The Sr atoms are located near the mirror plane *c* at $y \simeq \pm 0{\cdot}25$. Each cation is surrounded by four O atoms and four water molecules with Sr—O distances ranging from 2·539 to 2·655 Å. The SrO_8 polyhedra are distorted dodecahedra isolated from one another by P_4O_{12} rings. The shortest Sr—Sr distance is 6·5878 (6) Å. Each dodecahedron alternates with a P_4O_{12} ring *via* two common oxygen atoms so as to form arrays along the 2_1 axis parallel to **a** (Fig. 1).

The four water molecules O(*W*1), O(*W*2), O(*W*3) and O(*W*5) which participate in the Sr coordination are located in planes perpendicular to the ring planes at $x \simeq 0$ and $x \simeq 0{\cdot}5$, while the remaining water molecule O(*W*4) lies between the P_4O_{12}—SrO_8 arrays (Figs. 1 and 2).

Hydrogen bonds link together all the inorganic arrays and the organic groups. They form a three-dimensional network, the geometrical features of which are described in Table 2.

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Structure of Guanidinium Tris(oxalato)chromate(III) Monohydrate

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Abstract. $[C(NH_2)_3]_3[Cr(C_2O_4)_3].H_2O$, $M_r = 514{\cdot}3$, monoclinic, $P2_1/n$, $a = 11{\cdot}256\ (1)$, $b = 10{\cdot}831\ (1)$, $c = 16{\cdot}425\ (2)$ Å, $\beta = 91{\cdot}47\ (1)^\circ$, $V = 2001{\cdot}8\ (6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}707$, $D_m = 1{\cdot}69\ (1)$ Mg m^{-3} (by flotation), $\lambda(\text{Mo }K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}638$ mm^{-1}, $F(000) = 1048$, $T = 293\ (1)$ K, $R = 0{\cdot}040$ for 2539 observed reflections. The Cr atom is six-coordinated by O atoms from three slightly nonplanar oxalate groups in an octahedral configuration. The average Cr—O bond distance is 1·972 (5) Å. The coordination octahedra, guanidinium cations and one water molecule are interconnected by a net of hydrogen bonds.

Introduction. The first crystal structures of chromium(III) oxalate complexes with potassium and ammonium cations were studied by X-ray diffraction (van Niekerk & Schoening, 1952*a*,*b*). Owing to the moderate accuracy of the bond distances and the questionable water content the two structures were redetermined (Taylor, 1978; Merrachi, Mentzen & Chassagneux, 1986). Reinvestigation of ammonium tris(oxalato)chromate(III) trihydrate confirmed the presence of three water molecules as well as the expected isostructurality with ammonium tris(oxalato)gallate(III) trihydrate (Bulc, Golič & Šiftar, 1984).

X-ray structure determinations were also carried out on the chromium(III) complexes with monovalent cations (Bulc, Golič & Šiftar, 1982, 1985). In order to establish the influence of cations on the conformations and water content of the complexes, guanidinium tris(oxalato)chromate(III) monohydrate was prepared and its crystal structure determined.

Experimental. Dark violet crystals of the title compound were grown from an aqueous solution of chromium(III) oxalate and guanidinium oxalate (1:3). Crystal size 0·21 × 0·31 × 0·34 mm; Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo *Kα* radiation. Cell parameters by least-squares refinement of 90 reflections within $9 < \theta < 16^\circ$; intensity measurement by ω–2θ scan, ω-scan width (°) $= 0{\cdot}7 + 0{\cdot}3\tan\theta$, aperture (mm) $= 2{\cdot}4 + 0{\cdot}9\tan\theta$, max. scan time 40 s, $2\theta_{\max} = 56^\circ$, $\frac{1}{4}$ sphere measured, with equality test $(\pm h, +k, -l)$, $[(\sin\theta)/\lambda]_{\max} = 0{\cdot}66$ Å^{-1}, standard reflections $32\bar{7}$, $2,0,\overline{10}$, 530; remeasured every 216 reflections, 4805 unique reflections measured (h −14/14, k 0/14, l −21/0), 2539 observed $[I > 3\sigma(I)]$, no absorption correction applied. Patterson and Fourier methods, two-block-matrix least-squares refinement, anisotropic for all non-hydrogen atoms,

