its complexes (Blake & Scröder, 1990). By extension, interest has been aroused in the coordinating capabilities of related trithiamacrocycles, especially