density peak heights or thermal parameters) for any mutual disorder of C—Cl or C—O groups. The bond lengths and bond angles within the hydrotris(3,4,5-trimethyl-1-pyrazolyl)borate ligand resemble closely those of the hydrotris(3,5-dimethyl-1-pyrazolyl)borate ligand in complex (II) and show no unexpected features. The arrangement of the two carbonyl ligands [mean Mo—C 1·978 (5), mean C—O 1·163 (7) Å, mean Mo—C—O 175·3 (5), C(1)—Mo—C(2) 87·9 (3)°] is very similar to that found in complex (II) [mean Mo—C 1·992 (5), mean C—O 1·150 (6) Å, mean Mo—C—O 177·7 (5), C(1)—Mo—(2) 89·0 (2)°].

The chloromethylidyne ligand is bonded to molybdenum with Mo—C(3) 1·798 (5) and C(3)—Cl 1·680 (6) Å. The molybdenum–C(methylidyne) separation is thus essentially identical to that in the η^1-organothiomethylidyne complex (II). The much longer Mo—C(methylidyne) bond reported for (I) may be an artefact of some residual disordering of carbonyl and chloromethylidyne ligands in the crystal of that complex. The Cl—C(methylidyne) separation in (IV), 1·680 (6) Å, is close to the value (1·69 Å) calculated from the sum of the covalent radii of *sp*-carbon and chlorine (Cotton & Wilkinson, 1976). Whereas the η^1-organothiomethylidyne ligands in complexes (II) and (III) bond to the metal in an essentially linear fashion [*M*—C—S 179·5 (2) and 174·2 (6)° respectively] the Mo—C(3)—Cl fragment in (IV) is distinctly angular [165·7 (4)°]; this non-linearity probably arises from the effects of crystal packing forces. Thus, intermolecular distance calculations show that with the non-linear model, the Cl atom makes two contacts with neighbouring molecules Cl···C(18) (at $\frac{1}{2} - x$, $-\frac{1}{2} + y$, z) 3·887 (6) and Cl···C(26) (at $1 - x$, $-y$, $-\frac{1}{2} + z$) 3·728 (6) Å; these distances are in accord with the van der Waals radii sum for Cl and C(methyl) of approximately 3·8 Å. However, when the Cl atom is positioned geometrically so that the Mo—C—Cl bond is linear, the resulting Cl···C(18) and Cl···C(26) intermolecular contacts are reduced to 3·493 (6) and 3·501 (6) Å respectively, significantly less than the sum of the van der Waals radii.

The chloromethylidyne ligand in (IV) exerts a marked *trans* effect (the Mo—N bond *trans* to the ligand being *ca* 0·039 Å longer than those *trans* to CO) but the effect is less pronounced than that in (II) where the *trans* bond-lengthening is of the order of 0·074 Å.

In the crystal of (IV) the molecules are separated by normal van der Waals distances and show no unusual intermolecular contacts.

We thank the NSERC Canada for grants in Aid of Research.

References

Cotton, F. A. & Wilkinson, G. (1976). *Basic Inorganic Chemistry*, p. 87. New York: John Wiley.

Desmond, T., Lalor, F. J., Ferguson, G. & Parvez, M. (1983). *J. Chem. Soc. Chem. Commun.* pp. 457–459.

Desmond, T., Lalor, F. J., Ferguson, G. & Parvez, M. (1984). *J. Chem. Soc. Chem. Commun.* pp. 75–77.

