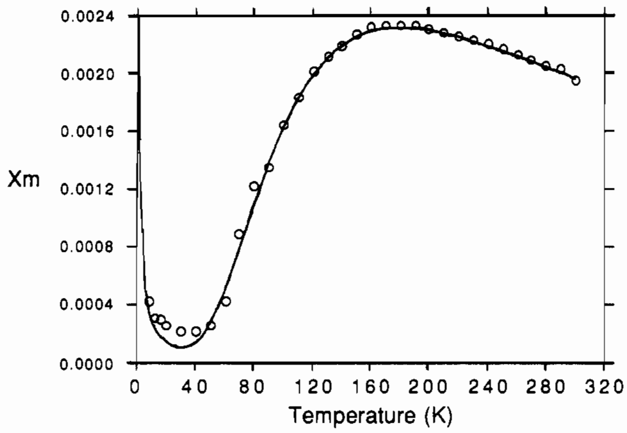

Figure 2. Plot of χ_m vs temperature.

used for the copper complex. The atomic coordinates are given in Tables II and III. The dinuclear complex is centrosymmetric and most of the bond lengths and angles (Tables IV and V) are compatible with D_{2h} symmetry within experimental error. In fact all atoms of the anion lie within 0.1 Å of the best mean plane, an indication of low strain throughout the complex. The cell parameters for the nickel complex are very similar to those of the palladium and copper complexes although in this case no intensity data were gathered. The tetrabutylammonium ion prevents close intermolecular stacking of the planar anions. We have reported on the effects of cation size on anion stacking elsewhere,[20] and further investigation is underway in this system. It is noteworthy, however, that the tetrabutylammonium ion adopts a relatively flat shape to accommodate to the shape of the rigid planar anion. The four terminal carbon atoms of the butyl groups are nearly coplanar, thus alleviating, in part, the problem of packing "basketballs and pizza pans". The bite angle of O–Pd–N is approximately the same as that found in the 4,5-dicarboxyimidazole complex with rhodium,[14] again indicating that a favorable geometry is available with this ligand.

An intriguing feature of the structure is the relatively short metal–metal separation of 3.89 Å (3.99 Å for Cu–Cu) resulting from the formation of a six-membered bimetallacyclic ring. This distance is very similar to the distance observed in a structurally related (aminotriazole)copper complex recently reported.[22] The copper ion's proximity leads to a significant coupling both through-space and through the π system of the heteroaromatic pyrazole rings. To test this factor, we investigated the magnetic behavior as a function of temperature. Figure 2 shows the data and the theoretical fitting to a modified Bleaney–Bowers relationship.[18] With use of a small correction for paramagnetic impurity (q = 0.004 (1), c = 0.375) and a value for g of 2.09 (14), an antiferromagnetic coupling constant of $2J = -200.2$ (8) cm^{-1} can be calculated. This value is lower than those observed for dinuclear copper complexes unsymmetrically bridged by a single pyrazole and a simple monoatomic bridge, but in those cases the Cu–Cu distances are nearly an 1 Å shorter.[23] Presumably this substantial interaction results from strong participation by the heteroaromatic pyrazole orbitals in the metal–nitrogen metallacyclic ring.

Attempts to partially oxidize the platinum complex were made by placing an acetonitrile solution into the anode compartment of an electrochemical cell with NBu_4Br as the supporting electrolyte. The current values were very low up to the oxidation potential of bromine, and no solid formed on the electrode. Subsequent attempts to carry out full oxidation with bromine gave products that analyzed for oxidative addition of two bromine atoms to each metal ion as well as addition of bromine to the 4-position of the pyrazole rings. Such reactions of pyrazole have been observed previously with chlorine.[24] Attempts at electrochemical oxidation of the sodium and potassium salts of the platinum complex, in the absence of supporting electrolyte, gave no reaction although these conditions yield "cation deficient" oxidation products with oxalates and cyanides.

