Mononuclear Trigonal Planar Trichloroargentate(I) and Tribromoargentate(I) Ions isolated as their Dibenzo-18-crown-6 Potassium and Rubidium Salts†‡

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Mononuclear trichloroargentate(I) and tribromoargentate(I) ions have been isolated with dibenzo-18-crown-6 potassium and rubidium cations and characterised by means of crystal structure determination. The four compounds prepared $[ML]_3[AgX_3]X$ [L = dibenzo-18-crown-6 (6,7,9,10,17,18,20,21-octahydrodibenzo[*b,k*][1,4,7,10,13,16]hexaoxacyclooctadecine); X = Cl, M = K **1** or Rb **2**; X = Br, M = K **3** or Rb **4**], crystallise in the hexagonal space group $P6_3/m$, with $Z = 2$, **1** and **3**, and **2** and **4** being isostructural, respectively [**1**, $a = 14.012(2)$ and $c = 18.958(2)$ Å; **2**, $a = 13.786(2)$ and $c = 19.507(2)$ Å; **3**, $a = 14.154(2)$ and $c = 19.045(4)$ Å; and **4**, $a = 14.000(1)$ and $c = 19.591(3)$ Å]. The anions exhibit perfect D_{3h} symmetry with Ag–Cl 2.463(2) Å in **1**, 2.447(2) Å in **2** and Ag–Br 2.561(2) Å in **3**, 2.550(1) Å in **4**. In compounds **2** and **4**, the rubidium ions appear to be somewhat too large for the crown cavity and are displaced towards the anion, such that each Rb^+ is involved in two short $Rb^+ \cdots X$ contacts [3.272(2) and 3.487(2) Å in **2**, 3.420(2) and 3.597(2) Å in **4**]. In the potassium compounds, **1** and **3**, however, K^+ is accommodated in the cavity of the crown and the cations are rotated relative to the anions so that there is only one short $K^+ \cdots X$ contact per potassium ion [3.019(3) Å in **1** and 3.199(5) Å in **3**]. The stronger outer-sphere co-ordination in the potassium compounds thus results in a slight lengthening of the Ag–X bond.

The co-ordination number of the metal in crystalline halogenocuprates(I) and halogenoargentates(I) has been shown to be dependent on the properties of the cation with which co-precipitation occurs.[1] Cation size, in particular, would appear to be of prime importance for the determination of a given metal(I) co-ordination number in the halogenocuprate(I) or halogenoargentate(I) anion in the crystalline phase.[1] Although a mononuclear $[AgI_3]^{2-}$ anion has been isolated recently with the methyltriphenylphosphonium cation and its structure determined,[2] the existence of mononuclear trigonal chloro- and bromo-argentate(I) counterparts in the solid state has not hitherto been documented. From our previous studies on halogenoargentates(I),[3] it seemed likely that this could be accomplished by employing fairly large cations with low effective positive charge. Thus, potassium and rubidium ions complexed with dibenzo-18-crown-6 ethers were selected as possible candidates for this purpose. We now report the preparation and characterisation, by means of crystal structure determination, of four compounds containing mononuclear trigonal $[AgX_3]^{2-}$ (X = Cl or Br) anions.

Table 1 Fractional atomic coordinates for the non-hydrogen atoms in $[KL]_3[AgCl_3]Cl$ **1**

Atom	*x*	*y*	*z*
Ag	0.6667	0.3333	0.2500
Cl(1)	0.4671(1)	0.2014(2)	0.2500
Cl(2)	0.0000	0.0000	0.0000
K(1)	0.3601(1)	−0.0466(1)	0.2500
O(1)	0.5305(3)	−0.0932(3)	0.2500
O(2)	0.4312(2)	−0.0812(2)	0.3784(1)
O(3)	0.2577(2)	−0.0604(2)	0.3776(1)
O(4)	0.1616(3)	−0.0416(3)	0.2500
C(1)	0.5901(3)	−0.0383(4)	0.3116(2)
C(2)	0.5260(3)	−0.0946(4)	0.3764(2)
C(3)	0.3698(3)	−0.1118(3)	0.4391(2)
C(4)	0.3949(4)	−0.1518(4)	0.4986(2)
C(5)	0.3276(5)	−0.1813(4)	0.5578(2)
C(6)	0.2363(4)	−0.1696(4)	0.5568(3)
C(7)	0.2097(4)	−0.1298(4)	0.4976(2)
C(8)	0.2760(3)	−0.1005(3)	0.4387(2)
C(9)	0.1641(3)	−0.0450(4)	0.3760(2)
C(10)	0.1732(3)	0.0208(4)	0.3125(3)