Greaves, W. W., Angelici, R. J., Helland, B. J., Klima, R. & Jacobson, R. A. (1979). *J. Am. Chem. Soc.* **107**, 7618–7620.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Sheldrick, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1990). C**46**, 61–64

Structure of Caesium Picrate

By A. Schouten and J. A. Kanters

Laboratorium voor Kristal- en Structuurchemie, Rijksuniversiteit Utrecht, Transitorium 3, *Padualaan* 8,
3584 *CH Utrecht, The Netherlands*

and N. S. Poonia

Institute for Research and Chemical Services, Vishnupuri, Indore 452001, *India*

(*Received* 15 *March* 1989; *accepted* 9 *May* 1989)

Abstract. $Cs[C_6H_2N_3O_7]$, $M_r = 361\cdot00$, monoclinic, $P2_1/c$, $a = 10\cdot811\,(1)$, $b = 4\cdot7011\,(4)$, $c = 19\cdot404\,(1)$ Å, $\beta = 101\cdot41\,(1)°$, $V = 966\cdot7\,(1)$ Å^3, $Z = 4$, $D_x = 2\cdot48$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 38\cdot3$ cm^{-1}, $F(000) = 680$, $T = 295$ K, $R = 0\cdot025$ for 1831 observed reflections with $I > 2\cdot5\sigma(I)$. In the

0108-2701/90/010061-04$03.00

crystal structure, which is isomorphous with that of the red polymorph of Tl^I picrate, four stacks of translationally equivalent picrates form channels in the [010] direction that contain columns of Cs cations. The Cs cations are coordinated to nine O atoms from seven different picrate anions to form a three-capped distorted trigonal prism (shortest $Cs^+\cdots O$ distance 3·028 Å). The phenyl ring of the picrate ion is significantly distorted from hexagonal symmetry.

Introduction. Several crystal structures of salts of picric acid with organic or metallic cations have been reported in recent years. The structures of the isomorphous anhydrous NH_4^+ and K^+ salts (Maartmann-Moe, 1969; Palenik, 1972) and the monohydrated Li^+ salt (Griffin & Coppens, 1973) are known. An article which describes the crystal structure of the red modification of Tl^I picrate (Herbstein, Kapon & Wielinski, 1977) also reports that Rb, Cs and red Tl^I picrates are isomorphous and different from the isomorphous NH_4 and K picrates. However, probably as a result of extinction and absorption effects, the refinement of Tl^I picrate did not proceed satisfactorily ($R = 0{\cdot}117$). Because of our interest in the coordination properties of the picrate anion and in particular in its deformation in salts, we undertook the structure analysis of Cs picrate. DTA measurements show that Cs picrate undergoes a phase transformation at 553 K (Stammler, 1968); the structure of this high-temperature polymorph is not yet known.

Experimental. Crystals of Cs picrate were prepared by reacting molar quantities of Cs carbonate and picric acid in 50% water–ethanol and slow evaporation at room temperature. A yellow, rod-shaped crystal of dimensions 0·2 × 0·2 × 0·5 mm was used for data collection. Enraf–Nonius CAD-4 diffractometer, Zr-filtered Mo *Kα* radiation. Lattice constants were determined from the setting angles of four quartets of equivalent reflections in the range $15{\cdot}07 \le \theta \le 17{\cdot}48°$. 2162 reflections were measured in the ω–2θ scan mode, $\Delta\omega = (0{\cdot}60 + 0{\cdot}35\tan\theta)°$; $2\theta_{max} = 55°$, $-12 \le h \le 12$, $0 \le k \le 6$, $0 \le l \le 25$, of which 1831 were above the $2{\cdot}5\sigma(I)$ level. Reference reflections ($0\bar{2}0$ and 300), measured every hour, showed insignificant changes. Intensities corrected for Lorentz–polarization, extinction and absorption effects (transmission factors ranged from 0·48 to 0·55). The structure was solved by Patterson and Fourier techniques. The positions of the H atoms were determined from difference syntheses and included in the refinement with individual isotropic thermal parameters. Anisotropic full-matrix least-squares refinement on F of 163 parameters converged at $R = 0{\cdot}025$ and $wR = 0{\cdot}024$ with $w = 1{\cdot}8892/\sigma^2(F_o)$, $S = 0{\cdot}98$, $(\Delta/\sigma)_{av} = 0{\cdot}0011$, $(\Delta/\sigma)_{max} = 0{\cdot}0108$. The isotropic extinction parameter converged to 0·0014. The final difference synthesis revealed regions of electron densities of about $\pm 0{\cdot}7$ e Å^{-3} at 1·0 Å from Cs, the other features were below that level. Scattering factors for non-H atoms were those of Cromer & Mann (1968) and for H atoms those of Stewart, Davidson & Simpson (1965); anomalous-dispersion corrections were from Cromer & Liberman (1970). Calculations were performed with *SHELX76* (Sheldrick, 1976) (structure determination and refinement) and the *EUCLID* package (Spek, 1982) (geometry and illustrations) on a microVAX II computer.*