The conditions necessary to form partially oxidized anisotropically conducting solids require delicate control of counterions and ligand electronic character. Although the dicarboxypyrazolate complexes are electronically and sterically very similar to the oxalate complexes that form conducting solids, it has not so far been possible to mimic those properties in our dinuclear systems. For example, the sodium, potassium, and alkaline-earth salts of our platinum complex are too insoluble to allow their use in electrochemical oxidations. In addition, it may be necessary to modify the electronic character of the ligand in order to observe the eclipsed stacking we have achieved in the imidazole systems.[14] These ligand modifications through substitution at the 4-position will be a part of our future work. In a very recent paper,[25] the authors stated that doubly bridging pyrazole–copper complexes were not known. We are pleased to be able to change the situation by this report. It is perhaps because of the additional charge compensation offered by the dicarboxy derivatives that these complexes form so readily. The availability of planar, dinuclear, anionic complexes opens many possibilities for studies of magnetism, catalysis, and intermolecular interactions.

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Supplementary Material Available: Tables of thermal parameters (1 page); tables of structure factors (13 pages). Ordering information is given on any current masthead page.

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Halogenoargentates(I) with Unusual Coordination Geometries. Synthesis and Structure of Potassium–Crypt Salts of Chloro-, Bromo-, and Iodoargentates(I), Including the First Example of a Two-Coordinated Chloroargentate(I) in the Solid State[1]

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The coordination number most commonly exhibited by silver(I) in crystalline halogenoargentates(I) is undoubtedly 4.[2] Thus, the majority of such compounds whose structures have been deter-

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Table I. Crystal Data for [K(crypt-2,2,2)][$AgCl_2$] (**1**), [K(crypt-2,2,2)]$_4$[Ag_4Br_8] (**2**), and [K(crypt-2,2,2)]$_2$[Ag_2I_4] (**3**)

	1	**2**	**3**
formula	$C_{18}H_{36}AgCl_2KN_2O_6$	$C_{72}H_{144}Ag_4Br_8K_4N_8O_{24}$	$C_{36}H_{72}Ag_2I_4K_2N_4O_{12}$
fw	594	2733	1555
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2/c$	$P2_1/c$	$P\bar{1}$
a, Å	14.242 (8)	16.557 (2)	11.330 (2)
b, Å	15.695 (4)	23.864 (2)	12.365 (2)
c, Å	11.614 (6)	14.070 (2)	10.343 (2)
α, deg	90	90	103.49 (1)
β, deg	95.63 (5)	107.446 (9)	101.72 (2)
γ, deg	90	90	86.66 (1)
V, Å^3	2584 (4)	5304 (2)	1379.5 (9)
Z	4	2	1
d_{calc}, g/cm^3	1.53	1.71	1.87
μ, cm^{-1}	11.7	39.3	31.2
abs cor	none	Gaussian[8]	Gaussian[8]
trans coeff		0.38–0.54	0.30–0.44
reflcns measd	$h,k,\pm l$	$\pm h,k,l$	$h,\pm k,\pm l$
no. of unique reflcns	4717	9587	4850
no. of obs reflcns	2868	3828	3538
no. of parms refined	272	541	271
R	0.037	0.043	0.060
R_w	0.045	0.044	0.068

mined hitherto contain polymeric anions comprised of silver(I) halide tetrahedra, and very few discrete halogenoargentate(I) ions have been reported.[2] Although two-coordinated [AgX_2]$^-$ species have been shown to exist in solution,[3] hitherto only one compound containing such an ion has been characterized structurally.[4] This compound, [$(Bu^n_2NCS)_2Au$][$AgBr_2$], contains, however, a rather short Ag–S distance of 3.16 Å.[4] Recently, an almost planar trigonal [AgI_3]$^{2-}$ monomer[5] and discrete dimeric [Ag_2X_4]$^{2-}$ ions (X = Cl, Br), in which silver(I) is three-coordinated,[6,7] have been prepared and characterized by means of crystal structure determinations.

We now wish to report the successful preparation and structural characterization of a monomeric two-coordinated dichloroargentate(I) ion in the solid state. Isolation of the [$AgCl_2$]$^-$ ion was achieved by using the cation K(crypt-2,2,2)$^+$. Replacement of chloride by bromide or iodide in the reactions also yielded new anions with the overall stoichiometry AgX_2^-, the bromoargentate(I) ion [Ag_4Br_8]$^{4-}$ being a tetranuclear anion containing both three- and four-coordinated silver(I) and the iodoargentate(I) ion [Ag_2I_4]$^{2-}$ being a dinuclear ion in which silver(I) is three-coordinated.

