8049 reflections
518 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0808P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from
*International Tables for
Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Ni—P2	2.1932 (8)	P1—C13	1.819 (3)
Ni—P1	2.1945 (7)	P1—C19	1.821 (3)
Ni—S2	2.2075 (8)	P1—C28	1.852 (3)
Ni—S1	2.2089 (8)	P2—C1	1.816 (3)
Cl—O1	1.373 (4)	P2—C7	1.821 (3)
Cl—O4	1.391 (5)	P2—C25	1.836 (3)
Cl—O2	1.392 (3)	N—C29	1.305 (4)
Cl—O3	1.406 (3)	N—C30	1.475 (5)
S1—C29	1.717 (3)	N—C32	1.490 (5)
S2—C29	1.707 (3)		
P2—Ni—P1	95.12 (3)	C26—C27—C28	115.4 (3)
S2—Ni—S1	78.38 (3)	C27—C28—P1	115.7 (2)
C29—S1—Ni	85.74 (10)	N—C29—S2	123.5 (3)
C29—S2—Ni	86.02 (10)	N—C29—S1	127.2 (2)
C26—C25—P2	115.0 (3)	S2—C29—S1	109.21 (15)
C25—C26—C27	115.1 (3)		

In one of the ethyl substituents of the dithiocarbamate, disorder was observed with respect to the C31 atom; two positions, C31*A* and C31*B*, were assigned site occupancies of 0.5. All the H atoms of the alkyl substituents were added with the *HADD* utility of *SHELXTL/PC* (Sheldrick, 1990). The two H atoms attached to C30 appear as four H atoms with equal site occupancies; the three terminal H atoms attached to C31*A*/C31*B* were included in six positions. Other H atoms were identified from the Fourier map and were refined isotropically.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC*. Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93*. Geometric calculations: *PARST* (Nardelli, 1983).

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Bis(thiourea)cadmium Halides

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Abstract

The crystals of dichlorobis(thiourea-*S*)cadmium, [CdCl$_2$\{SC(NH$_2$)$_2$\}$_2$], (I), and dibromobis(thiourea-*S*)cadmium, [CdBr$_2$\{SC(NH$_2$)$_2$\}$_2$], (II), are orthorhombic (*Pmn*2$_1$ and *Pnam*, respectively), while those of di-iodobis(thiourea-*S*)cadmium, [CdI$_2$\{SC(NH$_2$)$_2$\}$_2$], (III), are monoclinic (*P*2$_1$/*c*). In all these compounds, two S atoms from two thiourea molecules and two *X* (*X* = halogen) atoms coordinate to Cd in tetrahedral arrangements. Crystal packing is mainly determined by N—H···*X* hydrogen bonds, but is different in all three cases. The average Cd—*X* distance increases from 2.541 (1) Å in (I) to 2.655 (3) Å in (II) and 2.782 (1) Å in (III), whereas the average Cd—S distances in the three compounds are quite similar, their values being 2.517 (1), 2.522 (2) and 2.526 (2) Å, for (I), (II) and (III), respectively.

Comment

Thiourea is a chemically interesting ligand that has been widely studied [there are more than 700 structures of

metal–thiourea complexes in the August 1997 release of the Cambridge Structural Database (CSD; Allen *et al.*, 1991)] and its complexes with transition metals exhibit interesting properties. Bis(thiourea) compounds of cadmium halides are useful for obtaining cadmium sulfide for photovoltaic batteries by thermic decomposition at a moderate temperature (573 or 673 K) and in air atmosphere (Stoev & Ruseva, 1994).

The present investigation of the title compounds (I) (II) and (III) was undertaken with the purpose of studying the influence of the size of the halide ion on the crystal structures of the cadmium halide bis(thiourea) complexes. As far as we know, only the lattice parameters and space groups have been reported for the structures of the bis(thiourea)cadmium bromide and iodide (Durski *et al.*, 1975), while for $CdCl_2$.2thiourea, a new refinement of the crystal structure has now confirmed the results of the analysis carried out 40 years ago using two-dimensional projections (Nardelli *et al.*, 1957), giving more accurate structural data, as required for a comparison with the other halide derivatives.

