

Table 8. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (III)

Cd—I1	2.777 (1)	Cd—S2	2.514 (2)
Cd—I2	2.786 (1)	S1—C1	1.707 (8)
Cd—S1	2.538 (2)	S2—C2	1.727 (7)
I1—Cd—S1	111.78 (5)	Cd—S2—C2	105.5 (2)
I1—Cd—S2	110.62 (6)	S1—C1—N11	124.0 (6)
I2—Cd—S1	106.62 (5)	S1—C1—N12	118.0 (6)
I2—Cd—S2	114.82 (5)	S2—C2—N21	117.6 (6)
I1—Cd—I2	106.56 (3)	S2—C2—N22	122.3 (6)
S1—Cd—S2	106.47 (6)	N11—C1—N12	117.9 (7)
Cd—S1—C1	106.8 (3)	N21—C2—N22	120.1 (6)
I1—Cd—S1—C1	56.2 (3)	Cd—S1—C1—N12	-168.0 (6)
I1—Cd—S2—C2	-77.3 (3)	Cd—S2—C2—N21	135.5 (6)
I2—Cd—S1—C1	-59.8 (3)	Cd—S2—C2—N22	-43.9 (7)
I2—Cd—S2—C2	43.3 (3)	S2—Cd—S1—C1	177.1 (3)
Cd—S1—C1—N11	12.5 (8)	S1—Cd—S2—C2	161.0 (3)

Table 9. Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ) for (III)

D—H...A	D—H	H...A	D...A	D—H...A
N22—H22B...I2	0.86	3.00	3.762 (8)	148
N21—H21A...I2 <sup>i</sup>	0.86	2.91	3.672 (7)	148

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

The structures of (II) and (III) were solved by direct and Fourier methods, and refined anisotropically by full-matrix least squares. Refinement of (I) was carried out starting from the coordinates published by Nardelli *et al.* (1957). The H atoms of all three compounds were placed in calculated positions riding on the attached  $N_{sp^2}$  atoms, with isotropic displacement parameters 1.5 times those of the N atoms.

Data collection: local programs for (I); *CAD-4 EXPRESS* (Enraf–Nonius, 1994) for (II) and (III). Cell refinement: local programs for (I); *DIRDIF* (Beurskens *et al.*, 1992) for (II) and (III). Data reduction: local programs for (I); *REFLEX* (local program) for (II) and (III). For all compounds, program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *Xtal\_GX* (Hall & du Boulay, 1995); software used to prepare material for publication: *SHELXL93*; geometrical calculations: *PARST* (Nardelli, 1983).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1330). Services for accessing these data are described at the back of the journal.

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## Tetrabutylammonium and Caesium Salts of Trinitromethane

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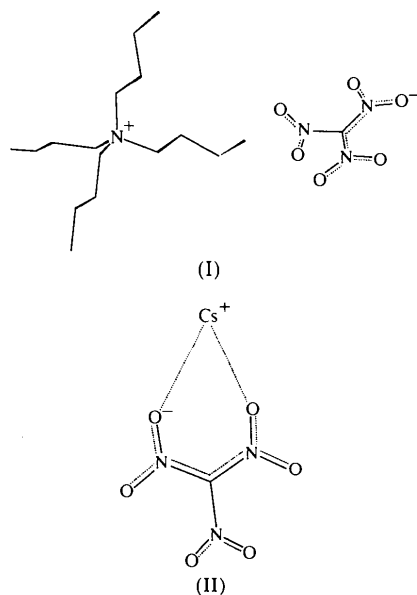
## Abstract

Two structures of the trinitromethane anion are reported. In tetra-*n*-butylammonium trinitromethanide,  $(C_4H_9)_4N^+.[C(NO_2)_3]^-$ , the  $[C(NO_2)_3]^-$  anion adopts the commonly observed  $C_{2v}$  conformation, while in the Cs salt, caesium trinitromethanide,  $Cs^+.[C(NO_2)_3]^-$ , it adopts a distorted propeller conformation. Both structures exhibit cation–anion interactions that may influence the structure of the anion.

