et al., 1978) and [Ni(sal)$_2$trien].6H$_2$O (Cradwick *et al.*, 1972). All the complexes have the same configuration of the hexadentate ligand, with the terminal O atoms mutually *cis*. The deviation from perfect octahedral geometry for the CoN$_4$O$_2$ unit, maximum angular distortion 6·8°, is comparable to that of the related iron complexes, which show maximum deviations of 6·5 and 6·2°. The NiN$_4$O$_2$ unit exhibits a much greater deviation, 15·6°. The metal–ligand distances for the Co$^{\text{III}}$ complex are somewhat shorter than those of the Fe$^{\text{III}}$ compounds, where Fe is in the low-spin state; mean Fe—O 1·883, Fe—N(imine) 1·931 and Fe—N(amine) 2·003 Å. However, the metal–ligand distances in the Ni$^{\text{II}}$ complex are much longer: Ni—O 2·058, Ni—N(imine) 2·029, Ni—N(amine) 2·159 Å.

The C—N bond lengths and the bond angles around the N atoms can be divided into two distinct groups. Angles at N(1) and N(4) add up to 359·9 and 359·8°, respectively, close to 360°, as expected for trigonal planar, while those at N(2) and N(3) are typical for tetrahedral bonding, mean 109·1° for N(2) and 108·4° for N(3). Both imine N atoms exhibit large distortions from ideal values in the angles Co(1)—N(1)—C(9) and Co(1)—N(4)—C(14) which are 112·7 (4) and 112·0 (4)°, respectively. This can be attributed to the electronic repulsion of the C=N double bond and to the participation of these atoms in the five-membered chelate rings. The angles Co(1)—N(1)—C(7) and Co(1)—N(4)—C(15) are concomitantly large at 126·3 (4)°.

The F atoms of the hexafluorophosphate counter-ion are disordered between two sets of atomic positions. The site occupancies refined to 0·65 (1) and 0·34 (1), and were then fixed at these values during the final cycle of refinement. The P—F lengths of the major orientation average 1·580 Å, some 0·03 Å larger than has generally been found previously (Banbery & Hamor, 1988).

The acetone molecule forms a weak hydrogen bond with one of the amine N atoms: N(2)···O(1*A*) = 2·995 (8), H(2N)···O(1*A*) = 2·05 Å.

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Structures of the Antiferrodistortive Layer Perovskites Bis(phenethylammonium) Tetrahalocuprate(II), Halo = Cl$^-$, Br$^-$

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Abstract. Bis(phenethylammonium) tetrachlorocuprate(II), $2\text{C}_8\text{H}_{12}\text{N}^+.\text{CuCl}_4^{2-}$, $M_r = 449\cdot8$, orthorhombic, *Pcab*, $a = 7\cdot328\ (1)$, $b = 7\cdot295\ (1)$, $c = 38\cdot618\ (5)$ Å, $V = 2064\cdot7\ (6)$ Å^3, $Z = 4$, $D_x = 1\cdot47$ g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1\cdot54178$ Å, $\mu = 63\cdot6$ cm^{-1}, $F(000) = 924$, $T = 295$ K, final $R = 0\cdot068$ for 1198 observed unique reflections. Bis(phenethylammonium) tetrabromocuprate(II), $2\text{C}_8\text{H}_{12}\text{N}^+.\text{CuBr}_4^{2-}$, $M_r = 627\cdot5$, orthorhombic, *Pcab*, $a = 7\cdot654\ (4)$, $b = 7\cdot756\ (4)$, $c = 38\cdot042\ (18)$ Å, $V = 2258\ (1)$ Å^3, $Z = 4$, $D_x = 1\cdot85$ g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1\cdot54178$ Å, $\mu = 97\cdot5$ cm^{-1}, $F(000) = 1212$, $T = 295$ K, final $R = 0\cdot067$ for 1207 observed unique reflections. Both salts contain layers of corner-shared tetragonally elongated octahedra sandwiched between layers of the organic cations. Each copper(II) ion forms four short Cu—X ($X = \text{Cl}^-$, Br^-) bonds in a planar arrangement. Two longer, semi-coordinate Cu—X bonds

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Table 1. *X-ray data-collection parameters*

