C(93*b*)	0.7778 (33)	0.8403 (19)	0.7817 (46)	0.146 (22)
N(1)	0.9722 (19)	0.1192 (10)	0.2453 (25)	0.203 (12)
C(2*s*)	0.9691 (20)	0.1040 (10)	0.3385 (27)	0.146 (11)
C(1*s*)	0.9681 (27)	0.0814 (12)	0.4504 (29)	0.261 (21)

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

Au(1)—P(4)	2.275 (4)	P(1)—S(1)	2.051 (6)
Au(1)—S(3)	2.894 (4)	P(1)—C(16)	1.835 (13)
P(1)—C(1)	1.753 (14)	P(2)—S(2)	1.982 (5)
P(1)—C(26)	1.818 (13)	P(2)—C(36)	1.823 (13)
P(2)—C(1)	1.765 (13)	P(3)—S(3)	1.993 (5)
P(2)—C(46)	1.809 (12)	P(3)—C(56)	1.829 (14)
P(3)—C(1)	1.787 (13)	P(4)—C(76)	1.818 (15)
P(3)—C(66)	1.830 (16)	P(4)—C(90)	1.818 (17)
P(4)—C(86)	1.840 (16)	C(2*s*)—C(1*s*)	1.494 (47)
Au(1)—S(1)	2.326 (4)	N(1)—C(2*s*)	1.206 (44)
P(4)—Au(1)—S(1)	161.4 (1)	C(1)—P(3)—C(56)	109.2 (6)
S(1)—Au(1)—S(3)	104.6 (1)	C(1)—P(3)—C(66)	108.0 (7)
S(1)—P(1)—C(16)	104.6 (4)	Au(1)—P(4)—C(76)	115.4 (5)
S(1)—P(1)—C(26)	106.3 (5)	C(76)—P(4)—C(86)	104.7 (7)
C(16)—P(1)—C(26)	102.9 (6)	C(76)—P(4)—C(90)	102.9 (7)
S(2)—P(2)—C(36)	111.7 (5)	Au(1)—S(1)—P(1)	112.3 (2)
S(2)—P(2)—C(46)	108.9 (5)	P(1)—C(1)—P(2)	119.9 (7)
C(36)—P(2)—C(46)	100.5 (6)	P(2)—C(1)—P(3)	122.4 (8)
S(3)—P(3)—C(56)	109.9 (5)	P(1)—C(16)—C(11)	119.8 (10)
S(3)—P(3)—C(66)	110.6 (5)	P(1)—C(26)—C(25)	120.7 (10)
C(56)—P(3)—C(66)	102.6 (7)	P(2)—C(36)—C(35)	121.9 (10)
Au(1)—P(4)—C(86)	108.0 (5)	P(2)—C(46)—C(45)	120.9 (10)
Au(1)—P(4)—C(90)	116.8 (6)	P(3)—C(56)—C(55)	118.6 (10)
C(76)—P(4)—C(90)	108.1 (7)	P(3)—C(66)—C(65)	122.4 (12)
Au(1)—S(3)—P(3)	97.2 (2)	P(4)—C(76)—C(75)	121.1 (11)
P(1)—C(1)—P(3)	117.2 (7)	P(4)—C(86)—C(85)	121.8 (12)
P(1)—C(16)—C(15)	119.7 (10)	P(4)—C(90)—C(91)	119.0 (12)
P(4)—Au(1)—S(3)	90.9 (1)	P(1)—C(26)—C(21)	120.0 (11)
S(1)—P(1)—C(1)	117.2 (4)	P(2)—C(36)—C(31)	121.5 (10)
C(1)—P(1)—C(16)	113.0 (6)	P(2)—C(46)—C(41)	121.6 (10)
C(1)—P(1)—C(26)	111.6 (6)	P(3)—C(56)—C(51)	122.9 (11)
S(2)—P(2)—C(1)	115.4 (5)	P(3)—C(66)—C(61)	117.0 (12)
C(1)—P(2)—C(36)	107.9 (6)	P(4)—C(76)—C(71)	120.7 (12)
C(1)—P(2)—C(46)	111.4 (7)	P(4)—C(86)—C(81)	118.2 (12)
S(3)—P(3)—C(1)	115.8 (4)	N(1)—C(2*s*)—C(1*s*)	175.4 (31)