## Comment

Trinitromethane and its salts have been known for almost 100 years, and are the subject of several structure-related publications, including an *ab initio* study predicting a propeller-type structure ( $D_3$ , Fig. 1a) for the anion (Cioslowski *et al.*, 1991). This computed

structure has a  $C_3$  axis through the C atom, perpendicular to the plane containing the C and N atoms ( $CN_3$ ). The nitro O atoms are predicted to be twisted out of the  $CN_3$  plane by  $27.5^\circ$ . There are several experimentally observed trinitromethane anion structures reported in the literature, but most exhibit a structure that differs greatly from that predicted, with two of the  $NO_2$  groups coplanar with the  $CN_3$  plane, and the final  $NO_2$  group perpendicular to this plane ( $C_{2v}$ , Fig. 1b). Of the few propeller-type structures reported, the closest to the calculated structure is the (iodomethyl)triphenylphosphonium salt (Scherfise *et al.*, 1985), yet the torsion angles between the  $CN_3$  plane and the  $NO_2$  groups range from  $15$  to  $30^\circ$ . Some of these deviations may be a result of specific anion-cation interactions. We sought to determine if the structure of the trinitromethane anion with the weakly coordinating tetrabutylammonium cation, (I), would more closely approach that



predicted by theory. We also redetermined the structure of caesium trinitromethanide, (II), since preliminary work suggested that the anion exhibited a propeller-type structure (Grigor'eva *et al.*, 1966).

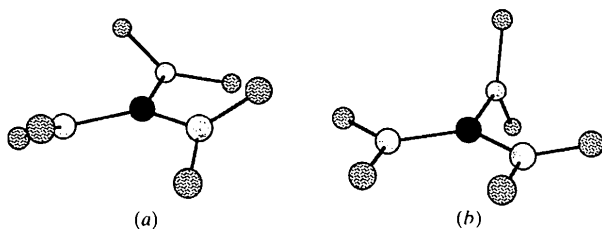


Fig. 1. Ball and stick representations of  $[C(NO_2)_3]^-$ , showing (a) the calculated  $D_3$  structure (Cioslowski *et al.*, 1991) and (b) the most commonly observed structure ( $C_{2v}$ ).

Despite rotational disorder about the normal to the  $CN_3$  plane, the  $[C(NO_2)_3]^-$  anion exhibits the more commonly observed  $C_{2v}$  structure in the tetrabutylammonium salt (Fig. 2). The absolute values of the O—C—N—N torsion angles for the dominant disorder component are all near  $0$ ,  $90$  or  $180^\circ$  (Table 1). Four butylammonium H atoms, attached to C atoms  $\alpha$  to the N atom, are positioned for potential hydrogen bonding to nitro O atoms (Table 2) (Steiner, 1996; Berkovitch-Yellin & Leiserowitz, 1984). While these interactions are undoubtedly weak, they may be significant enough to affect the conformation of the anion. These interactions appear to be strongest with O atoms in the  $CN_3$  plane, as has been observed previously (Ammon *et al.*, 1989, 1990). Only hydrogen bonds involving the major component are listed in Table 2, but hydrogen bonds to the minor components are also observed. This may be a factor contributing to the disorder.