(I) X=Cl
(II) X=Br
(III) X=I
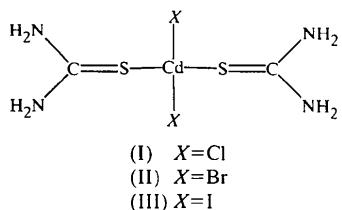
The crystal structures of the three compounds can be described as being made up of discrete complex molecules formed by Cd-centred coordination tetrahedra, each with two S atoms from two thiourea molecules and two halogens at the apices (Figs. 1, 2 and 3). The orientation of the thiourea ligands, defined by the X—Cd—S—C and Cd—S—C—N torsion angles, is determined by intramolecular N—H···X hydrogen-bonding interactions. In the chlorine and bromine derivatives, the crystallographic mirror symmetry imposes a symmetric orientation on the two thiourea ligands in each complex, and the X1—Cd—S—C [78.5 (1)° for (I) and −78.7 (3)° for (II)] and X2—Cd—S—C [−30.9 (1)° for (I) and 29.7 (3)° for (II)] torsion angles have opposite signs and are approximately equal. In contrast, in the iodine derivative, the local mirror symmetry is destroyed by the orientation of the thiourea, which is remarkably different in the two halves of the molecule, as shown by the values of the pairs of torsion angles I1—Cd—S2—C2 [−77.3 (3)°] and I2—Cd—S2—C2 [43.3 (3)°], and Cd—S1—C1—N11 [12.5 (8)°] and Cd—S2—C2—N22 [−43.9 (7)°]. This is a consequence of the larger size of the iodine ligands, resulting in much larger N—H···X intramolecular contacts for iodine than for bromine and chlorine; H2B···Cl2 = 2.40, H2B···Br2 = 2.53 and H22B···I2 = 3.00 Å.
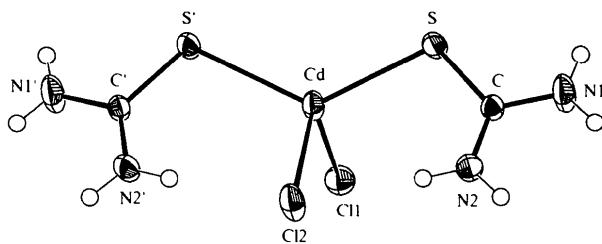

Fig. 1. *ORTEP* (Johnson, 1965) drawing of a molecule of (I). Ellipsoids are at the 50% probability level.
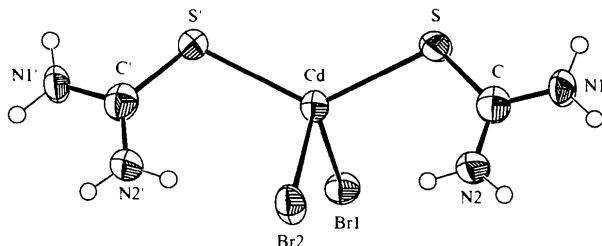
Fig. 2. *ORTEP* (Johnson, 1965) drawing of a molecule of (II). Ellipsoids are at the 50% probability level.
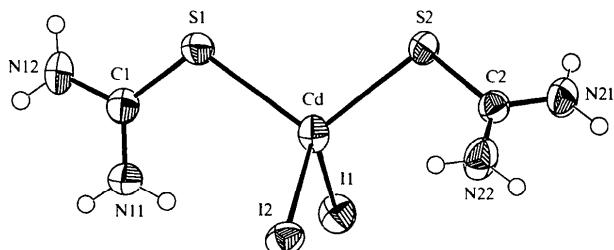
Fig. 3. *ORTEP* (Johnson, 1965) drawing of a molecule of (III). Ellipsoids are at the 50% probability level.

The tetrahedra in the three structures are distorted, with quadratic elongation values (Robinson *et al.*, 1971), based on the lengths of the edges, of 1.0028, 1.0016 and 1.0013, for (I), (II) and (III), respectively. No regular trend is observed for the displacements of the Cd atoms from the tetrahedra centroids, which are 0.236 (1), 0.279 (3) and 0.092 (2) Å, for (I), (II) and (III), respectively. As expected, the volumes of the tetrahedra increase with increasing size of the halogen, from 8.05 Å³ for (I) to 8.67 Å³ for (II) and 9.52 Å³ for (III).

