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Neutron Diffraction Study of Twinned Crystals of Ethylenediammonium Copper Tetrachloride and Ethylenediammonium Manganese Tetrachloride

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Isomorphous compounds $NH_3(CH_2)_2NH_3CuCl_4$ and $NH_3(CH_2)_2NH_3MnCl_4$ crystallize in the monoclinic space group No. 14, $P2_1/b$ with $Z = 2$. The unit-cell parameters are a = 8·109 (3), b = 7·158 (3), c = 7·363 (3) Å, γ = 92·37 (3)° for the Cu compound and a = 8·609 (2), b = 7·130 (2), c = 7·192 (2) Å, γ = 92·69 (2)° for the Mn compound. Both samples used for neutron (λ = 1·035 Å) measurement at room temperature were twinned; a maximum experimental resolution was achieved by measuring satellite reciprocal vectors in the equatorial plane of a four-circle diffractometer [Tichý & Beneš (1977). *Helv. Phys. Acta*, **50**, 459–466]. Full-matrix least-squares refinement yielded $R(F)$ = 0·0660 and $R_w(F)$ = 0·0422 for 1499 reflections of the Cu compound and $R(F)$ = 0·1038 and $R_w(F)$ = 0·0806 for 1317 reflections of the Mn one. The structure consists of parallel two-dimensional sheets of puckered perovskite-type layers of corner-sharing metal—Cl_6 octahedra interleaved by layers of ethylenediammonium chains nearly perpendicular to the layers. Ammonium groups at the ends of the chains fit into cavities of adjacent metal—Cl_4 layers and form hydrogen bonds N—H···Cl. Each in-plane Cl binds one H only (H···Cl = 2·286 Å in both structures), while out-of-plane Cl atoms are linked by two H bridges to two neighbouring organic chains. Their lengths are 2·291 (6) and 2·541 (8) Å for the Cu compound and for the Mn compound 2·300 (11) and 2·376 (12) Å. In-plane distances Cu—Cl are 2·308 (2) and 2·896 (2) Å and Mn—Cl are 2·579 (3) and 2·600 (3) Å: out-of-plane distances are Cu—Cl = 2·316 (2) and Mn—Cl = 2·508 (4) Å.

Introduction

Chloride perovskite layer compounds of the general formulae $(C_nH_{2n+1}NH_3)_2MCl_4$ and $NH_3(CH_2)_n$-NH_3MCl_4, with M = Cu, Mn, Fe, Cd have attracted a great deal of attention in recent years because of their magnetic properties and interesting structural phase transitions. They consist of parallel two-dimensional sheets of perovskite-type layers of corner-sharing metal—Cl_6 octahedra which are bonded together by aliphatic chains nearly perpendicular to the layers. In compounds of the first category the layers are held together essentially by van der Waals contacts between the aliphatic chains, which are hydrogen bonded to metal—Cl_4 layers, while in the compounds of the second category hydrogen bonds between NH_3 groups at both ends of the aliphatic chains and Cl atoms of the perovskite-type layer form a more rigid link between adjacent layers. Thermal motion of alkylammonium groups, deformation of metal—Cl_4 framework and changes in the hydrogen-bonding scheme were shown to be responsible for phase transitions (Heger, Mullen & Knorr, 1976; Depmeier, 1977; Chapuis, Arend & Kind, 1975).

The compounds ethylenediammonium copper and manganese tetrachlorides (subsequently abbreviated $EDACuCl_4$ and $EDAMnCl_4$) were chosen for neutron study in order to determine accurate H atom positions for the shortest organic chain possible in the second category of these compounds. In an X-ray study Birrell & Zaslow (1972) presented the structure of $EDACuCl_4$ without positions of H atoms, Willett & Riedel (1975) published neutron diffraction results about propylenediammonium manganese and ferrous tetrachlorides $NH_3(CH_2)_3NH_3MCl_4$, M = Mn, Fe, and Walpen (1976) solved X-ray structures of the compounds $NH_3(CH_2)_nNH_3CdCl_4$ with n = 2–7. Some preliminary results on $EDACuCl_4$ and $EDAMnCl_4$ were published elsewhere (Arend, Tichý, Baberschke & Rys, 1976; Tichý & Beneš, 1975).