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Table 1. *Final fractional coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors*, U_{eq} ($Å^2 \times 10^3$)

	x	y	z	U_{eq}
Cr	2126·3 (5)	255·9 (6)	2252·0 (3)	27·2 (2)
O(1)	−321 (3)	2815 (3)	2450 (3)	49 (2)
O(2)	1144 (2)	1513 (3)	2794 (2)	36 (1)
O(3)	471 (2)	2723 (3)	859 (2)	41 (1)
O(4)	1757 (2)	1294 (3)	1293 (1)	33 (1)
C(1)	540 (3)	2172 (4)	2289 (2)	33 (2)
C(2)	943 (3)	2099 (4)	1396 (2)	31 (2)
O(5)	−734 (2)	−1475 (3)	2875 (2)	46 (2)
O(6)	649 (2)	−698 (3)	2081 (1)	33 (1)
O(7)	1065 (3)	−1830 (4)	4052 (2)	50 (2)
O(8)	2242 (2)	−749 (3)	3248 (2)	38 (1)
C(3)	284 (3)	−1168 (4)	2750 (2)	32 (2)
C(4)	1266 (3)	−1278 (4)	3423 (2)	33 (2)
O(9)	5602 (2)	762 (3)	2170 (2)	45 (2)
O(10)	3699 (2)	995 (3)	2490 (2)	36 (1)
O(11)	4771 (2)	−752 (3)	892 (2)	43 (1)
O(12)	3060 (2)	−806 (3)	1536 (2)	33 (1)
C(5)	4553 (3)	520 (4)	2074 (2)	33 (2)
C(6)	4128 (3)	−424 (4)	1431 (2)	32 (2)
N(1)	6254 (3)	2262 (4)	393 (2)	48 (2)
N(2)	7806 (3)	3096 (4)	1116 (2)	48 (2)
N(3)	8087 (3)	2296 (5)	−160 (3)	60 (2)
C(7)	7386 (3)	2556 (4)	451 (3)	37 (2)
N(4)	7867 (3)	4181 (4)	4747 (2)	43 (2)
N(5)	7293 (3)	4616 (4)	3434 (2)	47 (2)
N(6)	5930 (3)	3886 (4)	4325 (2)	50 (2)
C(8)	7034 (3)	4224 (4)	4172 (2)	34 (2)
N(7)	7665 (4)	1368 (4)	3212 (2)	52 (2)
N(8)	9173 (3)	1425 (4)	4174 (2)	50 (2)
N(9)	7269 (3)	1025 (4)	4559 (2)	52 (2)
C(9)	8024 (4)	1286 (4)	3984 (3)	40 (2)
O(13)	4759 (3)	571 (4)	4121 (2)	59 (2)

final $R = 0{\cdot}040$ and $wR = 0{\cdot}058$; all hydrogen atoms from ΔF map and included in structure factor calculation. Empirical weighting function, $w = W_F \times W_S$, where $W_F(|F_o| < 10{\cdot}00) = |F_o|/10{\cdot}00$, $W_F(|F_o| > 14{\cdot}00) = 14{\cdot}00/|F_o|$, $W_F(10{\cdot}00 < |F_o| < 14{\cdot}00) = 1{\cdot}0$ and $W_S(\sin\theta < 0{\cdot}37) = \sin\theta/0{\cdot}37$, $W_S(\sin\theta > 0{\cdot}41) = (0{\cdot}41/\sin\theta)^2$, $W_S(0{\cdot}37 < \sin\theta < 0{\cdot}41) = 1{\cdot}0$, applied to keep $\sum w(\Delta F)^2$ uniform over ranges of $(\sin\theta)/\lambda$ and $|F_o|$; $(\Delta/\sigma)_{\max} = 0{\cdot}52$ (scale factor), $(\Delta/\sigma)_{\text{av}} = 0{\cdot}014$, $m/n = 13{\cdot}05$, $S = 1{\cdot}05$, largest peak in final ΔF map $0{\cdot}44$ e $Å^{-3}$, atomic scattering and dispersion factors for neutral Cr, O, N and C from Cromer & Mann (1968), Cromer & Liberman (1970) and for H atoms from Stewart, Davidson & Simpson (1965); DEC-10 computer at RCU Ljubljana, *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

Discussion. The final fractional coordinates with U_{eq} (Hamilton, 1959) for non-hydrogen atoms are listed in Table 1.* Relevant bond lengths and angles are listed in Table 2. Fig. 1 is an *ORTEP* (Johnson, 1965) stereo drawing with the numbering scheme of the asymmetric unit and Fig. 2 shows the unit-cell contents. A comparison of all specific parameters for chromium(III) complexes is presented in Table 3.

