The crystal structure gives direct evidence for the existence of the Cu^{I} species in the substituted pyridine/$CuBr_2$/HBr system. Unfortunately, the isolated mixed-valence species did not contain a brominated pyridine-ring system. Hence, it is not possible to tie the existence of the Cu^{I} ion to the bromination process. Indeed, the Cu^{I} ion may be simply generated by an inorganic reaction involving the decomposition of $CuBr_2$ to CuBr and Br_2. Nevertheless, the crystallization of organoammonium halocuprate(II) salts under anaerobic conditions appears to be a general method leading to the formation of mixed-valence copper halide systems.

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Structures of Ethylenediammonium Tetrabromocuprate(II) and Propylenediammonium Tetrabromocuprate(II)

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Abstract. $[C_2H_{10}N_2][CuBr_4]$, $M_r = 445{\cdot}3$, monoclinic, $P2_1/a$, $a = 7{\cdot}511$ (1), $b = 7{\cdot}803$ (1), $c = 8{\cdot}334$ (2) Å, $\beta = 92{\cdot}12$ (2)°, $V = 488{\cdot}1$ (1) Å^3, $Z = 2$, $D_x = 3{\cdot}02$ g cm^{-3}, $F(000) = 410$, $\mu = 184{\cdot}0$ cm^{-1}, numerical absorption correction, $T = 293$ K, 1417 unique reflections with 1094 with $F > 3\sigma(F)$ refined to $R = 0{\cdot}0504$ ($wR = 0{\cdot}0392$). $[C_3H_{12}N_2][CuBr_4]$, $M_r = 459{\cdot}3$, monoclinic, $P2_1/n$, $a = 8{\cdot}086$ (2), $b = 7{\cdot}566$ (2), $c = 17{\cdot}622$ (5) Å, $\beta = 96{\cdot}75$ (2)°, $V = 1071$ (1) Å^3, $Z = 4$, $D_x = 2{\cdot}85$ g cm^{-3}, $F(000) = 852$, $\mu = 167{\cdot}6$ cm^{-1}, empirical absorption correction assuming laminar crystal shape, $T = 293$ K, 864 unique reflections with 654 with $F > 3\sigma(F)$ refined to $R = 0{\cdot}0359$ ($wR = 0{\cdot}0473$). Both structures consist of antiferrodistortive perovskite layers with corner-shared Jahn–Teller elongated $CuBr_6$ octahedra with adjacent layers linked by the diammonium cations. The short Cu—Br distances average 2·440 Å while the longer semi-coordinate distances are 3·034 and 3·148 Å respectively for the two salts. The ethylenediammonium cation is in an all-*trans* conformation while the propylene analog has one *trans* and one *gauche* segment for a *tg* conformation. The layers are in a partially eclipsed conformation, leading to short interlayer Br···Br contacts of 3·602 and 4·065 Å respectively. Correlations between the structural parameters and magnetic behavior are discussed.

Introduction. Compounds of the type A_2CuX_4, where A^+ = alkali metal ion or a monosubstituted ammonium ion and $X = Cl^-$ or Br^-, typically form antiferrodistortive versions of the two-dimensional layer perovskite family (Steadman & Willett, 1970; Barendregt & Schenk, 1970; Larsen, 1974; Willett, 1964). In these compounds, adjacent layers are staggered with respect to each other, *e.g.* Cu ions in one layer are aligned above (or below) the A^+ cations on adjacent layers. In this manner, essentially no superexchange coupling can occur between layers, and dipolar interactions essentially cancel, leading to the formation of nearly ideal two-dimensional magnetic systems (de Jongh & Miedema, 1974). With the replacement of two A^+ cations by a diammonium cation, $^+H_3NC_nH_{2n}NH_3^+$, adjacent layers are now eclipsed in the sense that the copper ions in adjacent layers lie nearly directly above each other (Phelps, Losee, Hatfield & Hodgson, 1976; Ferguson & Zaslow, 1971; Tichy, Benes, Hälg & Arend, 1978). This allows for magnetic interactions to

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Table 1. *X-ray data collection parameters*