Discussion. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1, and bond distances, angles and selected torsion angles are listed in Table 2. A view of the molecule with atom numbering is shown in Fig. 1.

The structure is essentially isomorphous with that of red Tl^I picrate (Herbstein, Kapon & Wielinski, 1977).† In the crystal the Cs cations are coordinated to nine O atoms from seven different picrate anions to form a three-capped, slightly distorted trigonal prism with almost rectangular sides (see Fig. 2). Six O atoms are from the *o*-nitro groups, two from the phenoxide O and one from the *p*-nitro group. The edge of the prism is 4·701 (3) Å, the widths are 3·448 (3), 3·573 (4) and 4·110 (4) Å. The defining angles of the prism are 71·64 (8), 52·77 (6), 96·62 (7), 86·88 (7) and 92·83 (7)°, and these are similar to the angles in Tl^I picrate.

The $Cs^+\cdots O$ distances for the nine nearest O atoms range from 3·028 (3) to 3·372 (2) Å. The shortest distance involves an O atom of an *o*-nitro group, whereas in Tl^I picrate the shortest distance is to the phenoxide O atom. Four other O atoms within 4 Å of Cs^+ [at 3·534 (2), 3·540 (3), 3·847 (2) and 3·946 (3) Å] are not considered to belong to the coordination sphere because of their larger distances. The trigonal prism is parallel to [010] and the top and bottom faces are one translation apart along **b**. The prisms are so aligned that the top and bottom faces are shared, resulting in an infinite column of Cs polyhedra in the [010] direction. The phenyl rings of the picrate ions are inclined at 43·3 (1)° to the (010) plane. A stereoview of the molecular packing is shown in Fig. 3.

---

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and additional torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52213 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† Table 3 in that paper, which describes the coordination of Tl^I, contains an error in that it states that both O's of the *p*-nitro group coordinate to Tl^I. The atom corresponding to number 1 in that table, labelled O(3), should be labelled O(2).

Table 1. *Fractional coordinates and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

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

	x	y	z	U_{eq}
Cs	0·59866 (2)	0·54156 (5)	0·36089 (1)	0·0421 (1)
O(1)	0·3900 (2)	0·0830 (5)	0·3358 (1)	0·0473 (9)
O(2)	0·3811 (3)	−0·2939 (6)	0·4429 (2)	0·061 (1)
O(3)	0·3367 (3)	−0·0416 (6)	0·5268 (1)	0·059 (1)
O(4)	−0·0979 (2)	0·3362 (6)	0·4512 (1)	0·0484 (9)
O(5)	−0·1027 (2)	0·6898 (6)	0·3795 (1)	0·053 (1)
O(6)	0·1739 (3)	0·7222 (7)	0·2230 (1)	0·068 (1)
O(7)	0·3490 (2)	0·4984 (6)	0·2396 (1)	0·0522 (9)
N(1)	0·3274 (3)	−0·0943 (6)	0·4647 (2)	0·040 (1)
N(2)	−0·0525 (2)	0·4745 (6)	0·4084 (2)	0·0371 (9)
N(3)	0·2462 (3)	0·5452 (7)	0·2550 (1)	0·0393 (9)
C(1)	0·2925 (3)	0·1792 (7)	0·3517 (2)	0·033 (1)
C(2)	0·2475 (3)	0·0934 (7)	0·4145 (2)	0·033 (1)
C(3)	0·1386 (3)	0·1839 (7)	0·4335 (2)	0·033 (1)
C(4)	0·0642 (3)	0·3789 (7)	0·3906 (2)	0·032 (1)
C(5)	0·1016 (3)	0·4916 (7)	0·3325 (2)	0·033 (1)
C(6)	0·2115 (3)	0·3996 (7)	0·3141 (2)	0·031 (1)