Table 2. *Interatomic distances* (Å) *and angles* (°)

(*a*) Coordination octahedra			
Cr—O(1)	1·980 (3)	O(1)—Cr—O(3)	81·9 (1)
Cr—O(3)	1·971 (3)	O(1)—Cr—O(5)	86·9 (1)
Cr—O(5)	1·972 (3)	O(1)—Cr—O(7)	91·9 (1)
Cr—O(7)	1·967 (3)	O(1)—Cr—O(9)	98·1 (1)
Cr—O(9)	1·973 (3)	O(3)—Cr—O(5)	91·4 (1)
Cr—O(11)	1·968 (3)	O(3)—Cr—O(9)	95·5 (1)
		O(3)—Cr—O(11)	87·8 (1)
		O(5)—Cr—O(7)	82·3 (1)
		O(5)—Cr—O(11)	94·0 (1)
		O(7)—Cr—O(9)	91·1 (1)
		O(7)—Cr—O(11)	98·5 (1)
		O(9)—Cr—O(11)	82·3 (1)
Oxalate ligands			
Ligand 1			
C(1)—C(2)	1·548 (5)	O(1)—C(1)—C(2)	115·0 (3)
C(1)—O(1)	1·278 (5)	O(2)—C(1)—C(2)	119·1 (3)
C(1)—O(2)	1·227 (5)	O(1)—C(1)—O(2)	125·9 (3)
C(2)—O(3)	1·279 (5)	C(1)—C(2)—O(3)	112·9 (3)
C(2)—O(4)	1·222 (5)	C(1)—C(2)—O(4)	121·5 (3)
		O(3)—C(2)—O(4)	125·5 (3)
Ligand 2			
C(3)—C(4)	1·549 (5)	O(5)—C(3)—C(4)	113·7 (3)
C(3)—O(5)	1·288 (4)	O(6)—C(3)—C(4)	121·1 (3)
C(3)—O(6)	1·216 (5)	O(5)—C(3)—O(6)	125·2 (3)
C(4)—O(7)	1·278 (5)	C(3)—C(4)—O(7)	114·0 (3)
C(4)—O(8)	1·219 (5)	C(3)—C(4)—O(8)	119·8 (3)
		O(7)—C(4)—O(8)	126·1 (3)
Ligand 3			
C(5)—C(6)	1·538 (5)	O(9)—C(5)—C(6)	113·8 (3)
C(5)—O(9)	1·299 (4)	O(10)—C(5)—C(6)	121·0 (3)
C(5)—O(10)	1·216 (4)	O(9)—C(5)—O(10)	125·2 (4)
C(6)—O(11)	1·287 (4)	C(5)—C(6)—O(11)	113·3 (3)
C(6)—O(12)	1·211 (5)	C(5)—C(6)—O(12)	121·1 (3)
		O(11)—C(6)—O(12)	125·6 (4)
Guanidinium cations			
(I)			
C(7)—N(1)	1·315 (5)	N(1)—C(7)—N(2)	119·6 (4)
C(7)—N(2)	1·315 (6)	N(1)—C(7)—N(3)	119·3 (4)
C(7)—N(3)	1·323 (6)	N(2)—C(7)—N(3)	121·1 (4)
(II)			
C(8)—N(4)	1·314 (5)	N(4)—C(8)—N(5)	119·9 (4)
C(8)—N(5)	1·324 (5)	N(4)—C(8)—N(6)	120·7 (4)
C(8)—N(6)	1·326 (5)	N(5)—C(8)—N(6)	119·4 (3)
(III)			
C(9)—N(7)	1·324 (6)	N(7)—C(9)—N(8)	119·2 (4)
C(9)—N(8)	1·331 (6)	N(7)—C(9)—N(9)	121·0 (4)
C(9)—N(9)	1·317 (6)	N(8)—C(9)—N(9)	119·8 (4)
(*b*) Hydrogen bonds			
N—H···O			
N(1)—O(7)	2·955 (5)	N(5)—O(5)	2·984 (5)
N(1)—O(11)	2·888 (5)	N(5)—O(9)	2·874 (5)
N(2)—O(1)	3·018 (5)	N(6)—O(3)	3·117 (5)
N(2)—O(3)	3·067 (5)	N(6)—O(6)	2·912 (4)
N(2)—O(5)	2·933 (5)	N(7)—O(1)	3·051 (5)
N(3)—O(3)	3·160 (5)	N(7)—O(9)	2·924 (5)
N(3)—O(12)	3·040 (5)	N(8)—O(7)	2·965 (5)
N(4)—O(11)	2·883 (4)	N(9)—O(7)	3·043 (5)
N(4)—O(4)	2·905 (4)	N(9)—O(13)	2·940 (5)
O—H···O			
O(13)—O(10)	2·940 (4)		