	Ethylenediammonium tetrabromocuprate(II)	Propylenediammonium tetrabromocuprate(II)
Diffractometer system	Nicolet *R*3*m*/*E*	Upgraded Syntex $P2_1$
Systematic absences	*h* odd for *h*0*l* *k* odd for 0*k*0	*h* + *l* odd for *h*0*l* *k* odd for 0*k*0
Lattice constants	Based on 25 reflections in the range $26 < 2\theta < 37°$	Based on 25 reflections in the range $20 < 2\theta < 32.5°$
Crystal size (mm)	0·48 × 0·25 × 0·042	0·12 × 0·6 × 0·2
Type of absorption correction	Numerical	Laminar
Transmission range	0·110–0·442	0·346–0·913
Check reflections	$\bar{2}20$, $\bar{2}21$	040, 220
Total reflections	1653	1010
$(\sin\theta)/\lambda(\max)$ (Å^{-1})	0·703	0·538
Unique reflections	1417 with 1094 with $F > 3\sigma$	864 with 654 with $F > 3\sigma$
R for equivalent reflections	0·0218	0·0157
Structure solution package	Nicolet *SHELXTL* (Sheldrick, 1985)	Nicolet *SHELXTL* (Sheldrick, 1985)
Structure solution technique	Direct methods	Direct methods
R	0·0504	0·0359
wR	0·0392	0·0473
$w = 1/[\sigma^2(F) + g(F)^2]$	$g = 0.00011$	$g = 0.00246$
$\lvert\Delta/\sigma\rvert_{(mean)}$	0·001	0·013
$\lvert\Delta/\sigma\rvert_{(max)}$	0·004	0·045
Total parameters refined	44	69
Thermal parameters	Anisotropic on all non-hydrogen atoms	Anisotropic on Cu and Br atoms
H atoms	Constrained to C—H and N—H = 0·96 Å, thermal parameters fixed at 1·2 U_{eq} for the heavier atom	Constrained to C—H and N—H = 0·96 Å, thermal parameters fixed at 1·2 U_{eq} for the heavier atom
Largest peak on final difference map (e Å^{-3})	1·21 near Br(1)	0·64 near 0,0,0 special position
Extinction corrections	Yes	None
Goodness of fit	1·302	0·885

occur *via* Cu—*X*···*X*—Cu pathways which, for small *n*, may become quite significant. The effect is substantially larger for $X = Br^-$ than for $X = Cl^-$ since the interlayer distance is effectively fixed by the length of the C_nH_{2n} segment. However, the substantial increase in ionic radius leads to a larger overlap of electron density and thus to a stronger magnetic coupling (Snively, Seifert, Emerson & Drumheller, 1979; Snively, Tuthill & Drumheller, 1981; Block & Jansen, 1982; Rubenacker, Waplak, Hutton, Haines & Drumheller, 1985; Garland, Emerson & Pressprich, 1989). Since the structures of the first two members of the bromide series, $(NH_3C_2H_4NH_3)CuBr_4$ and $(NH_3C_3H_6NH_3)CuBr_4$, have not been determined, crystal structure analyses have been undertaken to determine the structural parameters associated with the Cu—Br···Br—Cu pathways, as well as details of the intralayer structure.

Experimental. Polycrystalline samples of $(C_2H_4N_2H_6)CuBr_4$ and $(C_3H_6N_2H_6)CuBr_4$ were prepared by partial evaporation of a 1:1 mixture of the appropriate diamine and $CuBr_2$ in dilute HBr solution. Single crystals for X-ray analysis were grown by a modified thermal gradient technique (Arend, Huber, Misckovsky & Van Leeuwen, 1978). The crystals, in general, tend to be badly twinned and exhibit large mosaic spreads. This is typical of the diammonium salts (Tichy *et al.*, 1978). After considerable searching however, satisfactory single crystals were obtained for the X-ray data collection.