A single crystal was mounted in a random orientation on a glass fiber with epoxy. The initial unit cell and orientation matrix were obtained from a rotation photograph. Orthorhombic symmetry was suggested on the basis of interaxial angles and confirmed by a Delaunay reduction and axial photographs. Backgrounds were estimated from a 96-step peak profile. All data processing, crystal solution and refinement were performed on a Data General Eclipse S140 mini computer using *SHELXTL* crystallographic software (Sheldrick, 1985). The space group was uniquely determined by the systematic absences. The position of the Au atom was determined by direct methods. All remaining non-H atoms were obtained by subsequent difference Fourier synthesis maps. The positions of H atoms on the phenyl rings were calculated with fixed C—H distances of 0.96 Å and refined with fixed temperature factors of 0.08 Å^2; their contributions were included in the structure-factor calculations. Au, P and S atoms, and one C atom were refined anisotropically, while the remaining atoms were refined isotropically. The butyl group was found to be disordered in the last two C atoms. These atoms were refined at 50% occupancy. A molecule of CH_3CN was found in the lattice.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: ST1090). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Co-Crystallized Bis(*μ*-*tert*-butylphosphido)-bis(di-*tert*-butylgallium) and Tetra-*tert*-butylcyclotetraphosphane

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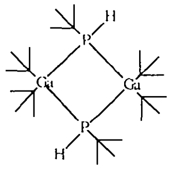
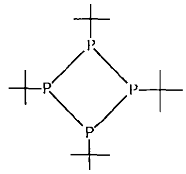
Abstract

Crystals of the title compound $[Ga_2(C_4H_9)_4(C_4H_{10}P)_2].(C_{16}H_{36}P_4)$ (1) consist of the two independent neutral molecules $[Ga\{\mu\text{-}PH({}^t Bu)\}{}^t Bu_2]_2$ (1*a*) and $[(P^t Bu)_4]$ (1*b*). Both molecules are situated on a crystallographically imposed mirror plane and their idealized molecular point group symmetries are $2/m$ (1*a*) and $\bar{4}2m$ (1*b*). (1*a*) is the *anti* isomer of a phosphido-bridged Ga dimer. It contains an almost planar Ga_2P_2 ring [P(1)—Ga—P(2)—Ga^i 0.90 (7)°] with Ga—P bond lengths of 2.466 (1) and 2.472 (1) Å. The coordination about both the Ga and P atoms is distorted tetrahedral, with much stronger distortion about P than Ga. (1*b*) posseses a non-planar P_4 ring [P(4^i)—P(3)—P(4)—P(5)

−22.34 (8)°] with equal P—P bond lengths of 2.213 (2) Å. The ^{t}Bu groups bonded to each of the P atoms are situated on alternative sides of the P$_4$ ring.



(1*a*)



(1*b*)

Comment

Interest in Group 13–15 compounds has grown dramatically in recent years because of their potential use as semiconductor precursors (see reviews: Cowley & Jones, 1989; Zanella, Rossetto, Brianese, Ossola, Porchia & Williams, 1991). Structures of dimeric compounds containing a four-membered Ga$_2$P$_2$ ring have been reported: [Ga(μ-P^{t}Bu$_2$)Me$_2$]$_2$, [Ga(μ-P^{t}Bu$_2$)^{n}Bu$_2$]$_2$ (Arif, Benac, Cowley, Geerts, Jones, Kidd, Power & Schwab, 1986), [Ga{μ-P(SiPh$_3$)}{2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$}]$_2$ (Cowley, Jones, Mardones, Ruiz, Atwood & Bott, 1990), [Ga(μ-PPh$_2$)(CH$_2$^{t}Bu)$_2$]$_2$ (Banks, Beachley, Buttrey, Churchill & Fettinger, 1991) and [Ga(μ-PEt$_2$)(^{t}Bu)(C≡CSiMe$_3$)]$_2$ (Lee, Higa, Nissan & Butcher, 1992). Nevertheless, only one X-ray structure of a dinuclear Ga complex with primary phosphido groups has been published [Ga{μ-PH(C$_5$H$_9$)}^{t}Bu$_2$]$_2$ (Heaton, Jones, Kidd, Cowley & Nunn, 1988).†

Among the numerous polyphosphorus compounds (Baundler & Glinka, 1993, and references therein) the following cyclic organophosphanes with the empirical formula (P*R*)$_4$ have been structurally characterized: [P{2-(MeO)C$_6$H$_4$}]$_4$ (Heuer, Sell, Schmutzler & Schomburg, 1987), [P{CH$_2$P(S)F$_2$}]$_4$ (Fild, Bunke & Schomburg, 1988), [P(C$_6$H$_{11}$)]$_4$ (Bart, 1969), [P(CF$_3$)]$_4$ (Palenik & Donohue, 1962), [P(C$_6$F$_5$)]$_4$ (Sanz & Daly, 1971) and [P^{t}Bu]$_4$ (Weigand, Cordes & Swepston, 1981), bond distances and angles of which are in good agreement with those of (1*b*).