Results and Discussion

Fractional co-ordinates for the four compounds $[ML]_3[AgX_3]X$ [L = dibenzo-18-crown-6 (6,7,9,10,17,18,20,21-octahydrodibenzo[*b,k*][1,4,7,10,13,16]hexaoxacyclooctadecine); X = Cl, M = K **1** or Rb **2**; X = Br, M = K **3** or Rb **4**] are given in Tables 1–4, and bond lengths within the $[AgCl_3]^{2-}$ and $[AgBr_3]^{2-}$ ions in Figs. 1 and 2. The anions have perfect D_{3h} symmetry since silver is situated on the six-fold inversion axis and the halogenide ligand in the mirror plane; the non-isostructurality of all four compounds can, however, be attributed to different outer-sphere co-ordination requirements associated with the potassium and rubidium ions. The arrangement of $[KL]^+$ and of $[RbL]^+$ cations around an $[AgX_3]^{2-}$ anion (X = Cl or Br) is illustrated in Figs. 1 and 2, respectively. As is apparent from Fig. 1, the potassium ions are accommodated in the cavity of the crown, each K^+ ion being involved in only one short $K^+ \cdots X$ contact, *viz*. 3.019(3) Å in **1** and 3.199(5) Å in **3**. The rubidium ion, on the other hand, appears to be slightly too large to fit into the crown cavity (Fig. 2) and the cations and anions are rotated relative to one another about the six-fold inversion axis such that two chloride

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‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 2 Fractional atomic coordinates for the non-hydrogen atoms in $[RbL]_3[AgCl_3]Cl$ **2**

Atom	*x*	*y*	*z*
Ag	0.666 7	0.333 3	0.250 0
Cl(1)	0.469 3(2)	0.282 4(2)	0.250 0
Cl(2)	0.000 0	0.000 0	0.000 0
Rb(1)	0.425 97(6)	0.026 46(6)	0.250 0
O(1)	0.496 5(6)	−0.142 1(6)	0.250 0
O(2)	0.438 0(3)	−0.086 4(3)	0.375 7(2)
O(3)	0.280 0(3)	−0.035 6(3)	0.376 5(2)
O(4)	0.183 8(4)	−0.022 1(4)	0.250 0
C(1)	0.561 8(9)	−0.113 9(10)	0.308 8(5)
C(2)	0.507 6(7)	−0.136 9(8)	0.370 7(4)
C(3)	0.381 2(5)	−0.104 6(4)	0.436 2(3)
C(4)	0.403 2(6)	−0.145 6(5)	0.494 5(4)
C(5)	0.340 4(8)	−0.162 2(4)	0.553 0(4)
C(6)	0.257 1(7)	−0.137 9(7)	0.553 0(4)
C(7)	0.234 0(6)	−0.095 5(6)	0.495 4(4)
C(8)	0.295 1(5)	−0.078 2(4)	0.436 6(3)
C(9)	0.181 1(5)	−0.025 5(5)	0.372 6(3)
C(10)	0.187 7(4)	0.038 2(5)	0.309 8(3)

Table 3 Fractional atomic coordinates for the non-hydrogen atoms in $[KL]_3[AgBr_3]Br$ 3

Atom	*x*	*y*	*z*
Ag	0.6667	0.3333	0.2500
Br(1)	0.4650(2)	0.1852(2)	0.2500
Br(2)	0.0000	0.0000	0.0000
K(1)	0.3432(3)	−0.0756(4)	0.2500
O(1)	0.5286(9)	−0.0957(9)	0.2500
O(2)	0.4250(6)	−0.0894(6)	0.3773(4)
O(3)	0.2528(7)	−0.0714(6)	0.3762(4)
O(4)	0.1583(8)	−0.051(1)	0.2500
C(1)	0.5864(9)	−0.039(1)	0.3114(6)
C(2)	0.523(1)	−0.097(1)	0.3755(6)
C(3)	0.366(1)	−0.117(1)	0.4390(6)
C(4)	0.395(1)	−0.1540(9)	0.4975(8)
C(5)	0.333(1)	−0.179(1)	0.5580(8)
C(6)	0.240(1)	−0.172(1)	0.5597(8)
C(7)	0.209(1)	−0.135(1)	0.500(1)
C(8)	0.272(1)	−0.1073(8)	0.4388(7)
C(9)	0.162(1)	−0.054(1)	0.3759(7)
C(10)	0.168(1)	0.010(1)	0.3125(7)