Experimental

Both substances were prepared by reacting the metal chloride with ethylenediammonium chloride in aqueous solutions according to the formula:

$$\mathrm{ClNH_3{-}(CH_2)_2{-}NH_3Cl} + M\mathrm{Cl_2} \rightarrow [\mathrm{NH_3{-}(CH_2)_2{-}NH_3}]M\mathrm{Cl_4} \quad (M = \mathrm{Cu, Mn}).$$

EDACuCl$_4$ is congruently soluble at room temperature whereas EDAMnCl$_4$ is not. The latter can be handled at 60°C, when it becomes congruently soluble. Crystals were prepared from aqueous solutions either by slow evaporation or by a temperature gradient technique (Arend, Huber, Mischgofsky & Richter-van Leeuwen, 1978).

The composition of the crystals was verified by volumetric analysis for metal and Cl atoms. Crystals grow in thin plates; EDACuCl$_4$ crystals are brown-green, EDAMnCl$_4$ are dark orange. Unit-cell

Table 1. *Crystal and experimental data for ethylenediammonium copper and manganese tetrachlorides*

Formula	$(NH_3)_2(CH_2)_2CuCl_4$	$(NH_3)_2(CH_2)_2MnCl_4$
Molecular weight	267·47	258·86
Space group	No. 14, $P2_1/b$ $hk0$, $k = 2n$ $00l$, $l = 2n$	No. 14, $P2_1/b$ $hk0$, $k = 2n$ $00l$, $l = 2n$
Unit-cell dimensions	a = 8·1086 (27) Å b = 7·1584 (25) c = 7·3627 (26) γ = 92·369 (29)° V = 427·00 (26) Å^3	a = 8·6089 (18) Å b = 7·1303 (16) c = 7·1921 (18) γ = 92·685 (24)° V = 441·00 (17) Å^3
Density	D_m = 1·993, D_c = 2·080 g cm^{-3}	D_m = 1·930, D_c = 1·949 g cm^{-3}
Molecules per unit cell	$Z = 2$	$Z = 2$
Principal growth face	plate parallel to (100)	plate parallel to (100)
Twinning		
relative volumes of twin individuals (based on scale factors)	0·440:0·560	0·434:0·566
twinning law	180° rotation around reciprocal vector 011	mirror plane perpendicular to a^*
indices of reflection satellites	$hkl_{\rm I}$ $\bar{h}lk_{\rm II}$	$hkl_{\rm I}$, $\bar{h}k\bar{l}_{\rm II}$
systematic coincidences of reflection satellites	$0kk$	$h0l$
number of orienting reflections for establishing unit cell and orientation of individuals	16, 16	14, 14
Data collection		
wavelength	1·0354 Å	1·0354 Å
monochromator	pyrolytic graphite	pyrolytic graphite
scan length (in degrees)	1·45 (0·44 + 2·26 tan θ)	1·45 (0·44 + 2·26 tan θ)
scanning mode	$\omega:2\theta$, 40 points per reflection	$\omega:2\theta$, 30 points per reflection
monitor count	10 000 or 40 000	40 000
$(\sin\theta/\lambda)_{\max}$ (Å^{-1})	0·50 (Å^{-1})	0·55
sample mounting	(100) plane parallel with diffractometer φ axis	(100) plane parallel with diffractometer φ axis
reference reflections	$300_{\rm I}$, $040_{\rm I}$, $004_{\rm I}$ $\bar{3}00_{\rm II}$, $040_{\rm II}$, $004_{\rm II}$	$300_{\rm I} \equiv \bar{3}00_{\rm II}$, $040_{\rm I}$ $040_{\rm II}$, $004_{\rm I} \equiv 00\bar{4}_{\rm II}$
interval between measurement of reference reflections	1–2 days	2–4 days
Crystal sample and absorption corrections		
weight	66·50 mg	22·67 mg
volume	31·97 mm^3	11·63 mm^3
shape	polyhedron, approximately 4·4 × 4·4 × 1·9 mm	polyhedron, approximately 3·2 × 2·9 × 1·6 mm
number of boundary planes	7	8
linear absorption coefficient μ (including incoherent scattering)	μ = 2·337 cm^{-1}	μ = 2·407 cm^{-1}
range of transmission factor	0·548–0·723	0·543–0·730
range of mean path length	0·1301–0·2464 cm	0·1274–0·2455 cm
Reflections		
number of reflections measured (excluding standard reflections)	1499	1317
number of symmetry-independent reflections for individuals I and II	463, 458	498, 498
total number of independent reflections (regardless of individuals I and II)	473 (all measured in $\sin\theta/\lambda < 0{\cdot}50$ Å^{-1})	567 (82 independent reflections in $\sin\theta/\lambda < 0{\cdot}55$ Å^{-1} were not measured because of accidental loss of the sample)
range hkl	±8, ±7, ±7	±9, ±7, ±7
range of intensities (relative scale)	4–1092	2–736