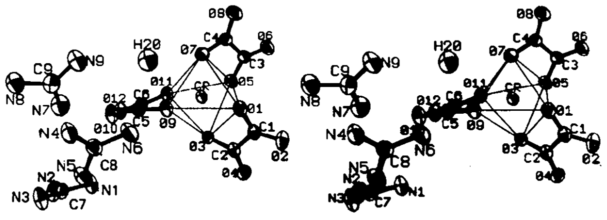

Fig. 1. *ORTEP* stereo drawing with the numbering of the asymmetric unit.

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51172 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Crystal data and dimensions of related compounds* $|A = \mathrm{Cr(C_2O_4)_3}|$

	$\mathrm{Na_3}A.\mathrm{5H_2O}$	$\mathrm{K_3}A.\mathrm{3H_2O}$	$\mathrm{Rb_3}A.\mathrm{3H_2O}$	$\mathrm{(NH_4)_3}A.\mathrm{3H_2O}$	$\mathrm{[N(CH_3)_4]_3}A.\mathrm{H_2O}$	$\mathrm{[C(NH_2)_3]_3}A.\mathrm{H_2O}$
Space group	$C2/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
Z	8	4	4	2	2	4
a (Å)	17·325 (1)	7·714 (1)	7·81	7·857 (1)	9·055 (2)	11·256 (1)
b (Å)	12·559 (1)	19·687 (4)	19·60	10·667 (2)	11·438 (7)	10·831 (1)
c (Å)	15·197 (2)	10·361 (3)	10·40	10·694 (2)	14·281 (4)	16·425 (2)
α (°)				83·27 (1)	100·51 (5)	
β (°)	100·39 (1)	108·06 (3)	108·0	70·06 (1)	96·14 (4)	91·47 (1)
γ (°)				70·54 (1)	96·97 (3)	
⟨Cr–O⟩ (Å)	1·972 (8)	1·969 (13)*		1·971 (6)	1·964 (3)	1·972 (5)
O–Cr–O (°) (range)	82·3 (1)– 95·8 (1)	81·8 (1)– 98·9 (1)		82·0 (2)– 95·2 (2)	82·2 (1)– 94·0 (1)	81·9 (1)– 98·5 (1)
⟨C–O$_{\mathrm{inner}}$⟩ (Å)	1·286 (5)	1·284 (6)		1·280 (8)	1·281 (6)	1·285 (8)
⟨C–O$_{\mathrm{outer}}$⟩ (Å)	1·220 (4)	1·223 (5)		1·220 (5)	1·218 (7)	1·219 (6)
⟨C–C⟩ (Å)	1·548 (8)	1·538 (16)		1·543 (9)	1·539 (3)	1·545 (6)
⟨O–C–O⟩ (°)	126·0 (6)	125·4 (3)		125·6 (7)	125·3 (3)	125·6 (3)
⟨O$_{\mathrm{inner}}$–C–C⟩ (°)	114·1 (3)	114·1 (3)		114·0 (5)	114·1 (4)	113·8 (7)
⟨O$_{\mathrm{outer}}$–C–C⟩ (°)	120·0 (5)	120·5 (4)		120·4 (5)	120·6 (5)	120·6 (9)
Torsion angles along C–C (°)	9·7 (4)	7·4 (4)		8·6 (6)	0·7 (6)	6·1 (4)
	3·4 (4)	7·9 (4)		0·4 (7)	1·4 (6)	8·3 (5)
	4·4 (4)	10·1 (4)		5·8 (7)	4·7 (7)	15·6 (5)

* Isostructural.