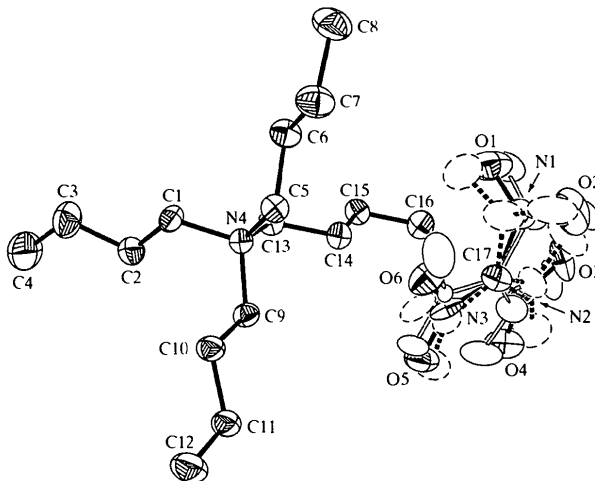


Fig. 2. The molecular structure of (I), showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity. The minor components of disorder are shown as boundary ellipsoids using solid or dashed lines.

$Cs^+$  forms more direct interactions with  $[C(NO_2)_3]^-$  in compound (II). There are 11 O atoms within  $3.4 \text{ \AA}$  of the  $Cs^+$  cation, and each nitro O atom has at least one  $Cs^+$  ion within  $3.4 \text{ \AA}$ . The result is a three-dimensional ionic network. The structure of the trinitromethane anion is therefore likely to be perturbed by its extensive binding to  $Cs^+$ .

The  $CN_3$  unit is planar in both structures. As calculated by *PLATON* (Spek, 1997), the interplanar angles formed between the  $NO_2$  groups and the  $CN_3$  plane are  $0$  and  $90^\circ$  (within  $3\sigma$ ) in (I), and range from  $9.7(3)$  to  $42.9(4)^\circ$  in (II). Longer central C—N bonds are observed when the  $NO_2$ — $CN_3$  interplanar angle is maximized, resulting from a loss of  $\pi$ -overlap between C and

N (Ammon *et al.*, 1989, 1990). Curiously, the anion structure in the caesium salt more closely approaches that predicted by theory.

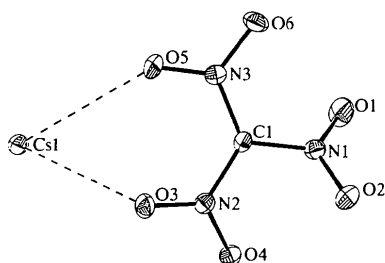


Fig. 3. ORTEP (Burnett & Johnson, 1996) plot of (II), showing 50% probability displacement ellipsoids.

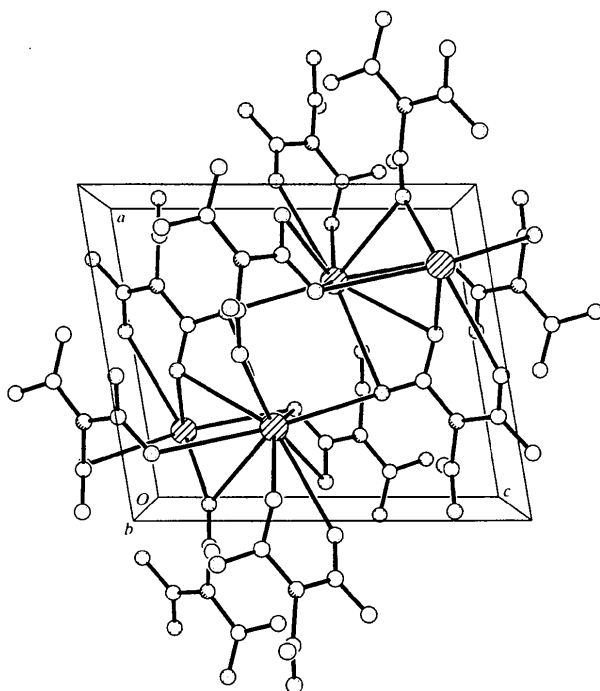


Fig. 4. The extended structure of (II). For clarity, all atoms are represented as circles. Cs atoms are shown shaded.