Table 2. *Final positional parameters* (× 10^4) *and isotropic or equivalent isotropic thermal parameters* (× 10^3)

	x	*y*	*z*	U/U_{eq}(Å^2)
$(C_2H_4N_2H_6)CuBr_4$				
Cu	0	0	0	22 (1)†
Br(1)	2664 (1)	−2905 (1)	403 (1)	30 (1)†
Br(2)	284 (1)	435 (1)	2903 (1)	31 (1)†
N	5022 (8)	−246 (7)	7258 (7)	32 (2)†
C	4545 (11)	483 (10)	5639 (8)	36 (3)†
$(C_3H_6N_2H_6)CuBr_4$				
Cu(1)	0	0	0	36 (3)†
Br(1)	−2068 (3)	2241 (4)	215 (2)	39 (2)†
Br(2)	835 (3)	−186 (4)	1374 (2)	42 (2)†
Cu(2)	−5000	5000	0	35 (3)†
Br(3)	−7155 (3)	2749 (4)	−191 (2)	37 (2)†
Br(4)	−4863 (4)	5147 (4)	−1380 (2)	43 (2)†
N(1)*	−7 (2)	507 (3)	378 (1)	34 (7)
C(2)*	−117 (3)	467 (4)	309 (2)	49 (10)
C(3)*	−71 (5)	550 (6)	235 (2)	127 (16)
C(4)*	54 (6)	477 (6)	202 (3)	155 (20)
N(5)*	60 (3)	504 (3)	121 (2)	54 (8)

* Parameters listed are multiplied by 10^3.

† Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Data collection (Campana, Shepherd & Litchman, 1981) with either a Nicolet *R*3*m*/*E* diffractometer or a Syntex $P2_1$ diffractometer upgraded to Nicolet *P*3*F* specifications. Mo $K\alpha$ radiation. $\lambda = 0.71069$ Å. Graphite monochromator. Data collection details given in Table 1. Structure solution *via* direct methods (Sheldrick, 1985) with C, N and H atoms located on difference synthesis maps. For the propylene-diammonium salt, it was apparent from the thermal parameters that two of the carbon atoms [C(3) and C(4)] were disordered. However, attempts to locate and refine individual sites for the disordered atoms were unsuccessful. For this reason, all C and N atoms were refined with isotropic thermal parameters. Refinement *via* blocked-diagonal cascading least-squares procedure. Scattering factors with dispersion corrections from *International Tables for X-ray Crystallography* (1974). H atoms constrained to idealized positions with isotropic thermal parameters fixed at approximately 20% larger than the corresponding heavier atom. Details summarized in Table 1. Final positional parameters and equivalent isotropic thermal parameters are listed in Table 2, pertinent bond distances and angles in Table 3, with interlayer and hydrogen-bonding contacts listed in Table 4.*

Discussion. Both structures consist of layers of square-planar $CuBr_4^{2-}$ ions linked together by semi-coordinate

* 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 51256 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bond distances* (Å) *and angles* (°)

$(C_2H_4N_2H_6)CuBr_4$			
Cu–Br(1^{i})	2·431 (1)	N–C	1·496 (9)
Cu–Br(2)	2·444 (1)	C–C^{ii}	1·492 (15)
Cu–Br(1)	3·034 (1)		
Br(1^{i})–Cu–Br(2)	90·4 (1)	N–C–C^{ii}	110·5 (8)
Cu–Br(1)–Cu^{i}	164·5 (1)		
$(C_3H_6N_2H_6)CuBr_4$			
Cu(1)–Br(1)	2·442 (3)	Cu(2)–Br(1)	3·148 (3)
Cu(1)–Br(2)	2·440 (3)	N(1)–C(2)	1·44 (4)
Cu(1)–Br(3^{iii})	3·148 (3)	C(2)–C(3)	1·55 (5)
Cu(2)–Br(3)	2·432 (3)	C(3)–C(4)	1·34 (7)
Cu(2)–Br(4)	2·450 (3)	C(4)–N(5)	1·46 (6)
Br(1)–Cu(1)–Br(2)	90·0 (1)	N(1)–C(2)–C(3)	116 (3)
Br(3)–Cu(2)–Br(4)	90·5 (1)	C(2)–C(3)–C(4)	116 (4)
Cu(1)–Br(3^{iii})–Cu(2^{iii})	165·6 (1)	C(3)–C(4)–N(5)	119 (4)
Cu(2)–Br(1)–Cu(1^{iii})	164·0 (1)		

Symmetry codes: (i) $0·5-x, -y, -z$; (ii) $1-x, -y, 1-z$; (iii) $1+x, y, z$.