parameters were refined by a least-squares fit to Cu $K\bar{\alpha}$ powder data from ground single crystals, space group extinctions were determined from Weissenberg photographs. The sample of $EDACuCl_4$ used for X-ray work was a single crystal; all examined samples of $EDAMnCl_4$ were twinned, but it was possible to determine the unit cell and space group unambiguously. Investigation of a thin slice cut perpendicular to the principal growth face of $EDAMnCl_4$ on a polarizing microscope revealed that the twins were of lamellar type. Non-deuterated samples used for neutron diffraction work were cut from thicker plates grown over a period of several months. Both samples were twinned.

Measurements were performed at the reactors Diorit and Saphir of the Swiss Federal Institute for Reactor Research at Würenlingen. A novel method for measuring twinned (and clustered) crystals was used. By bringing the measured reciprocal vector and its nearest reflection satellite into the equatorial plane of a four-circle diffractometer, a maximum resolution of peaks was achieved (Beneš & Tichý, 1975; Tichý & Beneš, 1977). We thus succeeded in measuring almost all the independent reflections because it was either possible to separate the reflection from its reflection satellite or (in the case of $EDAMnCl_4$) all systematically coincident reflections of the two single-crystal individuals had the same F_{calc}.

Integrated intensities were derived from reflection profiles and their standard deviations $\sigma(I)$ from counting statistics. When reflections with unequal F_{calc} were so close that they partly overlapped, their $\sigma(I)$ values were increased with increasing overlap. Intensities of unobserved reflections were given 50% of the 'threshold' of measurable intensity with $\sigma(I)$ of the same value and included in the subsequent least-squares refinement. Linear absorption coefficients μ were determined by a transmission of pin-hole-collimated neutrons through thicker crystal platelets and absorption corrections and mean path lengths (for extinction corrections) were computed assuming that both single-crystal individuals were evenly distributed over the whole volume of the sample. Crystal data and experimental details are summarized in Table 1.

Structure determination and refinement

Using phases of reflections in the range $\sin\theta/\lambda < 0{\cdot}35$ Å^{-1} computed for non-hydrogen atoms for the structure of $EDACuCl_4$ reported by Birrell & Zaslow (1972) and assuming isomorphy of $EDAMnCl_4$, all H atom positions were determined from several successive Fourier maps. In an early stage of refinement the necessity for including the extinction corrections was recognized. This was done only for isotropic secondary extinction according to Zachariasen (1967) with a modified version of the *ORFLS* program (Busing, Martin & Levy, 1962) on non-averaged sets of structure factors, to allow for different mean path lengths of the beam in the sample for symmetry-related reflections. Occupancy factors and all scattering lengths (Bacon, 1972) were kept fixed during full-

Table 2. *Summary of the least-squares refinement*

Extinction coefficient y is defined (Zachariasen, 1967) by $F^2_{measured} = yF^2_{kinematical}$, $F_{corr} = F_{obs}/\sqrt{y}$ is the observed structure factor corrected for extinction.