Table 4 Fractional atomic coordinates for the non-hydrogen atoms in $[RbL]_3[AgBr_3]Br$ **4**

Atom	*x*	*y*	*z*
Ag	0.6667	0.3333	0.2500
Br(1)	0.4645(1)	0.2826(2)	0.2500
Br(2)	0.0000	0.0000	0.0000
Rb	0.4212(1)	0.0195(1)	0.2500
O(1)	0.487(1)	−0.149(1)	0.2500
O(2)	0.4367(5)	−0.0883(6)	0.3762(4)
O(3)	0.2792(5)	−0.0397(5)	0.3763(3)
O(4)	0.1836(7)	−0.0281(7)	0.2500
C(1)	0.544(2)	−0.132(2)	0.308(1)
C(2)	0.506(1)	−0.137(1)	0.3715(7)
C(3)	0.3785(8)	−0.1076(8)	0.4337(6)
C(4)	0.403(1)	−0.1459(9)	0.4951(7)
C(5)	0.341(1)	−0.164(1)	0.5508(7)
C(6)	0.260(1)	−0.141(1)	0.5526(6)
C(7)	0.2343(9)	−0.100(1)	0.4949(7)
C(8)	0.2950(8)	−0.0821(7)	0.4358(6)
C(9)	0.1818(7)	−0.0318(8)	0.3716(6)
C(10)	0.1863(7)	0.0301(9)	0.3105(6)

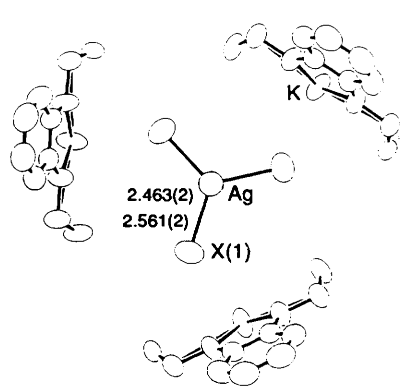

Fig. 1 View of the packing of $[KL]^+$ cations and $[AgX_3]^{2-}$ anions [X(1) = Cl(1) or Br(1)] in $[KL]_3[AgCl_3]Cl$ **1** and $[KL]_3[AgBr_3]Br$ **3**. The upper distance (Å) refers to Ag–Cl(1) and the lower to Ag–Br(1), respectively. Thermal ellipsoids enclose 50% probability

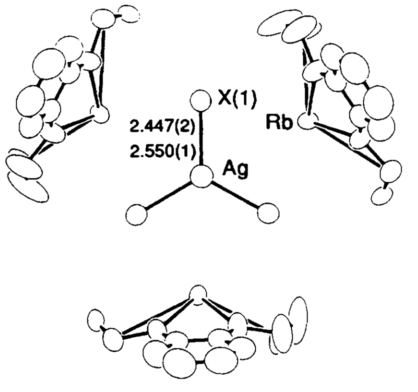

Fig. 2 View of the packing of $[RbL]^+$ cations and $[AgX_3]^{2-}$ anions [X(1) = Cl(1) or Br(1)] in $[RbL]_3[AgCl_3]Cl$ **2** and $[RbL]_3[AgBr_3]Br$ **4**. The upper distance (Å) refers to Ag–Cl(1) and the lower to Ag–Br(1), respectively. Thermal ellipsoids enclose 50% probability

or bromide ligands are in contact with each rubidium ion [3.272(2) and 3.487(2) Å in **2**, 3.420(2) and 3.597(2) Å in **4**]. Consequently, there is a relatively short $Rb^+ \cdots Ag$ contact in each compound, *i.e.* 3.8564(7) Å in **2** and 4.002(1) Å in **4**. The corresponding $K^+ \cdots Ag$ contacts in the potassium compounds **1** and **3** are 4.891(2) and 5.288(4) Å respectively.