The Cd—S distances [average 2.522 (4) Å] agree with the sum (2.52 Å) of the single-bond covalent radii (Pauling, 1960), indicating a fairly strong covalent interaction. The same applies to the Cd—X distances, which increase linearly with the size of the halogen and compare well with the sum of the single-bond covalent radii [2.47, 2.62 and 2.81 Å, for Cd—Cl, Cd—Br and Cd—I, respectively (Pauling, 1960)] and

with the CSD average data quoted by Orpen *et al.* (1989) [2.50(9), 2.61(6) and 2.75(8) for the same sequence]. The average C—S and C—N distances [1.713(3) and 1.314(3) Å, respectively] of the thiourea molecules agree well with the CSD values [1.725(19) and 1.322(16) Å] for terminally coordinated thiourea (Orpen *et al.*, 1989), which are respectively longer and shorter than the CSD values for uncoordinated thiourea [1.68(2) and 1.35(2) Å; Allen *et al.*, 1987], the variation probably being caused by the coordination to metal.

The Cd—S—C angles, ranging from 105.5(2) to 111.3(3)°, correspond well with those usually found in metal–thiourea complexes. Worthy of note is the systematic asymmetry of the two S—C—N angles, whose ranges are 117.6(1)–119.1(8)° for the smaller and 122.3(6)–124.1(7)° for the larger, the latter involving the N atom participating in the stronger N—H$\cdots$X interactions.

In conclusion, comparison of the structural data of bis(thiourea) compounds of cadmium halides shows that: (i) the crystals are not isostructural, with the crystals containing Cl^- or Br^- ions showing higher symmetry than that containing I^- (Durski *et al.*, 1975); (ii) the average Cd—X distances are in the sequence Cd—I 2.782(1) Å > Cd—Br 2.655(3) Å > Cd—Cl 2.541(1) Å, as expected; (iii) the average Cd—S distances in the three compounds are not significantly different, showing that the size and electronegativity of the halogen do not influence the metal–thiourea interaction; (iv) as expected, the volumes of the tetrahedra follow the sequence of the halogen radii; (v) the distortion of the cadmium coordination tetrahedra follows a reverse relation.

Experimental

Single crystals of the title compounds [CdBr$_2$\{SC(NH$_2$)$_2$\}$_2$] and [CdI$_2$\{SC(NH$_2$)$_2$\}$_2$] were grown by slow evaporation of aqueous solutions containing the cadmium halide and thiourea in the ratio 1:2. The crystals of [CdI$_2$\{SC(NH$_2$)$_2$\}$_2$] were obtained as described by Nardelli *et al.* (1956).

Compound (I)

Crystal data

[CdCl$_2$(CH$_4$N$_2$S)$_2$]
M_r = 335.54
Orthorhombic
$Pmn2_1$
a = 13.148(5) Å
b = 5.834(1) Å
c = 6.501(2) Å
V = 498.7(3) Å^3
Z = 2
D_x = 2.235 Mg m^{-3}
D_m = 2.320 Mg m^{-3}
D_m measured by flotation
  (Nardelli *et al.*, 1956)

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 30
  reflections
θ = 11.82–17.74°
μ = 3.091 mm^{-1}
T = 293(2) K
Prism
0.39 × 0.22 × 0.19 mm
Colourless

Data collection

Philips PW1100 diffractom-
  eter
ω–2θ scans
Absorption correction:
  ψ scan (North *et al.*,
  1968)
  T_{min} = 0.443, T_{max} = 0.556
4176 measured reflections
1198 independent reflections

1127 reflections with
  $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 35°
$h = -21 \rightarrow 21$
$k = -9 \rightarrow 9$
$l = 0 \rightarrow 10$
2 standard reflections
  every 100 reflections
  intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.018
$wR(F^2)$ = 0.043
S = 1.053
1198 reflections
56 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0682P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.059 e Å^{-3}
  (1.54 Å from Cd)
$\Delta\rho_{min}$ = −2.135 e Å^{-3}
  (0.75 Å from Cl1)

Extinction correction:
  SHELXL93 (Sheldrick,
  1993)
Extinction coefficient:
  0.127(4)
Scattering factors from
  *International Tables for
  Crystallography* (Vol. C)
Absolute structure: Flack
  (1983)
Flack parameter = 0.02(2)