Table 4. *Interlayer and primary hydrogen-bonding contacts* (Å,°)

$(C_2H_4N_2H_6)CuBr_4$			
Br(2)–Br(2^{i})	3·602 (1)	H(1*C*)–Br(2^{iii})	2·458
N(1)–Br(1^{ii})	3·391 (2)	N(1)–Br(2^{iv})	3·536 (2)
H(1*A*)–Br(1^{ii})	2·452	H(1*B*)–Br(2^{iv})	2·611
Cu–Br(2)–Br(2^{i})	155·7 (1)	N(1)–H(1^{iii})–Br(2^{iii})	161·2
C(1)–N(1)–Br(1^{ii})	100·7 (4)	C(1)–N(1)–Br^{iv})	100·7 (4)
N(1)–H(1*A*)–Br(1^{ii})	165·7	N(1)–H(1*B*)–Br(2^{iv})	162·0
C(1)–N(1)–Br(2^{iii})	109·3 (4)		
$(C_3H_6N_2H_6)CuBr_4$			
Br(2^{v})–Br(4)	4·063 (3)	N(1)–Br(2^{viii})	3·473 (5)
N(5)–Br(2^{vi})	3·624 (5)	H(1*C*)–Br(2^{viii})	2·550
H(5*B*)–Br(2^{vi})	2·704	N(1)–Br(3^{ix})	3·377 (4)
N(5)–Br(1)	3·365 (5)	H(1*A*)–Br(3^{ix})	2·508
H(5*C*)–Br(1)	2·503	N(1)–Br(4^{x})	3·666 (5)
N(5)–Br(3^{vii})	3·547 (5)	H(1*B*)–Br(4^{x})	2·709
H(5*A*)–Br(3^{vii})	2·828		
Cu(1)–Br(2)–Br(4)	155·8 (2)	N(5)–H(5*A*)–Br(3^{vii})	147·0
Cu(2)–Br(4)–Br(2)	174·2 (2)	C(2)–N(1)–Br(2^{vii})	116·2 (6)
C(4)–N(5)–Br(2^{vi})	94·0 (8)	N(1)–H(1C)–Br(2^{viii})	161·2
N(5)–H(5*B*)–Br(2^{vi})	160·8	C(2)–N(1)–Br(3^{ix})	90·8 (8)
C(4)–N(5)–Br(1)	109·4 (7)	N(1)–H(1*A*)–Br(3^{ix})	150·5
N(5)–H(5*C*)–Br(1)	149·5	C(2)–N(1)–Br(4^{x})	100·3 (6)
C(4)–N(5)–Br(3^{vii})	116·8 (7)	N(1)–H(1*B*)–Br(4^{x})	161·7

Symmetry codes: (i) $x, y, -1+z$; (ii) $0·5-x, 0·5+y, 1-z$; (iii) $0·5-x, -0·5+y, 1-z$; (iv) $1-x, -y, 1-z$; (v) $-0·5+x, 0·5-y, -0·5+z$; (vi) $x, 1+y, z$; (vii) $-x, 1-y, -z$; (viii) $0·5-x, 0·5+y, 0·5-z$; (ix) $0·5+x, 0·5-y, 0·5+z$; (x) $0·5+x, 1·5-y, 0·5+z$.

Cu···Br bonds with the latter completing the Jahn–Teller elongated octahedral coordination geometry for the Cu^{II} ions. Adjacent layers are bridged by the diammonium cations, providing three-dimensional stability to the lattice. Distances within the anions average 2·440 Å with semi-coordinate bond lengths averaging 3·034 and 3·148 Å for the C_2 and C_3 compounds respectively. The bridging Cu–Br···Cu angles range from 164·0 (1) to 165·6 (1)°. This non-linearity of the bridging linkages (shown in Fig. 1 for the C_3 compound) leads to the typical puckering or 'washboard' effect in the layer structure. This is due to the hydrogen bonding between the diammonium ions and the layers.