The stronger outer-sphere co-ordination in the potassium compounds results in a slight lengthening of the Ag–X bond relative to the corresponding rubidium compound, *i.e.* 2.463(2) *versus* 2.447(2) Å for $[AgCl_3]^{2-}$ in **1** and **2** respectively and 2.561(2) *versus* 2.550(1) Å for $[AgBr_3]^{2-}$ in **3** and **4** respectively. In the $[AgI_3]^{2-}$ ion in $[PMePh_3]_2[AgI_3]$, in which the anions and cations can be considered to be more well separated from one another, the Ag–I bond distances are 2.742(1), 2.746(1) and 2.755(1) Å and the silver(I) atom lies 0.036 Å from the ligand plane, the anion thus being very slightly distorted from the ideal D_{3h} symmetry.[2b]

In the $[KL]^+$ and $[RbL]^+$ cations the alkali metal and two of the oxygen ligands are situated in the crystallographic mirror plane. The K–O bond distances lie in the ranges 2.764(3)–2.816(4) and 2.736(7)–2.803(11) Å for **1** and **3** respectively, while those for the Rb–O distances are 2.934(6)–3.060(5) and 2.930(10)–3.049(8) Å for **2** and **4** respectively. The isolated halogenide ions [X(2)], *i.e.* Cl(2) in **1** and **2** and Br(2) in **3** and **4**, which are situated at the unit-cell origin, are remote from Ag, the closest contacts involving these ions being to the crown ether, *i.e.* $X(2) \cdots C(9)$ 3.557(4), 3.662(5), 3.63(1) and 3.760(9) Å for **1**–**4** respectively.

Three-co-ordinated halogenoargentate(I) species are still relatively rare. Apart from the mononuclear $[AgI_3]^{2-}$ ion,[2] and the chloro- and bromo-argentate(I) counterparts presented here, a dinuclear $[Ag_2Cl_5]^{2-}$ anion[4] and dinuclear $[Ag_2X_4]^{2-}$ species (X = Cl,[3b,e] Br[3b,e] or I[3f]) have been reported. The μ-chlorobis[dichloroargentate(I)] ion determined in $[NH_4]_6[AuCl_4][Ag_2Cl_5]$ has been described in terms of 'chlorine bridged $AgCl_2^-$',[4] and a similar description can be considered appropriate for the loose association of $AgCl_2$ moieties in the $[Ag_2Cl_4]^{2-}$ anions.[3b,e] In the di-μ-bromo-dibromodiargentate(I)[3b,e] and di-μ-iodo-diiododiargentate(I)[3f] anions, however, silver(I) exhibits more regular trigonal-planar co-ordination geometry. It is therefore perhaps somewhat surprising that, in the present compounds, mononuclear $[AgCl_3]^{2-}$ exhibits perfect trigonal-planar symmetry like its tribromoargentate(I) counterpart.

The present investigation provides a further example in which the adaptability of halogenoargentates(I) to cation dictates has been exploited for the preparation of anions with a desired silver(I) co-ordination number. The co-ordination number of the metal in halogenocuprate(I) ions and, to a lesser extent in halogenoargentate(I) ions, co-precipitated with bulky unipositive ions with well screened positive charge, has been shown to be dependent on cation size such that the metal(I) co-ordination number in the anion decreases with increasing size of the cation with which it is co-precipitated.[1] This is contrary to the usual principle of matching small anions with small cations and *vice versa*.[5]