## Experimental

Compound (I) was prepared *via* incomplete nitration of acetic anhydride (Liang, 1941), followed by cation exchange using tetrabutylammonium bromide in water. The crude compound was purified by slow precipitation from MeOH/H<sub>2</sub>O solutions to yield (I) as bright-yellow crystals. Crystals suitable for X-ray analysis were grown from MeOH/H<sub>2</sub>O at 273–278 K. Compound (II) was prepared by reacting compound (I) with CsF in MeOH at room temperature. The yellow precipitate was collected by filtration, washed several times with cold EtOH, and recrystallized twice from warm water (333–343 K).

Crystals of this salt suitable for X-ray analysis were grown from water at 278–283 K. Due to its instability at room temperature, a crystal of (II) was cooled on the diffractometer shortly after filtration.

## Compound (I)

### Crystal data

C<sub>16</sub>H<sub>36</sub>N<sup>+</sup>.CN<sub>3</sub>O<sub>6</sub><sup>-</sup>

*M<sub>r</sub>* = 392.50

Orthorhombic

*Pbca*

*a* = 16.923 (2) Å

*b* = 14.783 (2) Å

*c* = 17.6634 (13) Å

*V* = 4418.9 (9) Å<sup>3</sup>

*Z* = 8

*D<sub>x</sub>* = 1.180 Mg m<sup>-3</sup>

*D<sub>m</sub>* not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25

reflections

θ = 10.4–12.5°

μ = 0.09 mm<sup>-1</sup>

*T* = 163 (2) K

Prism

0.50 × 0.31 × 0.30 mm

Yellow

### Data collection

Enraf–Nonius CAD-4  
diffractometer

ω scans

Absorption correction: none

4163 measured reflections

3062 independent reflections

1742 reflections with

*I* > 2σ(*I*)

*R<sub>int</sub>* = 0.040

θ<sub>max</sub> = 25°

*h* = -20 → 18

*k* = -17 → 16

*l* = 0 → 20

3 standard reflections

frequency: 120 min

intensity decay: 5%

### Refinement

Refinement on *F*<sup>2</sup>

*R*(*F*) = 0.043

*wR*(*F*<sup>2</sup>) = 0.127

*S* = 1.13

3062 reflections

410 parameters

H atoms: see below

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0445*P*)<sup>2</sup>  
+ 1.7410*P*]

where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

(Δ/σ)<sub>max</sub> = 0.034

Δρ<sub>max</sub> = 0.18 e Å<sup>-3</sup>

Δρ<sub>min</sub> = -0.17 e Å<sup>-3</sup>

Extinction correction: none

Scattering factors from

*International Tables for  
Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °) for (I)

N4—C1	1.520 (4)	O4—N2	1.229 (17)
N4—C5	1.519 (3)	O5—N3	1.231 (17)
N4—C9	1.526 (3)	O6—N3	1.259 (19)
N4—C13	1.516 (3)	N1—C17	1.454 (10)
O1—N1	1.21 (2)	N2—C17	1.390 (19)
O2—N1	1.20 (2)	N3—C17	1.372 (18)
O3—N2	1.25 (2)		
C1—N4—C5	108.4 (2)	O3—N2—O4	124.7 (18)
C1—N4—C9	111.5 (2)	O3—N2—C17	115.5 (12)
C1—N4—C13	108.3 (2)	O4—N2—C17	119.6 (15)
C5—N4—C9	108.4 (2)	O5—N3—O6	125.3 (18)
C5—N4—C13	111.3 (2)	O5—N3—C17	121.6 (14)
C9—N4—C13	108.9 (2)	O6—N3—C17	113.0 (11)
N4—C1—C2	116.7 (2)	N1—C17—N2	115.4 (9)
O1—N1—O2	124.3 (13)	N1—C17—N3	117.3 (8)
O1—N1—C17	117.3 (12)	N2—C17—N3	126.9 (9)
O2—N1—C17	118.3 (12)		
O1—N1—C17—N2	85.6 (17)	O3—N2—C17—N3	177.6 (15)
O2—N1—C17—N2	-91.1 (19)	O4—N2—C17—N3	-6 (3)
O1—N1—C17—N3	-87.9 (18)	O5—N3—C17—N1	174.2 (15)
O2—N1—C17—N3	95.4 (18)	O6—N3—C17—N1	-1.4 (19)
O3—N2—C17—N1	5 (2)	O5—N3—C17—N2	2 (2)
O4—N2—C17—N1	-179.0 (15)	O6—N3—C17—N2	-174.1 (14)