The ethylenediammonium structure is isomorphous with the corresponding chloride salt (Tichy *et al.*, 1978) with the slight increase in unit-cell size (0·2–0·4 Å per edge) consistent with the larger radius for the Br ion. Many details appear relatively unchanged. The $CuBr_4^{2-}$ anions lie on centers of inversion, and so are rigorously planar. Both coordinate and semi-coordinate Cu–*X* bonds are approximately 0·15 Å longer in the Br salt, the increase being equal to the difference in ionic radii of the two halide ions. The ethylenediammonium ions lie on centers of inversion, causing adjacent layers to shift slightly (0·28 Å) so that the non-bridging bromide ions on adjacent layers are not totally eclipsed. As can be seen from Fig. 2, the $-NH_3$ groups interact with the layer such that two N–H···Br hydrogen bonds are formed to non-bridging bromide ions (N–H bonds essentially parallel to the layer). The third N–H···Br bond is to a bridging Br ion (the N–H bond in an

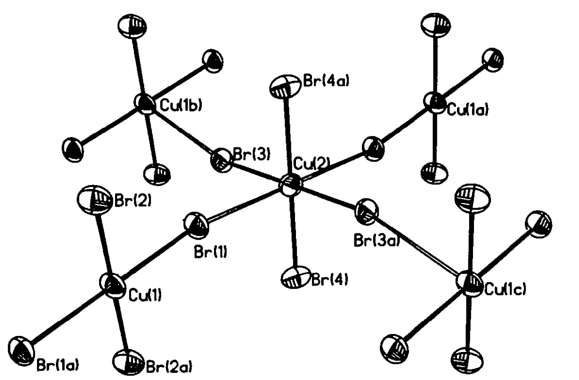

Fig. 1. Layer structure in $(C_3H_6N_2H_6)CuBr_4$. The *a* axis is horizontal.

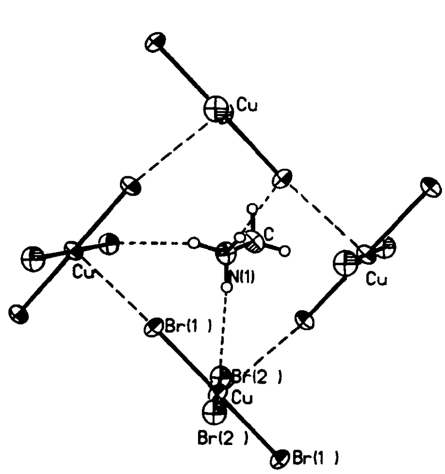

Fig. 2. Illustration of the relationship between the $-CH_2NH_3^+$ moieties and the halide layer in $(C_2H_4N_2H_6)CuBr_4$. View normal to *c* axis.

eclipsed conformation with the C atom). This is identical to the hydrogen-bonding scheme found in the neutron diffraction study of the corresponding chloride salt (Tichy *et al.*, 1978). The interlayer Br···Br distance is 3·602 Å, nearly 0·3 Å shorter than the sum of the van der Waals radii and 0·02 Å shorter than the Cl···Cl distance in the chloride salt. Thus this distance is dictated by the length of the cation rather than by halide–halide repulsions.