Table 2. *Bond distances* (Å), *bond angles* (°) *and selected torsion angles* (°) *with e.s.d.'s in parentheses*

N(1)—C(2)	1·463 (4)	N(3)—O(7)	1·227 (4)
N(2)—C(4)	1·444 (4)	O(1)—C(1)	1·241 (4)
N(3)—C(6)	1·447 (4)	C(1)—C(2)	1·457 (5)
N(1)—O(2)	1·223 (4)	C(1)—C(6)	1·456 (5)
N(1)—O(3)	1·213 (4)	C(2)—C(3)	1·369 (5)
N(2)—O(4)	1·232 (4)	C(3)—C(4)	1·384 (5)
N(2)—O(5)	1·230 (4)	C(4)—C(5)	1·375 (5)
N(3)—O(6)	1·223 (4)	C(5)—C(6)	1·377 (5)

O(2)—N(1)—O(3)	123·3 (3)	N(1)—C(2)—C(1)	118·3 (3)
O(2)—N(1)—C(2)	119·3 (3)	N(1)—C(2)—C(3)	115·7 (3)
O(3)—N(1)—C(2)	117·4 (3)	C(1)—C(2)—C(3)	125·9 (3)
O(4)—N(2)—O(5)	122·9 (2)	C(2)—C(3)—C(4)	118·2 (3)
O(4)—N(2)—C(4)	118·8 (3)	N(2)—C(4)—C(3)	119·6 (3)
O(5)—N(2)—C(4)	118·3 (3)	N(2)—C(4)—C(5)	119·2 (3)
O(6)—N(3)—O(7)	121·1 (3)	C(3)—C(4)—C(5)	121·2 (3)
O(6)—N(3)—C(6)	119·0 (3)	C(4)—C(5)—C(6)	120·0 (3)
O(7)—N(3)—C(6)	119·9 (3)	N(3)—C(6)—C(1)	120·6 (3)
O(1)—C(1)—C(2)	123·3 (3)	N(3)—C(6)—C(5)	115·5 (3)
O(1)—C(1)—C(6)	126·2 (3)	C(1)—C(6)—C(5)	123·9 (3)
C(2)—C(1)—C(6)	110·4 (3)		

O(1)—C(1)—C(2)—N(1)	6·1 (5)	O(4)—N(2)—C(4)—C(3)	−16·4 (5)
O(1)—C(1)—C(2)—C(3)	−177·5 (3)	O(4)—N(2)—C(4)—C(5)	165·9 (3)
O(1)—C(1)—C(6)—C(5)	177·5 (3)	O(5)—N(2)—C(4)—C(3)	164·2 (3)
O(1)—C(1)—C(6)—N(3)	−4·8 (5)	O(5)—N(2)—C(4)—C(5)	−13·4 (5)
O(2)—N(1)—C(2)—C(1)	−42·0 (5)	O(6)—N(3)—C(6)—C(1)	177·4 (3)
O(2)—N(1)—C(2)—C(3)	141·2 (3)	O(6)—N(3)—C(6)—C(5)	−4·8 (5)
O(3)—N(1)—C(2)—C(1)	137·9 (3)	O(7)—N(3)—C(6)—C(1)	−5·5 (5)
O(3)—N(1)—C(2)—C(3)	−38·9 (4)	O(7)—N(3)—C(6)—C(5)	172·3 (3)

The phenyl ring is significantly deformed from hexagonal symmetry and moderately planar (σ_{plane} = 0·035 Å).