Experimental Section

Preparation of Compounds. [K(crypt-2,2,2)][$AgCl_2$] (1). A 0.22-g (0.58-mmol) sample of crypt-2,2,2 (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) was dissolved in 15 mL of DMF (dimethylformamide); 0.043 g (0.58 mmol) of KCl was dissolved in a minimum amount of water (approximately 0.5 mL) and added to the DMF solution under gentle heating and stirring; AgCl was freshly precipitated from 0.10 g (0.58 mmol) of $AgNO_3$ and 0.5 M HCl and washed thoroughly before addition to the hot solution of [K(crypt-2,2,2)]Cl in DMF. The solution was stirred for 0.5 h, after which most of the silver(I) chloride had dissolved. After filtration, the resulting colorless solution was allowed to evaporate almost to dryness at room temperature, flat colorless needles, mp 158.4 °C, being deposited.

[K(crypt-2,2,2)]$_4$[Ag_4Br_8] (2). The compound was prepared in an analogous manner to **1** from 0.10 g (0.27 mmol) of crypt-2,2,2, 0.032 g (0.27 mmol) of KBr, 0.045 g (0.27 mmol) of $AgNO_3$, and 0.1 M HBr.

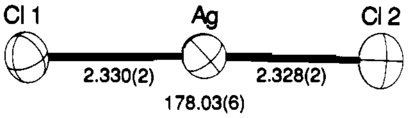

Figure 1. ORTEP[11] drawing of the [$AgCl_2$]$^-$ ion in [K(crypt-2,2,2)][$AgCl_2$]. Distances are in Å and angles in deg; estimated standard deviations are given in parentheses. The thermal ellipsoids enclose 50% probability.

After approximately 3 days, a large number of rhombic crystals had formed in the solution. These crystals were very unstable when isolated from the mother liquor and decomposed within minutes. On further evaporation of the solvent, the crystals gradually dissolved and a new crystal form consisting of colorless, elongated prisms of **2**, mp 168.8 °C, precipitated from the solution.

[K(crypt-2,2,2)]$_2$[Ag_2I_4] (3). A 0.062-g (0.27-mmol) sample of AgI was ground to a fine powder and added to a solution of 0.10 g (0.27 mmol) of crypt-2,2,2 and 0.044 g (0.27 mmol) of KI in DMF at ambient temperature. No heating was required in order to dissolve the silver(I) iodide; filtration of the solution was not considered necessary. The solution was allowed to stand for a few days at room temperature after which large colorless rhombic crystals, mp 169.8–170.3 °C, were formed.

X-ray Crystallography. Crystal and experimental data are summarized in Table I. Diffracted intensities for **1**–**3** were measured at 23 °C with a Rigaku AFC6R diffractometer using graphite-monochromated Mo Kα (λ = 0.71069 Å) radiation from a RU200 rotating anode operated at 9 kW (50 kV; 180 mA). The $\omega/2\theta$ scan mode was employed, and stationary background counts were recorded on each side of the reflection, the ratio of peak counting time vs background counting time being 2:1. Weak reflections ($I < 10.0\sigma(I)$) were rescanned up to three times and counts accumulated to improve counting statistics. The intensities of three reflections were monitored regularly after measurement of 150 reflections and indicated crystal stability in all three cases.

For **1**, data were measured for $3.5 < 2\theta < 50°$ from a crystal with dimensions 0.08 × 0.24 × 0.32 mm, using an ω scan rate of 16°/min^{-1} and a scan width of (1.26 + 0.30 tan θ)°. Correction was made for Lorentz and polarization effects but not for absorption. Of the 4717 unique reflections measured for $h,k,\pm l$, 2868 had $I > 3.00\sigma(I)$ and were considered observed. Cell constants were obtained from least-squares refinement by using the setting angles of 24 centered reflections in the range $37 < 2\theta < 40°$. The structure was solved by direct methods. Full-matrix least-squares refinement, including anisotropic temperature factors for all non-hydrogen atoms, with hydrogen atoms included in calculated positions, but not refined, gave a final R = 0.037 (R_w = 0.045) for 272 parameters and 2868 reflections. The maximum and minimum peaks in the final difference map were +0.64 and −0.52 e/Å^3, respectively; reflections were weighted according to $w = [\sigma^2(F_o)]^{-1}$.