In contrast, the structures of the Cl and Br salts with the propylenediammonium cation are not isomorphous. The chloride salt (Phelps *et al.*, 1976) is orthorhombic with the propylenediammonium cation assuming an all-*trans* conformation and lying athwart a mirror plane passing through the central C atom. Thus the adjacent layers are precisely eclipsed. Because the propylenediammonium cation is fully extended, the Cl···Cl distance is quite long (4·548 Å). In the bromide structure, this mirror plane is lost, and the structure becomes monoclinic. Two independent centrosymmetric $CuBr_4^{2-}$ anions are present in each layer and the semi-coordinate Cu···Br distances are substantially longer (3·148, 3·148 Å) than in the ethylenediammonium salt (3·034 Å). All of the atoms in the propylenediammonium cations lie in general positions and the cation backbone is no longer planar (Fig. 3), but the C(4)—N(5) bond assumes a *gauche* conformation with respect to the C(2)—C(3)—C(4) framework. Thus, the cation conformation is *tg* in contrast to the *tt* conformation in the chloride salt [the conformations in the $n = 4$ and $n = 5$ salts are *gtg* and *ttg* respectively (Garland *et al.*, 1989) for both $X = Cl^-$ and $X = Br^-$]. As seen in Fig. 4, one C—NH_3 end [the N(5) end] hydrogen bonds in a manner similar to that in the ethylenediammonium salt. However, the *gauche* bond existing at that end of the cation forces a different hydrogen-bond geometry at the other end with one N—H···Br bond to a terminal Br ion and two to bridging Br ions. This causes the layers to slide 1·03 Å out of the totally eclipsed configuration. More importantly, it moves the layers closer together and tilts the Cu(1) and Cu(2) chromophores in opposite senses (see Fig. 3) so that the Br···Br interlayer contacts are only 4·063 Å. This latter distance is nearly 0·5 Å shorter than the corresponding Cl···Cl distance in $(C_3H_6N_2H_6)CuCl_4$. The increased intralayer repeat distance in the Br salt is presumably responsible for allowing the cation out of the all-*trans* conformation.

The presence of the *gauche* bond in the propylenediammonium ion has important consequences with respect to the crystallographic symmetry of the metal halide layers. Adjacent CuX_4^{2-} anions within the layer of the ethylenediammonium salts are related by an *a* glide perpendicular to the *b* axis. This structural feature is seen for almost all other previously reported antiferrodistortive $(RNH_3)_2CuX_4$ or $(NH_3RNH_3)CuX_4$ salts (upon appropriate transformation of the crystallographic axes) (Willett, Place & Middleton, 1988). The presence of two crystallographically independent NH_3^+ groups in the propylene system destroys this symmetry element, leading to the presence of two independent $CuBr_4^{2-}$ anions. The only other structures with this lowering of symmetry within the layer are in the $[NH_3(CH_2)_5NH_3]CuX_4$ ($X = $ Cl, Br) system (Garland *et al.*, 1989).

One of the objects of the systematic study of the magnetic properties of materials is to delineate the origins of the magnetic behavior in terms of their structural and electronic properties (Willett, Gatteschi & Kahn, 1985). Copper(II) systems have been extensively studied in this respect because of their varied structural characteristics and the simplicity of their electronic structure. Table 5 tabulates the relevant structural and magnetic parameters for the first four members of the alkyldiammonium copper halide series and will provide data for several correlations.

The intralayer magnetic coupling, which occurs through a single halide ion and thus is denoted by J_{1h}, is ferromagnetic in nature since the magnetic orbitals on

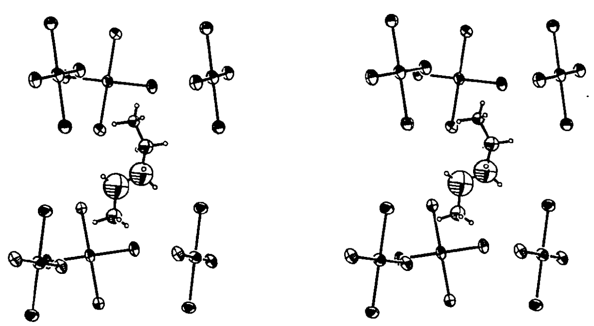

Fig. 3. Illustration of the conformation of the propylenediammonium ion. The *z* axis is to the left, *x* axis is down.

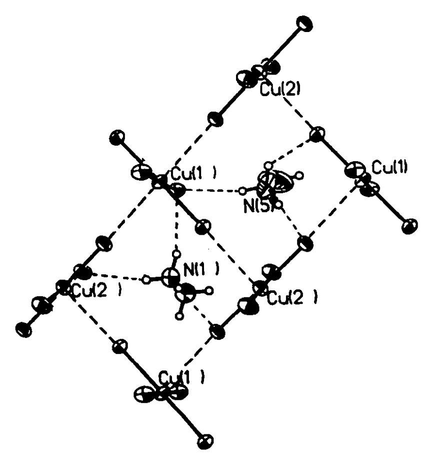

Fig. 4. Illustration of the relationship between the $-CH_2NH_3^+$ fragments and the halide layer in $(C_3H_6N_2H_6)CuBr_4$. View normal to *c* axis.