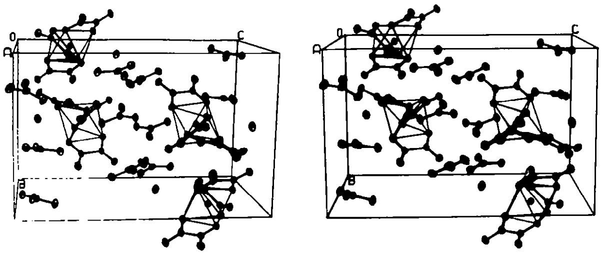

Fig. 2. Unit cell of $\mathrm{[C(NH_2)_3]_3[Cr(C_2O_4)_3].H_2O}$.

The Cr atom is coordinated by six O atoms from three oxalate groups in an octahedral configuration. The Cr—O bond distances are in the range 1·967 (3) to 1·980 (3) Å. A slight distortion of the octahedron is seen from the values of the O—Cr—O bond angles, from 81·9 (1) to 98·5 (1)°.

The three bidentate oxalate ligands are in general positions. The average bond lengths and bond angles are in the expected range for oxalate complexes. The ligands are slightly nonplanar. The maximum deviation of O atoms from the least-squares plane is 0·16 Å. The torsion angles along the C—C bond with the inner O atoms are 6·1 (4), 8·3 (5) and 15·6 (5)° (Stanford & Waser, 1972).

The three independent guanidinium cations in general positions are connected with the coordination octahedra through a net of hydrogen bonds. The C—N bond distances in the range 1·314 (5) to 1·331 (6) Å and bond angles from 119·2 (4) to 121·1 (4)° correlate well with corresponding values in other guanidinium ions (Adams, 1978).

In the stoichiometric unit there is one water molecule; it is involved in a weak O(13)—H···O(10) hydrogen bond of 2·940 (4) Å with the coordination octahedron and in a normal-value O(13)···H—N(9) hydrogen bond of 2·940 (5) Å with the guanidinium cation (Table 2*b*).

All the compounds characterized by the solved crystal structures seem to be of ionic character. The water content varies according to the type and size of the cation. The Cr atom is always six coordinated by oxygens of oxalate ligands. The average Cr—O bond distance is 1·97 (1) Å. The distortion of the coordination octahedra is shown by the values of the O—Cr—O bond angles which range from 81·8 (1) to 98·9 (1)°.

The oxalate groups act as bidentate ligands. The C—C bond distances are in the range 1·536 (6) to 1·553 (8) Å, except in the potassium-cation complex where one of C—C distances is rather short, 1·519 (6) Å. The average C—O bond distance is 1·283 (3) Å for inner O atoms and 1·220 (2) Å for outer O atoms. The values of the bond angles are very similar. Deviation from planarity is not related to the size of the cations. The maximum torsion angle of 15·6 (5)° along the C—C bond with the inner O atoms occurs in guanidinium tris(oxalato)chromate(III) monohydrate.

The cations are located between coordination octahedra. The $\mathrm{NH_4^+}$ and $\mathrm{C(NH_2)_3^+}$ cations and coordination octahedra are connected *via* hydrogen bonds of the type N—H···O ranging from 2·874 (5) to 3·168 (9) Å. $\mathrm{[N(CH_3)_4]^+}$ cations have a nearest contact to the anion of 3·22 (3) Å.

The $\mathrm{NH_4^+}$ cations exhibit disorder in ammonium tris(oxalato)chromate(III) trihydrate. One out of three $\mathrm{NH_4^+}$ cations is spread over two locations.

In the $\mathrm{Na^+}$ compound two of the $\mathrm{Na^+}$ cations are on the twofold axes while two are in general positions. The average Na—O(oxalate) distance is 2·57 (20) Å.