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

$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Cd	0	−0.26403(3)	0.00312(3)	0.0256(1)
S	−0.17216(3)	−0.1197(1)	0.1121(1)	0.0297(1)
Cl1	0	−0.2423(1)	−0.3890(1)	0.0295(2)
Cl2	0	−0.6899(1)	0.0759(2)	0.0397(2)
C	−0.2616(1)	−0.3318(3)	0.0785(3)	0.0218(4)
N1	−0.3582(2)	−0.2690(3)	0.0682(6)	0.043(1)
N2	−0.2398(1)	−0.5524(3)	0.0678(3)	0.0296(4)

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

Cd—S	2.517(1)	S—C	1.721(2)
Cd—Cl1	2.553(1)	C—N1	1.323(3)
Cd—Cl2	2.529(1)	C—N2	1.321(3)
Cl1—Cd—S	105.34(2)	Cd—S—C	109.8(1)
Cl2—Cd—S	106.02(1)	S—C—N1	117.6(1)
Cl1—Cd—Cl2	103.63(3)	S—C—N2	124.0(2)
S—Cd—S^i	128.14(2)	N1—C—N2	118.4(2)
Cl1—Cd—S—C	78.5(1)	Cd—S—C—N2	21.6(2)
Cl2—Cd—S—C	−30.9(1)	S^i—Cd—S—C	−157.1(1)
Cd—S—C—N1	−160.2(2)		

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

Table 3. *Hydrogen-bonding geometry (Å, °) for (I)*

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D\cdots A$	D—H$\cdots$$A$
N2—H2B$\cdots$Cl2	0.86	2.40	3.254(2)	175
N2—H2A$\cdots$Cl1^i	0.86	2.89	3.636(2)	147
N1—H1A$\cdots$Cl1^i	0.86	2.60	3.418(2)	158
N1—H1B$\cdots$Cl1^{ii}	0.86	2.72	3.529(2)	157

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

Compound (II)

Crystal data

[CdBr₂(CH₄N₂S)₂]	Mo $K\alpha$ radiation
$M_r = 424.46$	$\lambda = 0.71073$ Å
Orthorhombic	Cell parameters from 25
$Pnam$	reflections
$a = 13.052\ (18)$ Å	$\theta = 15-20°$
$b = 5.9892\ (19)$ Å	$\mu = 9.956$ mm^{-1}
$c = 13.542\ (3)$ Å	$T = 293\ (2)$ K
$V = 1059\ (2)$ Å^3	Tabular
$Z = 4$	$0.429 \times 0.198 \times 0.198$ mm
$D_x = 2.663$ Mg m^{-3}	Pale yellow
D_m not measured	

Data collection

Nonius CAD-4 diffractom-	1079 reflections with
eter	$I > 2\sigma(I)$
ω–2θ scan	$R_{int} = 0.033$
Absorption correction:	$\theta_{max} = 31.97°$
XABS2 (Parkin et al.,	$h = 0 \rightarrow 19$
1995)	$k = 0 \rightarrow 8$
$T_{min} = 0.027$, $T_{max} = 0.139$	$l = 0 \rightarrow 20$
1896 measured reflections	3 standard reflections
1896 independent reflections	every 200 reflections
	intensity decay: 3.9%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.055$	$\Delta\rho_{max} = 2.086$ e Å^{-3}
$wR(F^2) = 0.191$	(1.28 Å from Br2)
$S = 1.095$	$\Delta\rho_{min} = -1.777$ e Å^{-3}
1896 reflections	(1.56 Å from H12A)
55 parameters	Extinction correction: none
H atoms constrained	Scattering factors from
$w = 1/[\sigma^2(F_o^2) + (0.0921P)^2$	International Tables for
$\quad + 4.8853P]$	Crystallography (Vol. C)
where $P = (F_o^2 + 2F_c^2)/3$	

Table 4. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (II)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cd	0.3441 (1)	0.2187 (2)	3/4	0.0308 (3)
Br1	0.1395 (1)	0.2428 (2)	3/4	0.0359 (3)
Br2	0.3779 (1)	−0.2154 (2)	3/4	0.0460 (4)
S	0.3960 (2)	0.3659 (4)	0.5828 (2)	0.0392 (6)
C	0.3798 (6)	0.170 (2)	0.4935 (6)	0.043 (2)
N1	0.3841 (8)	0.230 (2)	0.4012 (7)	0.043 (2)
N2	0.3647 (7)	−0.048 (2)	0.5115 (6)	0.046 (2)