Table 2. Hydrogen-bonding geometry (Å, °) for (I)

D—H...A	D—H	H...A	D...A	D—H...A
C5—H5A...O2 <sup>i</sup>	0.99	2.50	3.47 (2)	167
C5—H5B...O6	0.99	2.36	3.344 (15)	170
C9—H9A...O4 <sup>ii</sup>	0.99	2.44	3.244 (12)	137
C13—H13B...O4 <sup>ii</sup>	0.99	2.58	3.293 (11)	129

Symmetry codes: (i)  $\frac{1}{2} - x, \frac{1}{2} + y, z$ ; (ii)  $-x, 1 - y, 1 - z$ .

O1—N1—C1—N2	139.3 (3)	O4—N2—C1—N1	-23.8 (4)
O1—N1—C1—N3	-45.4 (4)	O4—N2—C1—N3	161.1 (3)
O2—N1—C1—N2	-40.5 (4)	O5—N3—C1—N1	172.9 (3)
O2—N1—C1—N3	134.8 (3)	O5—N3—C1—N2	-12.1 (5)
O3—N2—C1—N1	156.3 (3)	O6—N3—C1—N1	-7.3 (4)
O3—N2—C1—N3	-18.8 (5)	O6—N3—C1—N2	167.7 (3)

Symmetry codes: (i)  $x - 1, y, z$ ; (ii)  $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$ ; (iii)  $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$ ; (iv)  $1 - x, -y, -z$ ; (v)  $1 - x, 1 - y, -z$ ; (vi)  $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$ ; (vii)  $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$ .**Compound (II)***Crystal data*Cs<sup>+</sup>.CN<sub>3</sub>O<sub>6</sub><sup>-</sup> $M_r = 282.93$ 

Monoclinic

 $P2_1/n$  $a = 8.1023 (5) \text{ \AA}$  $b = 8.3297 (4) \text{ \AA}$  $c = 9.4897 (9) \text{ \AA}$  $\beta = 99.208 (6)^\circ$  $V = 632.20 (8) \text{ \AA}^3$  $Z = 4$  $D_x = 2.973 \text{ Mg m}^{-3}$  $D_m$  not measuredMo  $K\alpha$  radiation $\lambda = 0.71073 \text{ \AA}$ 

Cell parameters from 25 reflections

 $\theta = 10.2\text{--}15.0^\circ$  $\mu = 5.8 \text{ mm}^{-1}$  $T = 163 (2) \text{ K}$ 

Chunk

 $0.21 \times 0.17 \times 0.13 \text{ mm}$ 

Yellow

*Data collection*

Enraf–Nonius CAD-4

diffractometer

 $\omega$  scans

Absorption correction:

 $\psi$  scan (Siemens, 1995) $T_{\min} = 0.314, T_{\max} = 0.478$ 

2278 measured reflections

1103 independent reflections

1039 reflections with

 $I > 2\sigma(I)$  $R_{\text{int}} = 0.034$  $\theta_{\text{max}} = 25^\circ$  $h = 0 \rightarrow 9$  $k = -9 \rightarrow 9$  $l = -11 \rightarrow 11$ 