Note added in proof. Our most recent literature search revealed the following compounds: [Ga{μ-PH(^{t}Bu)}^{t}Bu$_2$]$_2$ [Atwood, D. A., Cowley, A. H., Harris, P. R., Jones, R. A., Koschmieder, S. U. & Nunn, C. M. (1993). *J. Organomet. Chem.* **449**, 61–67]; [Ga(μ-PPh$_2$)(CH$_2$CMe$_3$)(PPh$_2$)]$_2$ [Beachley, D. T. Jr, Maloney, J. D. & Rogers, R. D. (1993). *Organometallics*, **12**, 229–232]; [Ga(μ-P^{i}Pr$_2$)^{i}Pr$_2$]$_2$ [Hoffmann, G. G., Fischer, R., Schubert, U. & Hirle, B. (1992). *J. Organomet. Chem.* **441**, 7–14]; [Ga{μ-P(SiMe$_3$)$_2$}Cl$_2$]$_2$ [Wells, R. L., Self, M. F., McPhail, A. T., Aubuchon, S. R., Woudenberg, R. C. & Jasinski, J. P. (1993). *Organomettallics*, **12**, 2832–2834]; [Ga(^{t}Bu)(Cl)(μ-P^{i}Pr$_2$)$_2$Ga(P^{i}Pr$_2$)(^{t}Bu)] [Atwood, D. A., Atwood, V. O., Cowley, A. H., Gobran, H. R., Jones, R. A., Smeal, T. M. & Carrano, C. J. (1993). *Organometallics*, **12**, 3517–3521].

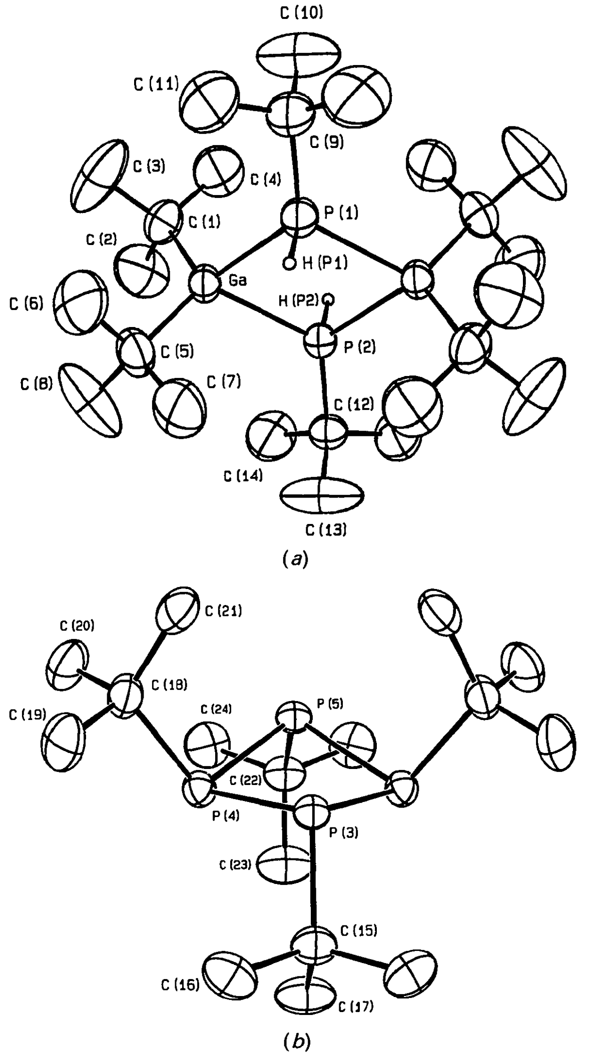


Fig. 1. *ORTEP* drawing and numbering scheme for (*a*) bis(μ-*tert*-butylphosphido)bis(di-*tert*-butylgallium) (1*a*) and (*b*) tetra-*tert*-butylcyclotetraphosphane (1*b*) showing 30% probability ellipsoids.

Experimental

The title compound was obtained by reaction of a solution of ^{t}BuPH$_2$ and three molar equivalents of ^{t}BuMgCl with GaCl$_3$ in ether. Crystals were obtained by recrystallization from toluene.