Compound	Bis(phenethylammonium) tetrachlorocuprate(II)	Bis(phenethylammonium) tetrabromocuprate(II)
Type of absorption correction	Empirical ψ scan	Empirical ψ scan (laminar)
transmission range	0·338–0·938	0·089–0·515
No. and θ range (°) of reflections for lattice parameters	25; 30–40	25; 30–40
Data-collection technique	ω scan	ω scan
Scan range (°)	0·8	0·80
Scan speeds (° min^{-1})	6–60	6–60
Check reflections monitored every 96 reflections	206, 028	040, 0,0,14
Total reflections	1579	2695
$2\theta_{max}$ (°)	110	110
Unique reflections	1289 with 1198 with $F > 3\sigma(F)$	1275 with 1207 with $F > 3\sigma(F)$
R for equivalent reflections		0·052
h,k,l range	$0 < h < 7$, $0 < k < 7$, $0 < l < 41$	$0 < h < 9$, $0 < k < 9$, $-40 < l < 40$
Structure-solution technique	Patterson	Patterson
R	0·0682 (0·0709 all data)	0·0669 (0·0689 all data)
wR	0·0917 (0·0937 all data)	0·0847 (0·0861 all data)
$w = 1/[\sigma^2(F) + g(F)^2]$; g	0·00313	0·001
Function minimized	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Goodness of fit	1·459	1·837
$\lvert\Delta/\sigma\rvert_{mean}$	0·000	0·007
$\lvert\Delta/\sigma\rvert_{max}$	0·002	0·028
Total parameters refined	107	107
Thermal parameters	Anisotropic on all non-H atoms, H atoms isotropic	Anisotropic on all non-H atoms, H atoms isotropic
Largest peak on final difference map (e $Å^{-3}$)	1·1 near Cu	1·1 near Br(1)
Most negative peak on final difference map (e $Å^{-3}$)	1·2	0·7
Extinction corrections	Yes	Yes

Table 2. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\times 10^3$)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}($Å^2$)
(*a*) $(PhC_2H_4NH_3)_2CuCl_4$				
Cu	0	0	0	27 (1)
Cl(1)	2239 (2)	2165 (2)	50 (1)	35 (1)
Cl(2)	109 (2)	277 (2)	−592 (1)	42 (1)
N	31 (5)	5113 (5)	551 (1)	40 (2)
C(1)	−404 (9)	4707 (8)	917 (2)	57 (2)
C(2)	871 (10)	5432 (11)	1161 (2)	82 (3)
C(3)	257 (10)	5170 (9)	1540 (2)	65 (3)
C(4)	964 (10)	3812 (12)	1738 (2)	81 (3)
C(5)	474 (11)	3667 (12)	2080 (2)	93 (3)
C(6)	−679 (14)	4835 (11)	2223 (2)	90 (3)
C(7)	−1470 (12)	6111 (14)	2029 (2)	101 (3)
C(8)	−995 (11)	6286 (13)	1685 (2)	96 (3)
(*b*) $(PhC_2H_4NH_3)_2CuBr_4$				
Br(1)	2264 (1)	2147 (1)	69 (1)	60 (1)
Br(2)	167 (1)	329 (1)	−640 (1)	68 (1)
Cu	0	0	0	51 (1)
N	124 (8)	5185 (11)	583 (3)	69 (3)
C(1)	−486 (14)	4631 (17)	939 (5)	114 (6)
C(2)	585 (19)	5376 (18)	1208 (4)	113 (6)
C(3)	−131 (17)	5079 (26)	1586 (5)	112 (7)
C(4)	−1364 (31)	6092 (33)	1690 (6)	196 (13)
C(5)	−2078 (31)	5840 (37)	2027 (9)	221 (16)
C(6)	−1414 (27)	4717 (33)	2235 (4)	152 (10)
C(7)	−196 (22)	3620 (31)	2100 (7)	153 (11)
C(8)	400 (19)	3749 (36)	1776 (5)	158 (11)

define the pseudo tetragonal axis for each copper ion. These lie in the plane of the layer, arranged in an antiferrodistortive manner. Hydrogen bonding between the RNH_3^+ moieties of the cations and the halide ions causes a puckering of the layers.

Introduction. As part of a continuing study of the properties of $(RNH_3)_2MX_4$ and $(NH_3RHN_3)MX_4$ salts (M = divalent metal ion, X = halide ion), an investigation of the electron paramagnetic resonance (EPR) behavior of the compounds $(PhC_nH_{2n}NH_3)_2CuX_4$ (n = 1,2,3) has been undertaken (Patyal, 1988; Patyal & Willett, 1990). The magnetic properties of the chloride salts have been reported (Dupas, Le Dang, Renard, Veillet, Daoud & Perret, 1976; Estes, Losee & Hatfield, 1980). These salts exhibit ferromagnetic coupling within the perovskite layers (J/k = 16·5, 19·0, and 16·3 K for n = 1, 2, and 3, respectively) with extremely weak, but likely, ferromagnetic interaction between layers. The corresponding bromide salts have not previously been investigated in detail, but preliminary data confirm similar behavior (Zhou, 1988; Zhou, Drumheller, Patyal & Willett, 1990). The EPR data of these $(PhC_nH_{2n}NH_3)_2CuX_4$ systems show numerous interesting features, including contributions to the line widths from magnetic spin anisotropies, two-dimensional spin diffusion, and magnetically inequivalent layers. For this reason, structural studies of these compounds were initiated. The results on the simplest of these crystallographically, the n = 2 salts, are reported in this paper.