	$EDACuCl_4$	$EDAMnCl_4$
Number of parameters refined (n)	89	89
Number of observations, including zero intensities (m)	1499	1317
$R(F) = \sum \lvert F_{corr} - \lvert F_{calc}\rvert\rvert / \sum F_{corr}$	0·0660	0·1038
$R_w(F) = [\sum w(F_{corr} - \lvert F_{calc}\rvert)^2 / \sum wF^2_{corr}]^{1/2}$	0·0422	0·0806
$S \quad = [\sum w(F_{corr} - \lvert F_{calc}\rvert)^2/(m-n)]^{1/2}$	4·7042	4·9417
y for reflection 022 (most affected by extinction)	0·213	0·414
Extinction parameter r^* (isotropic, secondary only)	21627·0	5022·0
Weighting scheme	$w = 1/\sigma^2(F)$ where $\sigma(F) \sim \sigma(I)/\sqrt{I}$	
Refinement based on	F	
Function minimized	$\sum w(F_{corr} - \lvert F_{calc}\rvert)^2$	
Neutron scattering lengths used in refinement (all $\times 10^{-12}$ cm)	$b_{Cu} = 0{\cdot}760$	$b_{Mn} = -0{\cdot}390$
	$b_{Cl} = 0{\cdot}960$	
	$b_C = 0{\cdot}665$	
	$b_N = 0{\cdot}940$	
	$b_H = -0{\cdot}374$	

Table 3. *Positional parameters* ($\times 10^5$) *of* $EDACuCl_4$ *and* $EDAMnCl_4$

Estimated standard deviations (in parentheses) refer to last significant figures; (*) indicates parameters not refined (atoms in special positions).

$EDACuCl_4$

	x	y	z
Cu	0 (*)	0 (*)	0 (*)
Cl(1)	−3497 (16)	22932 (24)	21135 (22)
Cl(2)	28046 (18)	2839 (24)	4032 (22)
C	43589 (29)	55338 (46)	−4938 (40)
H(1)	43363 (60)	52008 (112)	−19542 (75)
H(2)	45290 (62)	69274 (87)	−3953 (108)
N	26828 (24)	50176 (36)	1958 (35)
H(3)	25899 (57)	52804 (91)	15488 (83)
H(4)	18452 (62)	57784 (94)	−4448 (91)
H(5)	23951 (64)	37186 (107)	−21 (106)

$EDAMnCl_4$

	x	y	z
Mn	0 (*)	0 (*)	0 (*)
Cl(1)	−3233 (32)	27881 (41)	21772 (42)
Cl(2)	28681 (36)	2656 (44)	4380 (43)
C	43927 (49)	54878 (68)	−5364 (67)
H(1)	44161 (119)	52536 (200)	−19693 (129)
H(2)	44653 (122)	70186 (135)	−3147 (173)
N	28093 (41)	48996 (63)	1225 (64)
H(3)	26830 (103)	51532 (169)	14229 (160)
H(4)	20496 (133)	55669 (162)	−5924 (164)
H(5)	26594 (113)	34934 (173)	−85 (159)

matrix least-squares refinement which ended after all shift/e.s.d. ratios dropped below 0·05. Details of the refinement are given in Table 2. Difference Fourier maps computed at the end of the refinement from all reflections with F_{obs} corrected for extinction and F_{calc} showed no spurious peaks. Resultant atomic coordinates are given in Table 3.*

Description of the structures

Geometrical aspects of both structures are summarized in Tables 4–8 and in Figs. 1–3. For the sake of brevity, in the following text the numerical values for $\mathrm{EDACuCl_4}$ will be given as the 'numerator' and corresponding values for $\mathrm{EDAMnCl_4}$, separated by a ‖ sign, will be the 'denominator'. Estimated standard deviations (e.s.d.'s) in parentheses refer to the last significant figures.