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† See *Note added in proof.*

Crystal data

$[Ga_2(C_4H_9)_4(C_4H_{10}P)_2]$.-
$(C_{16}H_{36}P_4)$
$M_r = 898.46$
Monoclinic
$P2_1/m$
$a = 9.179$ (2) Å
$b = 16.978$ (4) Å
$c = 17.263$ (3) Å
$\beta = 102.84$ (3)°
$V = 2623$ (2) Å^3
$Z = 2$
$D_x = 1.14$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9$–12°
$\mu = 1.23$ mm^{-1}
$T = 294$ (1) K
Parallelepiped
0.25 × 0.20 × 0.20 mm
Pale yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: empirical
$T_{\min} = 0.934$, $T_{\max} = 0.995$
5679 measured reflections
5341 independent reflections

2687 observed reflections $[F_o^2 > 3\sigma(F_o^2)]$
$R_{\rm int} = 0.024$
$\theta_{\max} = 26.0°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 20$
$l = -21 \rightarrow 20$
3 standard reflections
frequency: 50 min
intensity variation: −8.5%

Refinement

Refinement on F
$R = 0.041$
$wR = 0.051$
$S = 1.59$
2687 reflections
241 parameters
$w = 1/\sigma^2(F_o)$

$(\Delta/\sigma)_{\max} = 0.02$
$\Delta\rho_{\max} = 0.41$ (7) e Å^{-3}
$\Delta\rho_{\min} = -0.26$ (7) e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$B_{\rm iso}$ for H; $B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$ for other atoms.

	x	y	z	$B_{\rm iso}/B_{\rm eq}$
Ga	0.58581 (6)	0.13823 (3)	0.33581 (3)	3.28 (1)
P(1)	0.6393 (2)	1/4	0.2552 (1)	3.65 (4)
P(2)	0.5361 (2)	1/4	0.4180 (1)	3.12 (4)
P(3)	0.0507 (2)	1/4	0.8183 (1)	3.32 (4)
P(4)	0.2285 (2)	0.34047 (8)	0.84259 (8)	3.57 (3)
P(5)	0.3763 (2)	1/4	0.9115 (1)	3.50 (4)
C(1)	0.7664 (6)	0.0786 (3)	0.3962 (3)	4.6 (1)
C(2)	0.7265 (7)	0.0390 (4)	0.4688 (4)	8.1 (2)
C(3)	0.8165 (8)	0.0185 (4)	0.3424 (5)	10.4 (2)
C(4)	0.8989 (6)	0.1331 (4)	0.4274 (4)	7.1 (2)
C(5)	0.4029 (6)	0.0802 (3)	0.2749 (3)	4.9 (1)
C(6)	0.4414 (8)	0.0385 (4)	0.2048 (4)	9.2 (2)
C(7)	0.2738 (7)	0.1339 (4)	0.2441 (4)	7.9 (2)
C(8)	0.3512 (9)	0.0213 (4)	0.3296 (5)	10.6 (2)
C(9)	0.7665 (8)	1/4	0.1840 (4)	5.0 (2)
C(10)	0.930 (1)	1/4	0.2341 (6)	10.2 (4)
C(11)	0.7415 (8)	0.1763 (4)	0.1328 (4)	9.4 (2)
C(12)	0.4085 (7)	1/4	0.4890 (4)	4.0 (2)
C(13)	0.2483 (9)	1/4	0.4409 (5)	9.7 (4)
C(14)	0.4401 (7)	0.1770 (4)	0.5410 (3)	7.6 (2)
C(15)	−0.0158 (8)	1/4	0.7068 (4)	4.5 (2)
C(16)	−0.1104 (6)	0.3247 (4)	0.6856 (3)	6.1 (2)
C(17)	0.1106 (8)	1/4	0.6617 (4)	6.3 (2)
C(18)	0.1748 (6)	0.4057 (3)	0.9201 (3)	5.0 (1)
C(19)	0.0448 (7)	0.4569 (3)	0.8751 (4)	7.0 (2)
C(20)	0.3138 (8)	0.4571 (4)	0.9540 (4)	7.2 (2)
C(21)	0.1284 (7)	0.3609 (3)	0.9883 (3)	6.2 (1)
C(22)	0.5437 (8)	1/4	0.8650 (4)	4.9 (2)
C(23)	0.5069 (8)	1/4	0.7748 (5)	7.1 (3)
C(24)	0.6330 (6)	0.3229 (4)	0.8963 (4)	7.0 (2)
H(P1)	0.501 (8)	1/4	0.196 (4)	8 (2)
H(P2)	0.657 (7)	1/4	0.489 (4)	5 (2)