Table 5. *Selected geometric parameters (Å, °) for (II)*

Cd—S	2.522 (2)	S—C	1.698 (10)
Cd—Br1	2.674 (4)	C—N1	1.302 (13)
Cd—Br2	2.636 (2)	C—N2	1.343 (17)
Br1—Cd—S	104.42 (7)	Cd—S—C	111.3 (3)
Br2—Cd—S	107.53 (6)	N1—C—S	119.1 (8)
Br1—Cd—Br2	102.48 (6)	N2—C—S	124.1 (7)
S—Cd—S^i	127.7 (1)	N1—C—N2	116.8 (9)
Br1—Cd—S—C	−78.7 (3)	Cd—S—C—N2	−14.5 (9)
Br2—Cd—S—C	29.7 (3)	S^i—Cd—S—C	159.8 (3)
Cd—S—C—N1	167.1 (8)		

Symmetry code: (i) $x, y, \frac{3}{2} - z$.

Table 6. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2B···Br2	0.86	2.53	3.386 (9)	172
N1—H1A···Br1^i	0.93	2.67	3.578 (11)	165

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

Compound (III)

Crystal data

[CdI₂(CH₄N₂S)₂]	Mo $K\alpha$ radiation
$M_r = 518.44$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25
$P2_1/c$	reflections
$a = 10.481\ (2)$ Å	$\theta = 15-18°$
$b = 7.640\ (2)$ Å	$\mu = 7.200$ mm^{-1}
$c = 15.133\ (4)$ Å	$T = 293\ (2)$ K
$\beta = 91.00\ (2)°$	Tabular
$V = 1211.6\ (5)$ Å^3	$0.231 \times 0.198 \times 0.198$ mm
$Z = 4$	Pale rose
$D_x = 2.842$ Mg m^{-3}	
D_m not measured	

Data collection

Nonius CAD-4 diffractom-	2350 reflections with
eter	$I > 2\sigma(I)$
ω–2θ scans	$R_{int} = 0.030$
Absorption correction:	$\theta_{max} = 31.96°$
XABS2 (Parkin et al.,	$h = -15 \rightarrow 15$
1995)	$k = 0 \rightarrow 11$
$T_{min} = 0.117$, $T_{max} = 0.240$	$l = 0 \rightarrow 22$
4200 measured reflections	3 standard reflections
4200 independent reflections	every 200 reflections
	intensity decay: 3.9%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.100$
$R[F^2 > 2\sigma(F^2)] = 0.051$	$\Delta\rho_{max} = 1.280$ e Å^{-3}
$wR(F^2) = 0.141$	(1.29 Å from Cd)
$S = 1.099$	$\Delta\rho_{min} = -3.751$ e Å^{-3}
4200 reflections	(0.03 Å from I2)
100 parameters	Extinction correction: none
H atoms constrained	Scattering factors from
$w = 1/[\sigma^2(F_o^2) + (0.0679P)^2]$	International Tables for
where $P = (F_o^2 + 2F_c^2)/3$	Crystallography (Vol. C)

Table 7. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (III)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cd	0.22442 (5)	−0.01472 (7)	0.11244 (4)	0.0388 (2)
S1	0.0608 (2)	0.0274 (3)	0.2322 (1)	0.0409 (4)
S2	0.1302 (2)	0.1180 (3)	−0.0260 (1)	0.0464 (5)
I1	0.28029 (5)	−0.36598 (7)	0.08636 (4)	0.0449 (2)
I2	0.44902 (4)	0.14257 (7)	0.17352 (4)	0.0429 (2)
C1	0.1205 (7)	−0.0716 (9)	0.3252 (5)	0.036 (2)
N11	0.2377 (7)	−0.124 (1)	0.3346 (5)	0.066 (2)
N12	0.0432 (7)	−0.095 (1)	0.3918 (4)	0.056 (2)
C2	0.2576 (6)	0.153 (1)	−0.0947 (4)	0.033 (1)
N21	0.2435 (6)	0.109 (1)	−0.1777 (4)	0.050 (2)
N22	0.3652 (6)	0.219 (1)	−0.0661 (5)	0.050 (2)

Table 8. *Selected geometric parameters (Å, °) 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 (Å, °) 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^i	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: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *Xtal_GX* (Hall & du Boulay, 1995); software used to prepare material for publication: *SHELXL*93; geometrical calculations: *PARST* (Nardelli, 1983).

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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 stuctures 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. 1*a*) for the anion (Cioslowski *et al.*, 1991). This computed