For **2**, 9587 unique reflections were measured for $3.5 < 2\theta < 50°$ ($\pm h,k,l$), using an ω scan rate of 32°/min^{-1} and a scan width of (1.21 + 0.30 tan θ)°. Data were corrected for Lorentz and polarization effects, and a Gaussian[8] correction was applied for absorption. Of the 9587 unique reflections measured, 3828 had $I > 3.0\sigma(I)$ and were considered observed. Cell constants were obtained as for **1** from 24 reflections in the range $25 < 2\theta < 50°$. Crystal dimensions (distance to face from vertex chosen as origin for absorption correction): 0.000 (001, 010, 100), 0.168 ($\bar{1}00$), 0.254 ($0\bar{1}0$), 0.336 ($00\bar{1}$) mm. The positions of the silver and bromine atoms were located from a Patterson map and those of the remaining atoms from subsequent difference Fourier maps. Full-matrix least-squares refinement as for **1** gave a final R = 0.043 (R_w = 0.044) for 541 parameters and 3828 reflections. Maximum and minimum residual electron densities were +0.50 and −0.69 e/Å^3, respectively.

For **3**, an ω scan rate of 32°/min^{-1} and a scan width of (1.47 + 0.30 tan θ)° were employed, a total of 4850 unique reflections being measured for $h,\pm k,\pm l$ and $3.5 < 2\theta < 50°$. Correction was made for Lorentz and polarization effects and a Gaussian[8] correction was applied for absorption; the number of observed reflections ($I > 3.0\sigma(I)$) was 3538. Cell constants were obtained as for **1** and **2** from 24 reflections in the range $44 < 2\theta < 50°$. Crystal dimensions (distance to face from vertex chosen as origin for absorption correction): 0.000 (010, 100, $\bar{1}03$), 0.522 ($0\bar{1}0$), 0.389 ($\bar{1}00$), 0.309 ($10\bar{3}$) mm. The structure was solved by direct methods. Refinement as for **1** and **2** yielded a final R = 0.060 (R_w = 0.068) for 271 parameters and 3538 reflections. The maximum and minimum peaks in the final difference maps were +2.10 and −1.87 e/Å^3, respectively, the highest peak being located in the vicinity of I(1). All calculations for **1**–**3** were carried out with the TEXSAN[9] program package.

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Table II. Final Positional Parameters for [K(crypt-2,2,2)][AgCl$_2$] (**1**)

Atom	*x*	*y*	*z*
Ag	0.24824 (3)	0.26261 (3)	0.72144 (4)
Cl(1)	0.1868 (1)	0.12563 (9)	0.6952 (1)
Cl(2)	0.3109 (1)	0.3984 (1)	0.7544 (1)
K(1)	0.5000	0.2051 (1)	0.2500
O(1)	0.3574 (2)	0.1102 (2)	0.3437 (3)
O(2)	0.3477 (3)	0.1381 (2)	0.1009 (3)
O(3)	0.4761 (2)	0.3594 (2)	0.3646 (3)
N(1)	0.4873 (3)	0.2046 (3)	0.5068 (4)
C(1)	0.4235 (4)	0.1366 (3)	0.5376 (4)
C(2)	0.3337 (4)	0.1307 (3)	0.4577 (4)
C(3)	0.2742 (4)	0.0954 (4)	0.2687 (5)
C(4)	0.3020 (4)	0.0693 (3)	0.1523 (5)
C(5)	0.3641 (4)	0.1193 (4)	−0.0147 (4)
C(6)	0.4173 (4)	0.1914 (4)	−0.0647 (4)
C(7)	0.5118 (4)	0.4337 (3)	0.3141 (4)
C(8)	0.4932 (4)	0.3635 (4)	0.4885 (5)
C(9)	0.4507 (4)	0.2869 (3)	0.5413 (5)
K(2)	0.0000	0.2861 (1)	0.2500
O(4)	−0.1691 (3)	0.3708 (2)	0.2851 (3)
O(5)	−0.1231 (3)	0.3484 (2)	0.0577 (3)
O(6)	−0.0480 (3)	0.1304 (2)	0.3513 (3)
N(2)	−0.0680 (3)	0.2885 (3)	0.4862 (4)
C(10)	−0.1397 (4)	0.3550 (4)	0.4902 (5)
C(11)	−0.2135 (4)	0.3549 (4)	0.3884 (5)
C(12)	−0.2369 (4)	0.3792 (4)	0.1887 (5)
C(13)	−0.1889 (4)	0.4105 (4)	0.0882 (5)
C(14)	−0.0749 (4)	0.3769 (4)	−0.0375 (5)
C(15)	−0.0118 (5)	0.3071 (4)	−0.0728 (5)
C(16)	0.0009 (4)	0.0582 (4)	0.3134 (6)
C(17)	−0.0490 (4)	0.1306 (4)	0.4740 (6)
C(18)	−0.1072 (4)	0.2043 (5)	0.5090 (5)