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

Ga—P(1)	2.466 (1)	Ga—Ga$^{\rm i}$	3.7953 (7)
Ga—P(2)	2.472 (1)	P(3)—P(4)	2.213 (2)
Ga—C(1)	2.023 (5)	P(3)—C(15)	1.886 (7)
Ga—C(5)	2.027 (5)	P(4)—P(5)	2.213 (2)
P(1)—C(9)	1.875 (8)	P(4)—C(18)	1.885 (6)
P(2)—C(12)	1.874 (8)	P(5)—C(22)	1.884 (8)
P(1)—H(P1)	1.44 (6)	P(3)—P(5)	3.064 (2)
P(2)—H(P2)	1.46 (5)	P(4)—P(4$^{\rm i}$)	3.072 (2)
P(1)—P(2)	3.158 (3)		
P(1)—Ga—P(2)	79.52 (5)	Ga—P(2)—Ga$^{\rm i}$	100.30 (7)
P(1)—Ga—C(1)	115.7 (2)	C(9)—P(1)—H(P1)	96 (3)
P(1)—Ga—C(5)	109.1 (2)	C(12)—P(2)—H(P2)	86 (3)
P(2)—Ga—C(1)	108.8 (2)	P(3)—P(4)—P(5)	87.62 (6)
P(2)—Ga—C(5)	115.7 (2)	P(3)—P(4)—C(18)	104.1 (2)
C(1)—Ga—C(5)	120.9 (2)	P(5)—P(4)—C(18)	104.6 (2)
Ga—P(1)—C(9)	126.96 (7)	P(4)—P(3)—C(15)	104.5 (2)
Ga—P(2)—C(12)	126.68 (7)	P(4)—P(5)—C(22)	103.4 (2)
Ga—P(1)—H(P1)	99 (2)	P(4)—P(5)—P(4$^{\rm i}$)	87.90 (7)
Ga—P(2)—H(P2)	106 (2)	P(4)—P(3)—P(4$^{\rm i}$)	87.92 (8)
Ga—P(1)—Ga$^{\rm i}$	100.64 (8)		
P(1)—Ga—P(2)—Ga$^{\rm i}$	0.90 (7)	P(4$^{\rm i}$)—P(3)—P(4)—P(5)	−22.34 (8)

Symmetry code: (i) $x, \frac{1}{2} - y, z$.

The H atoms bonded to P(1) and P(2) were located and refined isotropically. The other H atoms were calculated in idealized positions and included in the refinement with fixed $U_{\rm iso} = 1.3 \times U$ of the bonding atom. Anisotropic displacement parameters were used for non-H atoms. Calculations were carried out on a VAX11/750 computer using *SDP* (Frenz, 1978). The figure was produced with *ORTEP* (Johnson, 1974).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71799 (41 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1073]

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

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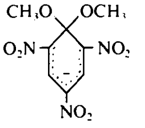
Abstract

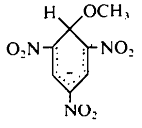
The title compound crystallizes as a centrosymmetric dimer, bis(μ-4-trichloromethyl-1,3,5-trinitro-2,5-cyclohexadien-1-ido)-$1\kappa^2O^1,O^{1'}:2\kappa O^3;1\kappa O^3:2\kappa^2O^1,O^{1'}$-bis-[(1,4,7,10,13,16-hexaoxacyclooctadecane-κ^6O)potassium], $[\{K(C_{12}H_{24}O_6)\}_2(\mu\text{-}C_7H_3Cl_3N_3O_6)_2]$, 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

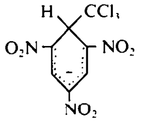
Meissenheimer (1902) presented the first chemical evidence for the molecular structures of the brightly coloured solutions formed by the interaction of aromatic nitro compounds with bases. There are recent reviews of the behaviour of these compounds in solution (Bunsel, Norris & Russell, 1968; Terrier, 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.



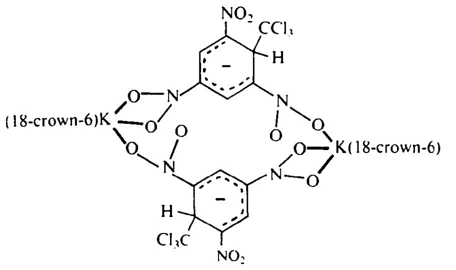
(I)



(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 $C(24^i)—C(25^i)$ 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

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