In order to compare the distortion of the title compound with that of reported picrate geometries, a search was made in the Cambridge Structural Database (Allen, Kennard & Taylor, 1983). The search yielded 48 hits of crystal structures containing picrate fragments with R below 0·06. As can be seen below, the distortion of the phenyl ring of the title compound is in very good agreement with the average values of the pertinent geometric data (given in square brackets) retrieved from the database: the bond angle at the phenolic site is decreased, 110·4 (3)° [112 (1)°], the angles subtended at the *o*-C atoms are enlarged, 123·9 (3), 125·9 (3)° [124·1 (7), 125 (1)°], the two C—C bonds at the phenolic site are lengthened, 1·457 (5), 1·456 (5) Å [1·45 (1),

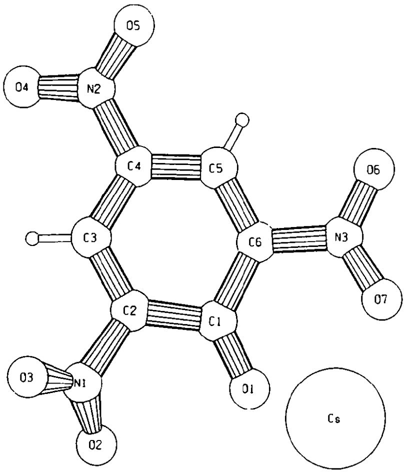


Fig. 1. Perspective view of the molecule with atom numbering.

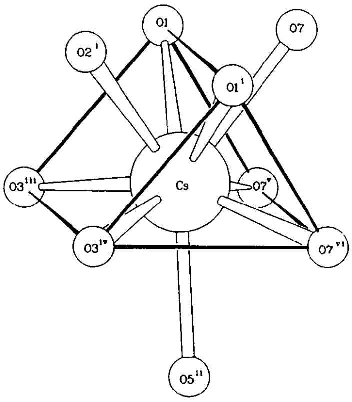


Fig. 2. View of the coordination polyhedron of O atoms about the Cs$^+$ ion. Symmetry code: (i) x, $1 + y$, z; (ii) $1 + x$, y, z; (iii) $1 - x$, $-y$, $1 - z$; (iv) $1 - x$, $1 - y$, $1 - z$; (v) $1 - x$, $-\frac{1}{2} + y$, $\frac{1}{2} - z$; (vi) $1 - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$.

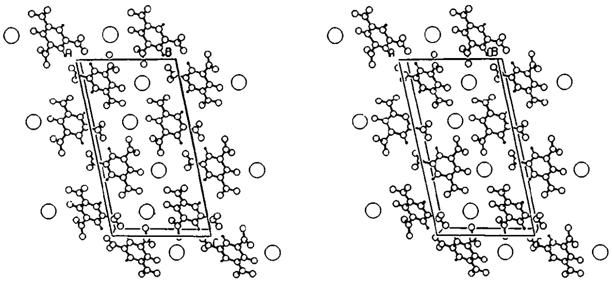


Fig. 3. Stereoplot of the unit cell viewed down the b axis, showing the molecular packing.

1·45 (2) Å], and the four remaining C—C bonds are shortened, av. 1·376 (6) Å [1·38 (1) Å].

The three nitro groups display various degrees of twisting, moderate for one of the *o*-nitro groups [9·0 (4)°] and the *p*-nitro group [15·0 (4)°], but large for the other *o*-nitro group [41·8 (4)°].

References

Allen, F. H., Kennard, O. & Taylor, R. (1983). *Acc. Chem. Res.* **16**, 146–153.

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* **A24**, 321–324.

Griffin, J. F. & Coppens, P. (1973). Am. Crystallogr. Assoc. Winter Meet. *Program and Abstracts*, p. 30.

Herbstein, F. H., Kapon, M. & Wielinski, S. (1977). *Acta Cryst.* **B33**, 649–654.

Maartmann-Moe, K. (1969). *Acta Cryst.* **B25**, 1452–1460.

Palenik, G. J. (1972). *Acta Cryst.* **B28**, 1633–1635.