In potassium tris(oxalato)chromate(III) trihydrate the potassium cation was somewhat unexpectedly found to have a disorder similar to the disposition of the $\mathrm{NH_4^+}$ cation. The average distance K—O(oxalate) of 2·76 (8) Å is, as expected, slightly longer than the Na—O distance.

The water molecules in all the complexes are hydrogen bonded between coordination octahedra and cations. With increasing ionic radius of cation, the water content decreases from five for $\mathrm{Na^+}$, three for $\mathrm{K^+}$,

Rb^+, NH_4^+ to one water molecule for the $[N(CH_3)_4]^+$ and $C(NH_2)_3^+$ cations. In the compound with ammonium and potassium cations disorder of one water molecule is present – as in ammonium tris(oxalato)gallate(III) trihydrate (Bulc, Golič & Šiftar, 1984).

There are no significant differences between the crystal structures of the complexes discussed, except for the disorder of the cations and water molecules. The disorder of the water molecules in the ammonium and potassium compounds could be expected, but the disorder of the monovalent cations in the abovementioned compounds is unusual.

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Structures of Catalytically Related Species Involving Copper(II) Halides. VI. Tetrakis(3-aminopyridinium) Decabromodicuprate(I)dicuprate(II)

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Abstract. $[C_5H_7N_2]_4[Cu_4Br_{10}]$, $M_r = 1433\cdot8$, triclinic, $P\bar{1}$, $a = 8\cdot389\ (5)$, $b = 9\cdot563\ (2)$, $c = 12\cdot015\ (3)$ Å, $\alpha = 98\cdot04\ (2)$, $\beta = 91\cdot61\ (4)$, $\gamma = 106\cdot18\ (4)^\circ$, $V = 914\cdot3\ (6)$ Å^3, $Z = 1$, $D_x = 2\cdot60$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot71069$ Å, $\mu = 131\cdot6$ cm^{-1}, $F(000) = 670$, $T = 293$ K, $R = 0\cdot0647$ for 2368 unique observed reflections with $F \geq 3\sigma(F)$. The title compound contains mixed-valence binuclear copper(I)/copper(II) bromide species weakly linked together into tetranuclear units. The Cu^{II} ion assumes a square pyramidal coordination (two Br^- and two amino ligands in the equatorial positions and a Br^- in the axial position). The Cu^I ion is disordered between two positions; one with trigonal coordination, the other with tetrahedral coordination. The Cu^I and Cu^{II} ions are bridged by one Br^- ion, while the two Cu^I ions are bridged by two Br^- ions.

Introduction. In the past several years in this laboratory, we have been investigating the structural and magnetic properties of substituted aminopyridinium salts of copper(II) halides. This has resulted in the synthesis of a large number of oligomeric and polymeric species including a variety of planar, bibridged $Cu_nX_{2n+2}^{2-}$ oligomers (Willett, Grigereit, Halvorson & Scott, 1987), infinite bibridged $(CuX_3^-)_n$ chains (Geiser, Gaura, Willett & West, 1987), as well as isolated CuX_4^{2-} anions (Place & Willett, 1988). Particularly with $X = Br^-$, and occasionally with $X = Cl^-$, the reaction process has led to the halogenation of the pyridine ring (Willett & West, 1987; Place & Willett, 1987). It has been surmised that this involves the reduction of copper(II) to copper(I) during the halogenation process and subsequent reoxidation by O_2. Indirect evidence for such a process can be inferred from the anaerobic recrystallization of $(R_4N)CuCl_3$ salts which have led to the isolation of several mixed-valence Cu^I/Cu^{II} species: a bibridged $(Cu_2Cl_4^-)_n$ chain in $(Et_4N)Cu_2Cl_4$ (Willett, 1987), and isolated $Cu_2Cl_6^{2-}$ and $CuCl_2^-$ anions in $(Bu_4N)_3Cu_3Cl_8$ (Willett, Geiser & Ramakrishna, 1988). In this paper we report the crystal structure of a new mixed-valence Cu^I/Cu^{II} bromide salt obtained in an investigation of the 3-aminopyridine/$CuBr_2$/HBr system. In dilute HBr solution, the system yields $(3\text{-aminopyridinium})_2Cu_2Br_6.H_2O$ (Blanchette &

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