Table 5. *Structural and magnetic parameters for* $[NH_3(CH_2)_nNH_3]CuX_4$ *salts* ($n=2$–5)

$X = Br^-$

n	Cu–Br (Å)	Cu···Br (Å)	Cu–Br···Cu (°)	J_{1h}/k (K)	Cu–Br (Å)	Br···Br (Å)	Cu–Br···Br (°)	J_{2h}/k (K)	References*
2	2·431	3·034	164·5	39	2·444	3·602	155·7	−68·4	RWHHD
3	2·444	3·148	164·0	26	2·440	4·063	155·8	−26	SHED
	2·431	3·148	165·6		2·450		174·2		
4	2·442	3·185	166·3	29	2·431	4·801	154·9	−5	GEP,SHED
5	2·429	3·164	164·2	23	2·442	6·234	167·3	−2	GEP,SHED
	2·430	3·179	166·3		2·450		149·2		

$X = Cl^-$

n	Cu–Cl (Å)	Cu···Cl (Å)	Cu–Cl···Cu (°)	J_{1h}/k (K)	Cu–Cl (Å)	Cl···Cl (Å)	Cu–Cl···Cl (°)	J_{2h}/k (K)	References*
2	2·288	2·882	166·5	23·0	2·294	3·623	159·6	−13·7	TBHA,SSED
3	2·275	2·946	165·7	15·4	2·314	4·548	171·3	−1·7	PLHH
4	2·308	3·100	166·2	13·0	2·280	4·941	154·8	−0·16	GEP,STD
5	2·279	3·058	164·5	14·1	2·299	6·525	167·6	−0·04	GEP,STD
	2·307	3·020	166·1		2·307		149·6		

* Letters are the initials of the last names of the authors.

adjacent CuX_4^{2-} anions are nearly orthogonal. This can be seen by the bridging Cu–X···Cu angles. For a given halide ion, the magnitude of J_{1h} depends on the extent of differential overlap between the two magnetic orbitals. Thus a strong dependence upon the semi-coordinate bond length is expected, as has been observed experimentally (Landee, Halvorson & Willett, 1987). The data in Table 5 readily confirm those ideas, with J_{1h} much larger for the ethylenediammonium salts, where the Cu···X distances are 0·1–0·2 Å shorter than in the other salts.

It is observed that J_{1h}(Br) is considerably larger than J_{1h}(Cl). It is possible that this is related to the increased delocalization of the unpaired electron out onto the halide ion in the $CuBr_4^{2-}$ anion as compared to the $CuCl_4^{2-}$ anion. This latter fact has been demonstrated by EPR studies of the Cu^{2+} ion doped into the K_2PdX_4 lattice ($X = Cl^-$, Br^-) (Chow, Chang & Willett, 1973; Aramuburu & Moreno, 1985). A similar ligand dependence has been observed for the antiferromagnetic contribution to the exchange coupling in bibridged oligomers and chains (Willett, 1986; Scott & Willett, 1987) where this contribution is about twice as large for the Br complexes as for the Cl complexes. This latter effect has been ascribed to the lower energy of the charge-transfer transition in the Br salts.

The dependence of the interlayer magnetic coupling, which occurs *via* an exchange pathway involving two halide ions and thus is labeled J_{2h}, is strongly dependent upon the X···X contact distance between layers, the geometry of the Cu–X···X–Cu linkage, and upon the halide ion. In both the $X = Cl$ and the $X = Br$ series, $|J_{2h}|$ decreases monotonically with the X···X distance as can be seen in the ln–ln plot in Fig. 5. However, the apparent slope of 6·5 for the Br salts is considerably smaller than the apparent slope of 10 for the Cl salts. In both series, the $n = 4$ point lies significantly below the best straight line. For the Cl series, the non-regular behavior has been attributed to changes in the non-