3 standard reflections

frequency: 120 min

intensity decay: 4%

*Refinement*Refinement on  $F^2$  $R(F) = 0.018$  $wR(F^2) = 0.047$  $S = 1.10$ 

1103 reflections

101 parameters

 $w = 1/[\sigma^2(F_o^2) + (0.0209P)^2$  $+ 0.2810P]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\text{max}} < 0.001$  $\Delta\rho_{\text{max}} = 0.60 \text{ e \AA}^{-3}$  $\Delta\rho_{\text{min}} = -0.76 \text{ e \AA}^{-3}$ 

Extinction correction:

 $SHELXL93$  (Sheldrick, 1993)

Extinction coefficient:

0.0417 (12)

Scattering factors from

*International Tables for Crystallography* (Vol. C)

Anisotropic displacement parameters were used for all non-H atoms. All H atoms were placed in calculated positions, refined using a riding model, and given an isotropic displacement parameter equal to 1.2 (CH<sub>2</sub>) or 1.5 (CH<sub>3</sub>) times the equivalent isotropic displacement parameter of the atom to which they were attached. Methyl H atoms were allowed to rotate about C—C. The nitro groups in (I) are modeled as being disordered over three sites (52:26:22). The relative occupancies were determined by assigning all disordered atoms a variable common isotropic displacement parameter, and allowing an occupancy factor for each component to vary, whilst restraining the sum of the three occupancy factors to be equal to 1. The resulting occupancy factors were rounded to two significant figures, and fixed in the subsequent refinement. The actual disorder in (I) is probably more complex than that modeled here, but attempts to resolve the disorder further were not productive. Between the disordered components, all equivalent bond distances and angles were restrained to be equal; for example, C17—N1 was restrained to be equal to C17—N1A, but not to C17—N2. Additionally, the  $U^j$  components of bonded atoms, or of atoms within 0.7 Å of each other, were restrained to be similar. Despite these restraints, some of the disordered atoms exhibited unusual anisotropic displacement parameters. As a result of the disorder in (I), the data-to-parameter ratio was low (7.5). This was partially compensated for by the large number of restraints (798) applied to the parameters.

For both compounds, data collection: *CAD-4-PC* (Enraf–Nonius, 1993); cell refinement: *CAD-4-PC*; data reduction: *XCAD4* (Harms, 1995); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *SHELXTL* (Siemens, 1995); software used to prepare material for publication: *PLATON* (Spek, 1997).

The research was sponsored by the Newly Independent States–Initiatives for Proliferation Prevention (NIS–IPP) Program, USA, and by the Division of Chemical Sciences, Office of Basic Energy Sciences, US Department of Energy, under contract DE-AC05-96OR22464 with the Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corporation.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1207). Services for accessing these data are described at the back of the journal.

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Ammon, H. L., Choi, C. S., Bashir-Hashemi, A., Moriarty, R. M. & Khosrowshahi, J. S. (1989). *Acta Cryst.* **C45**, 319–321.

Table 3. Selected geometric parameters (Å, °) for (II)

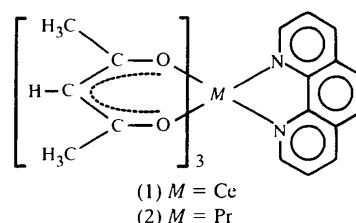
Cs1—O3	3.029 (2)	Cs1—O1 <sup>iii</sup>	3.252 (3)
Cs1—O5	3.155 (3)	O1—N1	1.224 (4)
Cs1—O1 <sup>i</sup>	3.105 (3)	O2—N1	1.225 (4)
Cs1—O4 <sup>ii</sup>	3.147 (2)	O3—N2	1.234 (3)
Cs1—O6 <sup>iii</sup>	3.254 (2)	O4—N2	1.250 (3)
Cs1—O5 <sup>iv</sup>	3.333 (3)	O5—N3	1.237 (4)
Cs1—O6 <sup>v</sup>	3.246 (3)	O6—N3	1.244 (3)
Cs1—O2 <sup>v</sup>	3.374 (3)	N1—C1	1.439 (4)
Cs1—O3 <sup>vi</sup>	3.346 (2)	N2—C1	1.383 (4)
Cs1—O4 <sup>vi</sup>	3.260 (2)	N3—C1	1.384 (4)
O1—N1—O2	123.2 (3)	O5—N3—O6	122 (3)
O1—N1—C1	119.1 (3)	O5—N3—C1	120 (3)
O2—N1—C1	117.7 (3)	O6—N3—C1	118 (3)
O3—N2—O4	121.3 (3)	N1—C1—N2	117.1 (3)
O3—N2—C1	121 (3)	N1—C1—N3	119.1 (3)
O4—N2—C1	117.7 (3)	N2—C1—N3	123.7 (3)