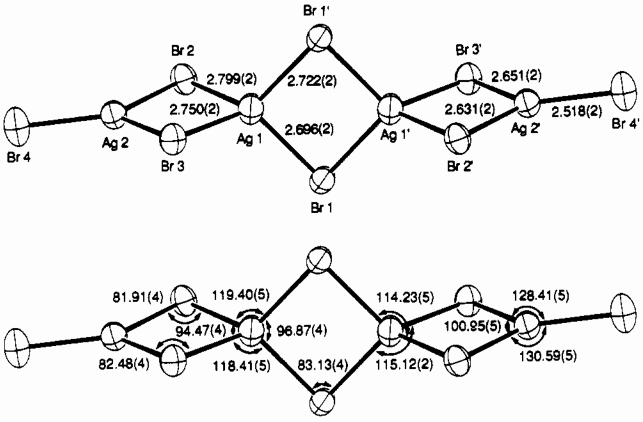

Figure 2. The [Ag$_4$Br$_8$]$^{4-}$ ion in [K(crypt-2,2,2)]$_4$[Ag$_4$Br$_8$]. Distances given are in Å, angles in deg. Thermal ellipsoids enclose 50% probability. A primed atom is related to an unprimed by the symmetry operation $-x$, $-y$, $1 - z$.

Atomic scattering factors and anomalous dispersion correction factors were taken from ref 10. Structural illustrations have been drawn with ORTEP.[11]

Results and Discussion

Final positional parameters for the three compounds are listed in Tables II–IV. The [AgCl$_2$]$^-$ ion determined in **1** is almost linear (Figure 1), the Cl–Ag–Cl angle being 178.03 (6)° and the Ag–Cl(1) and Ag–Cl(2) distances being 2.330 (2) and 2.328 (2) Å, respectively, making the molecular symmetry C_{2v}. It is interesting that the Ag–Cl bond distances are longer than the corresponding distances in the dichloroaurate(I) anion, e.g. 2.281 (5) and 2.282 (5) Å.[12] The [AgCl$_2$]$^-$ ion is well separated from the cation and there are no K$^+$···Cl contacts of <4 Å. Cs$_2$AgAuCl$_6$ has been reported to contain monomeric [AgCl$_2$]$^-$.[13] This structure is, however, best described as a distorted close-packed array of cesium and chloride ions in which alternate octahedral interstices are occupied by silver(I) and gold(III) ions, the interpretation of the structure as containing monomeric dichloroargentate(I) ions having been disputed in a recent study.[14]

Table III. Positional Parameters for [K(crypt-2,2,2)]$_4$[Ag$_4$Br$_8$] (**2**)