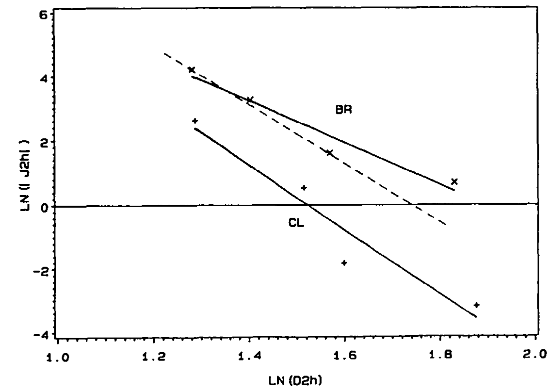

Fig. 5. Plot of ln $|J_{2h}/k|$ *vs* ln $d(X\cdots X)$ for $NH_3(CH_2)_nNH_3CuX$ salts. Solid lines: best least-squares lines for $X = Br$ (×) and $X = Cl$ (+). Dashed line: line through $n = 2$ and $n = 4$ data points for $X = Br$.

linearity of the Cu–X···X interaction (Snively *et al.*, 1981; Block & Jansen, 1982; Straatman, Block & Jansen, 1984). Since the unpaired electron is primarily delocalized into ligand p_σ orbitals, the two-halide exchange interaction will be a maximum when the Cu–X···X angle is 180°. In fact, the calculation of Block & Jansen (1982) indicates this interaction drops off very rapidly as this angle deviates from 180°, with J_{2h} going to zero when the related Cu···Cu–X angle reaches 30°.

From examination of the non-regular variations in the Cu–X···X angles given in Table 5, a linear ln–ln relation between $|J_{2h}/k|$ and d_{2h} (the X···X distance) cannot be expected. For the Br series, it is more appropriate to analyze the data in the following manner. The $n = 2$ and $n = 4$ Br salts have nearly equal Cu–Br···Br angles, and thus can be reasonably compared. A line through those data points gives a slope of 10, in good agreement with the calculated slope of 9 ± 0·6 (Straatman *et al.*, 1984). The $n = 3$ salt lies somewhat above this line, as would be predicted by the larger average Cu—Br···Br angle. The data point for $n = 5$ lies further from the line than would be predicted from its geometrical parameters and it appears that the experimental value of $|J_{2h}|$ may have been overestimated for this latter case.

Straatman *et al.* (1984) have also shown that J_{2h} depends strongly upon the lengths of the Cu—X bonds involved in the two-halide bridges with $|J_{2h}|$ increasing as the Cu—X length shortens. For the bromide series, there is little variation in these lengths, so it would not appear to be an important factor. For the chlorides, in contrast, there are significant differences which need to be taken into account when discussing those correlations.

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The Synthesis and Structure of (*N*-{2-[2-(2-Ammonioethylamino)ethylamino]ethyl}-salicylideneaminato-*O*,*N*,*N*′,*N*″)nickel(II) Perchlorate

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Abstract. $[Ni(C_{13}H_{22}N_4O)](ClO_4)_2$, $M_r = 507.9$, triclinic, $P\bar{1}$, $a = 8.699$ (1), $b = 10.029$ (1), $c = 11.923$ (1) Å, $\alpha = 94.34$ (3), $\beta = 108.63$ (4), $\gamma = 96.10$ (3)°, $V = 973.4$ (4) Å^3, $Z = 2$, $D_x = 1.73$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 12.5$ cm^{-1}, $F(000) = 524$, $T = 298$ K, final $R = 0.055$ and $wR = 0.061$ for 2900 independent reflections $[I > 3\sigma(I)]$. The coordination polyhedron around Ni is an irregular square pyramid with the protonated saltrien [saltrien = $2\text{-}O^-\text{—}C_6H_4CH{=}N(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$] acting as tetradentate ligand through one O and three N atoms.

Introduction. Structural, electronic and magnetic properties of Schiff-base coordination compounds have been measured in depth and form a significant part of our knowledge of the inorganic chemistry of chelate systems (Holm & O'Connor, 1971). In recent years Schiff-base complexes have been proposed as a model to describe energy transfer in naturally occurring systems,

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