Sheldrick, G. M. (1976). *SHELX76*. Program for structure determination. Univ. of Cambridge, England.

Spek, A. L. (1982). *The EUCLID Package*. In *Computational Crystallography*, edited by D. Sayre, p. 528. Oxford: Clarendon Press.

Stammler, M. (1968). *Explosivstoffe*, **16**, 154–163.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1990). C**46**, 64–66

Dimethylbis(5-methylfurfuryl)ammonium Chloride

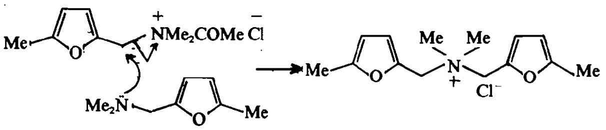
By D. S. Brown, C. A. Burns, H. Heaney, G. Papageorgiou and R. F. Wilkins

*Department of Chemistry, Loughborough University of Technology, Loughborough, Leics. LE*11 3*TU*, *England*

(*Received* 24 *February* 1989; *accepted* 24 *April* 1989)

Abstract. $C_{14}H_{20}NO_2^+.Cl^-$, $M_r = 269{\cdot}8$, monoclinic, $C2/c$, $a = 6{\cdot}24\ (1)$, $b = 14{\cdot}47\ (1)$, $c = 15{\cdot}96\ (1)$ Å, $\beta = 92{\cdot}3\ (2)°$, $V = 1439{\cdot}8$ Å^3, $Z = 4$, $D_x = 1{\cdot}25\ \text{g cm}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 2{\cdot}17\ \text{cm}^{-1}$, $F(000) = 576$, $T = 293$ K. The structure was refined to $R = 0{\cdot}034$ for 1141 observed reflections [$F/\sigma(F) > 6$]. The compound is a by-product from the interaction of a Mannich base with acetyl chloride resulting in the quaternary ammonium salt. The salt possesses a twofold axis of symmetry with N and Cl occupying special positions, the quaternary nitrogen having two short and two long C—N bonds [1·533 (2) and 1·496 (2) Å].

Introduction. Mannich reactions of furan had been reported not to proceed using classical methodology (Eliel & Peckham, 1950; Eliel & Fisk, 1963). As part of a recent study (Heaney, Papageorgiou & Wilkins, 1988), reactions of pre-formed methyleneimonium salts were carried out using both furan and 2-methylfuran. The normal method of isolating the Mannich bases involves extraction with diethyl ether. However, isolation of 2-dimethylaminomethyl-5-methylfuran (1) by extraction using dichloromethane gave rise to variable quantities of a quaternary ammonium salt which was shown to have the structure (2). Although the majority of the physical properties of (1) and (2) were different, we were unable to establish the molecular weight of the salt (2) using electron-impact mass spectrometry. It was for this reason that X-ray crystallographic studies were initiated. Although the electron-impact mass spectra of the compounds (1) and (2) were essentially identical, we were eventually able to obtain a fast-atom-bombardment spectrum which did establish the structure.



(1) (2)

It is assumed that the quaternary salt (2) is formed by the displacement of dimethylamine from the hydrochloride derived from (1). The salt (2) was subsequently prepared in 98% yield by the reaction of acetyl chloride with 2-dimethylaminomethyl-5-methylfuran (2 mol equivalents).

Experimental. Preparation by the method of Heaney *et al.* (1988); colourless acicular crystal, 1·0 × 0·4 × 0·3 mm, mounted about *c*; Stoe Stadi-2 Weissenberg diffractometer, $(\sin\theta)\lambda < 0{\cdot}6$ Å^{-1}; lattice parameters from optimum fit of axial row reflections ($15 < 2\theta < 40°$); 1631 unique reflections measured of which 1141 had $F/\sigma(F) > 6$ and were classed as observed; h $-6\rightarrow6$, k $0\rightarrow16$, l $0\rightarrow18$; standard reflections on each layer measured every 50 reflections, no signifi-

0108-2701/90/010064-03$03.00