Atom	*x*	*y*	*z*
Ag(1)	0.10102 (6)	0.03469 (4)	0.53505 (7)
Ag(2)	0.30206 (6)	0.10193 (4)	0.61720 (7)
Br(1)	0.01292 (7)	−0.01387 (5)	0.64596 (8)
Br(2)	0.26725 (7)	−0.00442 (5)	0.57502 (9)
Br(3)	0.14759 (7)	0.14514 (5)	0.57103 (9)
Br(4)	0.44190 (8)	0.15090 (5)	0.6886 (1)
K(1)	0.3011 (1)	0.0772 (1)	0.1155 (2)
K(2)	0.8053 (2)	0.2370 (1)	0.1379 (2)
O(1)	0.1795 (5)	0.0690 (4)	0.2151 (6)
O(2)	0.1668 (5)	0.0000 (3)	0.0417 (7)
O(3)	0.1458 (5)	0.0016 (3)	0.0715 (6)
O(4)	0.4312 (4)	0.0312 (3)	0.2727 (5)
O(5)	0.2595 (5)	0.1499 (3)	−0.0507 (6)
O(6)	0.3274 (5)	0.1913 (3)	0.1450 (6)
O(7)	0.7263 (6)	0.1826 (3)	−0.0437 (6)
O(8)	0.6938 (5)	0.1885 (3)	0.2385 (6)
O(9)	0.8682 (6)	0.1692 (4)	0.2993 (6)
O(10)	0.7278 (7)	0.3414 (3)	0.0865 (6)
O(11)	0.9050 (6)	0.1951 (3)	0.0213 (7)
O(12)	0.9005 (6)	0.3365 (4)	0.2035 (6)
N(1)	0.2615 (6)	0.0296 (4)	−0.0924 (6)
N(2)	0.3379 (5)	0.1228 (4)	0.3216 (6)
N(3)	0.9915 (6)	0.2295 (5)	0.2280 (9)
N(4)	0.6161 (6)	0.2433 (4)	0.0477 (8)
C(1)	0.2047 (8)	0.0756 (5)	0.3207 (9)
C(2)	0.2577 (8)	0.1267 (5)	0.3456 (8)
C(3)	0.1305 (7)	−0.0011 (5)	−0.064 (1)
C(4)	0.1981 (8)	−0.0150 (5)	−0.1079 (8)
C(5)	0.3417 (9)	0.0081 (5)	−0.102 (1)
C(6)	0.3873 (7)	−0.0289 (5)	−0.019 (1)
C(7)	0.4508 (8)	−0.0331 (5)	0.154 (1)
C(8)	0.4938 (8)	0.0014 (5)	0.243 (1)
C(9)	0.2309 (9)	0.0751 (6)	−0.1659 (8)
C(10)	0.2739 (9)	0.1303 (6)	−0.139 (1)
C(11)	0.295 (1)	0.2054 (6)	−0.028 (1)
C(12)	0.282 (1)	0.2248 (5)	0.062 (1)
C(13)	0.3256 (8)	0.2164 (5)	0.235 (1)
C(14)	0.3738 (7)	0.1793 (5)	0.3193 (9)
C(15)	0.4673 (8)	0.0644 (6)	0.3582 (9)
C(16)	0.3977 (8)	0.0873 (5)	0.3959 (8)
C(17)	0.134 (1)	0.0162 (7)	0.189 (1)
C(18)	0.104 (1)	0.0071 (7)	0.090 (1)
C(19)	0.731 (1)	0.1391 (6)	0.289 (1)
C(20)	0.814 (1)	0.1491 (6)	0.353 (1)
C(21)	0.952 (1)	0.1785 (6)	0.361 (1)
C(22)	1.0114 (9)	0.1825 (7)	0.299 (1)
C(23)	0.775 (1)	0.3884 (5)	0.135 (1)
C(24)	0.865 (1)	0.3833 (6)	0.140 (1)
C(25)	1.0314 (8)	0.2192 (6)	0.149 (1)
C(26)	0.986 (1)	0.1762 (7)	0.074 (1)
C(27)	0.640 (1)	0.3456 (6)	0.078 (1)
C(28)	1.023 (1)	0.282 (1)	0.278 (1)
C(29)	0.5760 (9)	0.2306 (7)	0.123 (1)
C(30)	0.643 (1)	0.2010 (6)	−0.100 (1)
C(31)	0.5890 (9)	0.2029 (5)	−0.035 (1)
C(32)	0.608 (1)	0.1803 (7)	0.183 (1)
C(33)	0.780 (1)	0.1765 (6)	−0.106 (1)
C(34)	0.863 (1)	0.1540 (6)	−0.050 (1)
C(35)	0.593 (1)	0.2996 (6)	0.007 (1)
C(36)	0.988 (1)	0.3328 (8)	0.221 (2)

The [Ag$_4$Br$_8$]$^{4-}$ ion in **2** is comprised of two three-coordinated and two four-coordinated silver(I) centers and is very similar to the [Ag$_4$I$_8$]$^{4-}$ ion isolated previously with the tetraphenylphosphonium and tetraphenylarsonium cations.[7] A copper(I)

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Table IV. Positional Parameters for $[K(crypt\text{-}2,2,2)]_2[Ag_2I_4]$ (3)