Experimental. Crystals were grown by slow evaporation of acidic aqueous or alcoholic solutions containing stoichiometric ratios of the phenethylammonium halide and the copper(II) halide (Daoud, Thrierr-Sorel, Perret, Chaillot &

Table 3. *Selected interatomic lengths* (Å) *and angles* (°) *for the* $(PhC_2H_4NH_3)_2CuX_4$ *salts*

	X = Cl	X = Br		X = Cl	X = Br		X = Cl	X = Br
Cu—X(1)	2·286 (1)	2·418 (1)	C(1)—C(2)	1·43 (1)	1·43 (2)	C(5)—C(6)	1·32 (1)	1·28 (4)
Cu—X(2)	2·296 (1)	2·449 (1)	C(2)—C(3)	1·54 (1)	1·55 (2)	C(6)—C(7)	1·33 (1)	1·36 (3)
Cu—X(1a)	2·899 (1)	3·057 (1)	C(3)—C(4)	1·36 (1)	1·29 (3)	C(7)—C(8)	1·38 (1)	1·32 (3)
N—C(1)	1·48 (1)	1·50 (2)	C(4)—C(5)	1·37 (1)	1·41 (4)	C(8)—C(3)	1·35 (1)	1·32 (3)
X(1)—Cu—X(2)	89·9 (1)	89·9 (1)	C(2)—C(3)—C(4)	121·1 (6)	117 (2)	C(7)—C(8)—C(3)	121·8 (8)	118 (2)
X(2)—Cu—X(1a)	91·6 (1)	92·6 (1)	C(3)—C(4)—C(5)	120·1 (8)	119 (2)	C(8)—C(3)—C(4)	117·8 (8)	122 (2)
X(1)—Cu—X(1a)	89·9 (1)	89·0 (1)	C(4)—C(5)—C(6)	121·3 (8)	120 (2)	C(8)—C(3)—C(2)	121·2 (7)	121 (2)
N—C(1)—C(2)	114·5 (1)	111 (1)	C(5)—C(6)—C(7)	119·6 (7)	118 (2)	Cu—X(1)—Cu(a)	171·2 (1)	168·5 (1)
C(1)—C(2)—C(3)	112·9 (6)	114 (1)	C(6)—C(7)—C(8)	120·0 (8)	123 (2)			

The symbol a denotes an atom related by the a-glide operation.

Guerchais, 1975). The crystals grow as thin flat platelets which are extremely difficult to manipulate without destroying their suitability for diffraction experiments. It proved impossible to cut large crystals so as to obtain appropriate-sized samples for X-ray studies. A technique which finally proved to be successful involved immersing clusters of crystals in a liquid in which the crystals were only slightly soluble. The solvent properties of the liquid allowed the clusters to be broken apart into their individual component crystals. Gentle swirling of the solution then allowed the gradual dissolution of the crytals until they reached a suitable size. An ethanol/n-propanol mixture was used for the chloride salt while pure n-propanol was used for the corresponding bromide. X-ray diffraction data were collected on a Nicolet *R*3*m*/*E* diffractometer system with Cu $K\alpha$ radiation so as to provide adequate resolution of individual reflections. Details of the data-collection technique (Campana, Shepherd & Litchman, 1981) are given in Table 1. Structure solution and refinement were accomplished with the *SHELXTL* package (Sheldrick, 1985) operating on a Data General S/140 computer, with pertinent parameters also given in Table 1. Scattering factors, corrected for anomalous dispersion, were taken from *International Tables for X-ray Crystallography* (1974). The irregular shape of the crystals obtained *via* the dissolution process precluded the usuage of numerical absorption corrections. Final positional parameters for the two compounds are given in Table 2 with selected interatomic distances and angles given in Table 3.*

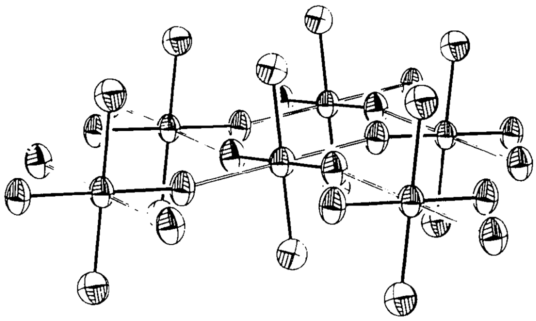

Fig. 1. Illustration of the layer structure in $(PhC_2H_4NH_3)_2CuBr_4$. The a axis is coming out of the plane of the illustration.