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arrangement. The ligands span the opposite edges of the two square faces of the coordination antiprism. Important bond-distance ranges are: Ce—O 2.434 (7)–2.499 (7), Ce—N 2.70 (1)–2.767 (9), Pr—O 2.392 (5)–2.437 (6) and Pr—N 2.659 (5)–2.690 (6) Å.

### Comment

Rare earth metal complexes are of growing importance because of their chemical (Cotton, 1991), industrial (Niinisto, 1987), and biochemical and medicinal applications (Evans, 1990). As part of our study on rare earth metal complexes with N-donor and O-donor ligands, we report here the preparation and crystal structures of the title compounds, tris(acetylacetonato)(1,10-phenanthroline)cerium(III), (1), and tris(acetylacetonato)(1,10-phenanthroline)praseodymium(III), (2).



There are two crystallographically independent molecules in the asymmetric unit of compound (1) (Fig. 1), but only one molecule in the asymmetric unit of compound (2) (Fig. 2). In both compounds, the metal atom is eightfold coordinated by six O and two N atoms in a slightly distorted square-antiprismatic arrangement. The acetylacetonato and 1,10-phenanthroline (phen) ligands behave as bidentate chelates. One of the two square faces of the coordination antiprism, denoted as the *O*-face, is formed exclusively by O atoms [O1, O2, O3 and O4 for the first molecule of compound (1) and the molecule of compound (2), and O7, O8, O9 and O10 for the second molecule of compound (1)]. The other square face, denoted the *NO*-face, is formed by two N and two O atoms [N1, N2, O5 and O6 for the first molecule of compound (1) and the molecule of compound (2), and N3, N4, O11 and O12 for the second molecule of compound (1)]. These square faces are almost parallel, the angles between them being 2.1 (2), 2.9 (2) and 3.4 (2)° for the two molecules of compound (1) and the molecule of compound (2), respectively.

The antiprismatic arrangement is common among eight-coordinate rare earth metal complexes. In some compounds, as in (1) and (2), and in the analogous  $\text{Eu}^{\text{III}}$  complex (Watson *et al.*, 1972), the ligands span the opposite edges of the two square faces of the coordination antiprism (*s* edges). In other complexes, as in tris(thenoyltrifluoroacetylacetonato)europium(III) dihydrate, the ligands span the edges of the triangular faces of the antiprism (*l* edges) (Lippard, 1967).

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## Tris(acetylacetonato)(1,10-phenanthroline)cerium(III) and Tris(acetylacetonato)(1,10-phenanthroline)praseodymium(III)

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### Abstract

The crystal structures of the title compounds,  $[\text{Ce}(\text{C}_5\text{H}_7\text{O}_2)_3(\text{C}_{12}\text{H}_8\text{N}_2)]$ , (1), and  $[\text{Pr}(\text{C}_5\text{H}_7\text{O}_2)_3(\text{C}_{12}\text{H}_8\text{N}_2)]$ , (2), have been determined. There are two independent molecules in the asymmetric unit of (1), but only one molecule in the asymmetric unit of (2). In both compounds, the metal atom is eightfold coordinated by six O and two N atoms in a slightly distorted square-antiprismatic