Atom	*x*	*y*	*z*
Ag	0.43440 (8)	0.63322 (7)	0.49295 (9)
I(1)	0.36736 (7)	0.47087 (6)	0.61061 (8)
I(2)	0.31568 (6)	0.82087 (5)	0.45904 (8)
K(1)	0.1611 (1)	0.2647 (1)	0.1118 (2)
O(1)	0.2465 (5)	0.4522 (5)	0.0411 (6)
O(2)	0.0858 (6)	0.4771 (5)	0.2178 (6)
O(3)	0.1675 (5)	0.1572 (4)	0.3253 (5)
O(4)	0.3787 (5)	0.1716 (5)	0.2241 (6)
O(5)	0.1326 (5)	0.1168 (5)	−0.1528 (5)
O(6)	−0.0704 (5)	0.1887 (5)	−0.0335 (6)
N(1)	0.3624 (6)	0.2327 (6)	−0.0370 (7)
N(2)	−0.0453 (6)	0.2924 (6)	0.2508 (7)
C(1)	0.369 (1)	0.330 (1)	−0.093 (1)
C(2)	0.361 (1)	0.439 (1)	0.004 (1)
C(3)	0.241 (1)	0.5489 (8)	0.145 (1)
C(4)	0.119 (1)	0.5676 (7)	0.170 (1)
C(5)	−0.022 (1)	0.4954 (8)	0.269 (1)
C(6)	−0.0366 (9)	0.4057 (8)	0.340 (1)
C(7)	−0.0366 (9)	0.2108 (9)	0.332 (1)
C(8)	0.088 (1)	0.1981 (8)	0.415 (1)
C(9)	0.2866 (8)	0.1373 (7)	0.3969 (9)
C(10)	0.3641 (8)	0.0920 (7)	0.301 (1)
C(11)	0.4659 (8)	0.138 (1)	0.144 (1)
C(12)	0.4742 (8)	0.221 (1)	0.061 (1)
C(13)	0.3431 (9)	0.1316 (9)	−0.144 (1)
C(14)	0.218 (1)	0.1242 (8)	−0.2317 (9)
C(15)	0.0134 (8)	0.1165 (7)	−0.2298 (8)
C(16)	−0.0722 (8)	0.0981 (7)	−0.148 (1)
C(17)	−0.1617 (8)	0.1809 (9)	0.038 (1)
C(18)	−0.1588 (8)	0.2803 (9)	0.153 (1)

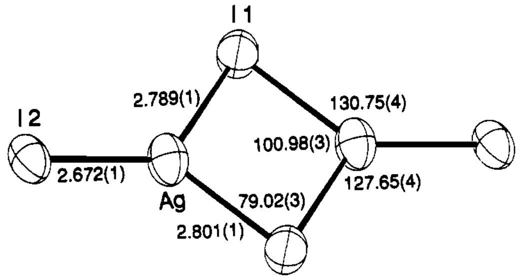

Figure 3. The $[Ag_2I_4]^{2-}$ ion in $[K(crypt\text{-}2,2,2)]_2[Ag_2I_4]$. The anion is centrosymmetric. Distances are in Å and angles in deg. The thermal ellipsoids enclose 50% probability.

analogue also exists.[15] Relevant bond distances and angles for the anion are given in Figure 2. Although there is considerable difference between the silver(I)–bromide distances associated with the trigonal and tetrahedrally coordinated silver(I) atoms, this is less pronounced than in the $[Ag_4I_8]^{4-}$ counterpart.[7] As in the $[Ag_2Br_4]^{2-}$ dimer,[6,7] the terminal Ag–Br bond is markedly shorter than the bridging Ag–Br bonds. The $Ag\text{–}Br_{terminal}$ distance (2.518 (2) Å) is slightly longer than the terminal bonds determined for $[Ag_2Br_4]^{2-}$ (2.491 (1) and 2.481 (1) Å),[6,7] but considerably longer than those for two-coordinated silver(I) in $[AgBr_2]^-$ (2.450 (4) Å).[4] The bridging distances associated with the trigonal center are very similar (2.631 (2) and 2.651 (2) Å), which is quite different from the situation in the $[Ag_2Br_4]^{2-}$ dimers where the corresponding distances differ by approximately 0.13 Å from each other.[6,7] The Ag···Ag separations are 3.562 (1) Å [Ag(1)···Ag(2)] and 3.595 (2) Å [Ag(1)···Ag(1′)], respectively (for the symmetry code see Figure 2).