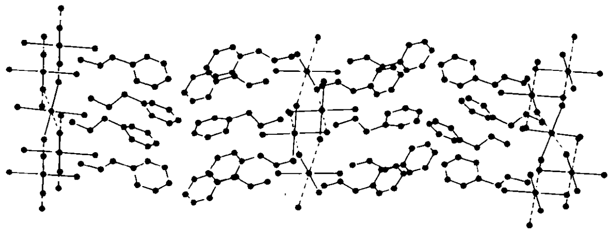

Fig. 2. Unit-cell packing diagram for $(PhC_2H_4NH_3)_2CuBr_4$. The a axis is vertical and the c axis is horizontal.

Discussion. Both compounds assume an antiferrodistortion version of the layer perovskite structure. The structure of the layers is shown in Fig. 1. The copper(II) ions assume an elongated 4 + 2 coordination geometry with four short Cu—X bonds in a plane (Cu—Cl_{av} = 2·291, Cu—Br_{av} = 2·434 Å) and two longer, semi-coordinate interactions (Cu···Cl = 2·900, Cu···Br = 3·057 Å). These longer bonds lie approximately parallel to the 110 and $1\bar{1}0$ directions, respectively, for the copper ions at the corners of the unit cell and centers of the ab face. The hydrogen-bonding interactions of the cations with the halide ions cause pleating of the layers parallel to the a axis, creating the typical washboard effect found in the $(RNH_3)_2MX_4$ layer perovskites. The bridging Cu—X···Cu angles are 171·2 and 168·5° for the Cl and Br salts, respectively. The hydrogen bonding in related $(NH_3RNH_3)CuX_4$ salts, has been discussed in detail recently for $(NH_3RNH_3)CuX_4$ salts (Garland, Emerson & Pressprich, 1990) and in the present cases appears to involve one hydrogen bond to a terminal halide ion and two to bridging halide ions. The

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52432 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

sandwiching of the perovskite layers between the organic cations is shown in Fig. 2. The plane of the phenyl ring in the cation is rotated approximately 90° to the plane of its aliphatic tail. Interdigitation of the phenyl groups between layers is not observed, in accord with the very delicate nature of the crystals.

The structural characteristics of the copper(II) halide layer perovskites have recently been reviewed (Willett, Place & Middleton, 1989). The non-conventional choice of the *Pcab* space group allows direct comparison with that summary. The $PhC_2H_4NH_3^+$ salts reported here are isostructural with $(EtNH_3)_2CuCl_4$ (Steadman & Willet, 1970) and $(PrNH_3)_2CuCl_4$ (Barendregt & Schenk, 1970). The stacking of layers is of the staggered arrangement, with copper ions located at the corners and face centers of the unit cell. The *Pcab* space group is derived from the parent *I4/mmm* structure of the undistorted tetragonal layer perovskites (Heger, Mullen & Knorr, 1975) *via* a descent of symmetry involving (1) the loss of the fourfold axis, (2) a rotation of the in-layer axes by 45°, doubling the unit-cell volume, and (3) a loss of the mirror operation in the plane of the layer. The layer group is $P2_1/a$, where the *a*-glide operation generates the pleated nature of the structure parallel to the *a* axis.

The Cu—*X* distances compare very favorably with those of the other salts in the layer perovskite series, where the Cu—Cl and Cu—Br distances average 2·291 and 2·439 Å, respectively. The semi-coordinate distances are among the shortest reported. It is expected theoretically, and demonstrated experimentally, that the value of the ferromagnetic interlayer coupling, *J*, should increase monotonically as the semi-coordinate Cu···*X* distances decrease (Willett *et al.*, 1989). The value of J/k = 19·0 K for the chloride salts for a Cu···Cl distance of 2·899 Å is in accord with several other salts where J/k = 19·0 ± 0·4 K for Cu···Cl values of 2·90 ± 0·03 Å. The only bromide salt with a similarly short semi-coordinate distance is $(NH_3C_2H_4NH_3)CuBr_4$ (Cu···Br = 3·034 Å), where J/k = 38·2 K.

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Dichlorobis(*N*,*N*-dimethylacetamide)oxovanadium(IV)

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Abstract. $[VCl_2O(C_4H_9NO)_2]$, M_r = 312·09, orthorhombic, $P2_12_12_1$, a = 8·635 (2), b = 12·237 (2), c = 13·683 (2) Å, V = 1445·8 Å^3, Z = 4, D_x = 1·43 g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 9·80 cm^{-1}, $F(000)$ = 644, T = 295 K, R = 0·043 for 1409 unique observed reflections [$F_o > 4\sigma(F_o)$]. The compound has a trigonal bipyramidal structure with the two chloro ligands and the vanadyl oxygen in the trigonal plane and the O atoms of the acetamide groups near the axis with O—V—O = 156·6°.

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