For both halogenocuprates(I) and halogenoargentates(I) crystallising with comparable unipositive cations, a correlation has been found between the co-ordination number of the metal and the concentration of halogenide ligand in the solid, suggesting that dilution of the ligand ions by the cations is a determinating factor for the attainment of a particular metal(I) co-ordination number and thus for the resulting anionic configuration.[1,6] For crystalline halogenocuprates(I) it has been suggested that cation–halogenide ligand packing may be the primary process occurring during crystal nucleation, copper(I) attaining the appropriate co-ordination number by diffusion into available interstices, subsequent rearrangement then resulting in the specific anion.[7] This would imply a rapid ligand exchange rate for copper(I) in solution, the dihalogenocuprate(I) ion thus providing a source of the 'naked' metal ion.[1,7] A similar explanation might be considered appropriate for the analogous correlation between metal(I) co-ordination number and cation size in halogenoargentates(I).[1] Further indirect evidence for such a mechanism of formation has been provided by, for example, the preparation of a heteronuclear $[Ag_2Cu_2I_8]^{4-}$ cluster, in which copper(I) is three-co-ordinated, whereas silver(I) is four-co-ordinated, simply by dissolving the metal(I) iodides in an acetonitrile solution of tetraphenylphosphonium iodide.[8] With tetraphenylphosphonium iodide and the individual metal iodides(I) in acetonitrile, a $[Cu_2I_4]^{2-}$ anion in which copper(I) is three-co-ordinated,[9] and an $[Ag_4I_8]^{4-}$ ion containing both three- and four-co-ordinated silver(I),[3e] are precipitated, respectively. Yet another example of anion design by pertinent choice of cation is the isolation of linear, monomeric $[AgCl_2]^-$, containing two-co-ordinated silver(I), and of $[Ag_2I_4]^{2-}$, in which silver(I) is three-co-ordinated, with the bulky $[KL']^+$ cation [L′ = cryptand 222 (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane)].[1,3f] The tuning of anionic configurations to cation properties in halogenocuprates(I) and halogenoargentates(I) reflects the versatility in co-ordination not only of copper(I) or silver(I) but also of the ligands. Indeed, the importance of the bonding requirements imposed by bridging halogenides and, in particular, by bromide, in determining the geometry of halogenocuprate(I) anions has been demonstrated in a recent theoretical study.[10]

Experimental

Preparation of Compounds.—Dibenzo-18-crown-6 (0.36 g, 1.0 mmol) was dissolved in dimethylformamide (*ca.* 20 cm^3). An equimolar amount of potassium chloride (0.074 g) (for **1**), rubidium chloride (0.12 g) (**2**), potassium bromide (0.12 g) (**3**) or rubidium bromide (0.17 g) (**4**), dissolved in a minimum amount of water, was added dropwise to the solution under gentle heating and stirring. Freshly precipitated silver(I) chloride (0.14 g, 1.0 mmol) (for **1** and **2**) or silver bromide (0.19 g, 1.0 mmol) (**3** and **4**) was dissolved in the solution by stirring and heating the mixture gently for *ca.* 30 min. Colourless prisms of **1**–**4** were deposited from the solution within a few days; m.p.: **1**, 161; **2**, 186; **3**, 153; **4**, 158 °C.

Crystallography.—*Crystal data.* **1**. $C_{60}H_{72}AgCl_4K_3O_{18}$, $M = 1448.2$, hexagonal, $a = 14.012(2)$, $c = 18.958(2)$ Å, $U = 3223.3(9)$ Å^3 (by least-squares refinement on diffractometer setting angles for 25 automatically centred reflections, $\lambda = 0.710\,69$ Å), space group $P6_3/m$, $Z = 2$, $D_c = 1.49$ g cm^{-3}, $F(000) = 1496$. Colourless hexagonal prisms. Crystal dimensions (distance to faces from origin at crystal centroid): 0.181 (001, 00−1) × 0.164 (010, 0−10) × 0.080 (1−10, −110) × 0.133 (110, −1−10) mm, μ(Mo-Kα) = 7.36 cm^{-1}.

2. $C_{60}H_{72}AgCl_4Rb_3O_{18}$, $M = 1578.3$, hexagonal, $a = 13.786(2)$, $c = 19.507(2)$ Å, $U = 3211.0(8)$ Å^3 (by least-squares refinement on diffractometer setting angles for 25 automatically centred reflections, $\lambda = 0.710\,69$ Å), space group $P6_3/m$, $Z = 2$, $D_c = 1.64$ g cm^{-3}, $F(000) = 1604$. Colourless hexagonal prisms. Crystal dimensions (distance to faces from origin at crystal centroid): 0.208 (001, 00−1) × 0.270 (100, −100) × 0.261 (1−30, −130) mm, μ(Mo-Kα) = 27.43 cm^{-1}.

3. $C_{60}H_{72}AgBr_4K_3O_{18}$, $M = 1626.0$, hexagonal, $a = 14.154(2)$, $c = 19.045(4)$ Å, $U = 3304(1)$ Å^3 (by least-squares refinement on diffractometer setting angles for 20 automatically centred reflections, $\lambda = 0.710\,69$ Å), space group $P6_3/m$, $Z = 2$, $D_c = 1.64$ g cm^{-3}, $F(000) = 1640$. Colourless, irregular-shaped prisms. Approximate crystal dimensions: 0.24 × 0.24 × 0.26 mm, μ(Mo-Kα) = 29.50 cm^{-1}.