Distances and angles within the $[Ag_2I_4]^{2-}$ ion in 3 are given in Figure 3. The anion is similar to the $[Ag_2Br_4]^{2-}$ and the $[Ag_2Cl_4]^{2-}$ ions mentioned earlier,[6,7] viz., a centrosymmetric, approximately planar, dimer. Silver(I) is displaced 0.123 Å from the plane formed by the ligands, and the Ag···Ag separation is 3.557(2) Å. It is noteworthy that in going from Cl to I as ligand, the difference between the two $Ag\text{–}X_{bridging}$ bonds gradually decreases from approximately 0.36 Å for Cl and 0.13 Å for Br down to 0.012 Å for I. The largest Ag–Cl distance in $[AsPh_4]_2[Ag_2Cl_4]$, 2.809 (2) Å,[7] is in fact slightly longer than the corresponding distance in $[Ag_2I_4]^{2-}$. The terminal Ag–I bond is appreciably shorter than the Ag–I bonds in the mononuclear trigonal $[AgI_3]^{2-}$ ion, viz., 2.742 (1), 2.746 (1), and 2.755 (1) Å.[5]

The $[K(crypt\text{-}2,2,2)]^+$ ion shows no abnormalities in any of the three compounds. The most interesting feature is that the potassium ions in **1** are situated on crystallographic 2-fold axes, giving the cation C_2 symmetry. This is also the situation in [K(crypt-2,2,2)]I.[16] In **1** and **2**, in which there are two crystallographically independent $K(crypt\text{-}2,2,2)^+$ ions, the K–N and K–O distances are slightly longer than in **3**, which may indicate the presence of weak long-range interactions between cation and anion in the former compounds.

Anionic configurations in halogenoargentates(I) appear to be dependent on the nature of the cation such that there is a trend toward a lower metal coordination number with increasing size of the cation.[2] This has been demonstrated, e.g., by comparison between the resulting anionic configurations in a series of halogenoargentates(I) crystallizing with symmetrically substituted quaternary ammonium and phosphonium cations.[7] While rather small cations like NMe_4^+ and NEt_4^+ produce infinite chain structures composed of edge-sharing Ag–X tetrahedra,[17-21] larger and more bulky cations such as PPh_4^+ and $AsPh_4^+$ promote the formation of discrete anions in which the coordination number of silver(I) is 3 or, in some cases, a mixture of 3 and 4.[6,7] An even stronger correlation between cation size and metal coordination number has been found for halogenocomplexes of copper(I).[2] In a series of halogenocuprates(I) crystallized as tetraalkylammonium and phosphonium salts, in which the size of the cation was gradually increased by adding carbon atoms to the alkyl chain, it was possible to produce halogenocuprates(I) in which the coordination number of copper(I) decreased from 4 to 2.[22] It has been suggested that cation–halide packing is the primary process at the solution–crystal interface, copper(I) then diffusing into available interstices, with subsequent rearrangement resulting in the specific anion with the appropriate copper(I) coordination number, such a mechanism implying a rapid ligand-exchange rate for copper(I) in solution.[23] Previous results on halogenoargentates(I) crystallizing with large, bulky, unipositive cations suggest that a similar mechanism might also be applicable to the formation of halogenoargentates(I)[7] and, consequently, that it ought to be possible to isolate mononuclear dihalogenoargentate(I) anions by using large unipositive cations of spherical type.

The present results appear to support this hypothesis. By employment of $[K(crypt\text{-}2,2,2)]^+$ as the cation, a discrete monomeric dichloroargentate(I) anion has been isolated, while an iodoargentate(I) consisting of solely three-coordinated silver(I) has been prepared. The only discrepancy is the bromoargentate(I), which, according to previously observed trends,[6,7,21] might have been expected to adopt a configuration more closely resembling that of the chloroargentate(I), with a silver(I) coordination number of 2.

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Supplementary Material Available: Tables S1–S9, listing positional parameters for the hydrogen atoms, anisotropic thermal parameters, and distances and angles within the cations (26 pages); listings of calculated and observed structure factors (127 pages). Ordering information is given on any current masthead page.

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