4. $C_{60}H_{72}AgBr_4Rb_3O_{18}$, $M = 1765.1$, hexagonal, $a = 14.000(1)$, $c = 19.591(3)$ Å, $U = 3325.2(8)$ Å^3 (by least-squares refinement on diffractometer setting angles for 25 automatically centred reflections, $\lambda = 0.710\,69$ Å), space group $P6_3/m$, $Z = 2$, $D_c = 1.76$ g cm^{-3}, $F(000) = 1748$. Colourless, irregular-shaped prisms. Approximate crystal dimensions: 0.30 × 0.40 × 0.20 mm, μ(Mo-Kα) = 48.67 cm^{-1}.

Data collection and processing. **1**. Rigaku AFC6R diffractometer, *ca.* 290 K, ω–2θ scan mode with an ω scan rate of 4° min^{-1} and a scan width of (0.94 + 0.30 tan θ)°, graphite-monochromated Mo-Kα radiation from a RU200 rotating anode operated at 9 kW (50 kV; 180 mA); weak reflections [$I < 10\sigma(I)$] were rescanned twice and counts accumulated to improve counting statistics. Stationary backgrounds were recorded on each side of the reflection; ratio of peak counting time *vs.* background counting time 2:1; 1996 unique reflections ($3.5 < 2\theta < 50°$); Gaussian absorption correction[11] (max., min. transmission factors = 0.892, 0.817); 1270 reflections with $I > 3\sigma(I)$.

2. As for **1**, ω scan rate 4° min^{-1}, scan width (1.05 + 0.30 tanθ)°, 1967 unique reflections ($3.5 < 2\theta < 50°$); Gaussian absorption correction[11] (max., min. transmission factors = 0.380, 0.307); 1281 reflections with $I > 3\sigma(I)$.

3. As for **1**, ω scan rate 4° min^{-1}, scan width (0.92 + 0.30 tanθ)°, 2014 unique reflections ($3.5 < 2\theta < 50°$); empirical correction for absorption correction based on azimuthal scans for several reflections (max., min. transmission factors = 1.00, 0.64); 654 reflections with $I > 3\sigma(I)$.

4. As for **1**, ω scan rate 4° min^{-1}, scan width (1.37 + 0.30 tanθ)°, 2029 unique reflections ($3.5 < 2\theta < 50°$); empirical correction for absorption correction based on azimuthal scans for several reflections (max., min. transmission factors = 1.00, 0.74); 1098 reflections with $I > 3\sigma(I)$.

Structure analysis and refinement. **1**. The coordinates of the silver, chlorine and potassium atoms were determined by direct methods (MITHRIL)[12] and those of the remaining atoms from subsequent electron-density maps. Full-matrix least-squares refinement, including anisotropic thermal parameters for all non-hydrogen atoms and with hydrogen atoms as a fixed contribution (C–H 0.95 Å, $B = 1.2B_{eq}$ of the carrying carbon atom) gave final $R = 0.039$, $R' = 0.048$ for 137 parameters and 1270 reflections; maximum residual electron density = 0.50 e Å^{-3}. Weighting scheme $w = [\sigma^2(F_o)]^{-1}$.

2. Although the cell constants and the space group suggested isostructurality with **1**, the Patterson maps differed somewhat and refinement using the coordinates of **1** as starting point diverged. The structure was therefore solved using direct methods (MITHRIL)[12] followed by successive electron density calculations. Full-matrix least-squares refinement as for **1** gave final $R = 0.043$, $R' = 0.046$ for 137 parameters and 1281 reflections; maximum residual electron density = 0.71 e Å^{-3}. Weighting scheme as above.

3. The coordinates of **1** were used as starting point for the refinement of the structure, refinement as for **1** yielding final $R = 0.045$, $R' = 0.042$ for 137 parameters and 654 reflections; maximum residual electron density = 0.49 e Å^{-3}. Weighting scheme as above.

4. The coordinates of **2** were used as starting point for the refinement of the structure; refinement as for **1** yielded final $R = 0.044$, $R' = 0.050$ for 137 parameters and 1098 reflections; maximum residual electron density = 0.49 e Å^{-3}. Weighting scheme as above.

For atomic scattering factors, anomalous dispersion corrections, and computer programs used, see ref. 13. Figs. 1 and 2 were drawn using ORTEP.[14]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond distances and angles.

Acknowledgements

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