The main features of the structure are parallel two-dimensional perovskite-type metal–tetrachloride layers interleaved by layers of ethylenediammonium ions. Ammonium groups at both ends of the ethylene chains fit into cavities of the metal—$\mathrm{Cl_4}$ layer (see Fig. 1) and hydrogen bonds —N—H···Cl thus bind the ethylene chains to the layer. Organic chains are extended along the longest *a* axis and exhibit large thermal vibrations.

(*a*) *Metal—tetrachloride framework*

This perovskite-type layer consists of metal—$\mathrm{Cl_4}$ planar ions so oriented that metal atoms and Cl(1) atoms form a puckered plane and that the metal—Cl(2) bond is nearly perpendicular to this plane [82·08 (06)‖ 82·53 (13)°]. The planarity of metal—$\mathrm{Cl_4}$ ions is imposed by metal atoms occupying the centres of symmetry. Neighbouring ions are approximately at

Table 4. *Interatomic distances* (Å) *and angles* (°)

The values were calculated with the program *ORFFE* (Busing, Martin & Levy, 1964) with variance–covariance matrices and e.s.d.'s of cell parameters. Bond lengths C—H and N—H were corrected for riding motion, all other bond lengths for independent vibration of atoms. E.s.d.'s in parentheses refer to last significant figures. Roman numerals as superscripts refer to the equivalent positions which should be applied to the coordinates of the atom.

None	x,	y,	z	(vii)	$-x$,	$\frac{3}{2}-y$,	$\frac{1}{2}+z$
(i)	$-x$,	$\frac{1}{2}-y$,	$-\frac{1}{2}+z$	(viii)	x,	$\frac{3}{2}+y$,	$\frac{1}{2}-z$
(ii)	$-x$,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$	(ix)	$1-x$,	$1-y$,	$1-z$
(iii)	x,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$	(x)	x,	y,	$1+z$
(iv)	$-x$,	$-y$,	$-z$	(xi)	$1+x$,	y,	z
(v)	$-x$,	$1-y$,	$-z$	(xii)	x,	$\frac{1}{2}+y$,	$-\frac{1}{2}-z$
(vi)	x,	$1+y$,	z				

	$\mathrm{EDACuCl_4}$		$\mathrm{EDAMnCl_4}$	
	Uncorrected	Corrected	Uncorrected	Corrected
Metal—$\mathrm{Cl_4}$ framework				
Metal—Cl(1)	2·288 (2)	2·308 (2)	2·556 (3)	2·579 (3)
Metal—Cl(2)	2·294 (2)	2·316 (2)	2·488 (3)	2·508 (4)
Metal—Cl(1^{i})	2·882 (2)	2·896 (2)	2·578 (3)	2·600 (3)
Cl(1)—Cl(1^{i})	3·735 (1)	3·748 (1)	3·665 (1)	3·683 (1)
Cl(1)—Cl(2)	3·240 (2)	3·257 (2)	3·579 (4)	3·594 (4)
Cl(2)—Cl(1^{i})	3·623 (2)	3·637 (2)	3·537 (4)	3·554 (4)
Cl(1)—Metal—Cl(1^{i})	91·77 (3)		91·10 (3)	
Cl(2)—Metal—Cl(1)	90·01 (6)		90·40 (10)	
Cl(2)—Metal—Cl(1^{i})	88·07 (5)		88·56 (9)	
Metal—Cl(1)—Metal$^{\mathrm{ii}}$	166·46 (6)		161·04 (12)	
Chlorine environment of N atom				
Hydrogen-bonded chlorines				
N—Cl(2^{iii})	3·247 (3)	3·265 (3)	3·204 (5)	3·221 (6)
N—Cl(1^{v})	3·237 (3)	3·253 (3)	3·219 (5)	3·236 (5)
N—Cl(2)	3·398 (3)	3·409 (3)	3·315 (6)	3·333 (6)
Chlorines not H-bonded				
N—Cl(1^{i})	3·348 (3)	3·361 (3)	3·515 (5)	3·531 (5)
N—Cl(1)	3·383 (3)	3·398 (3)	3·368 (5)	3·385 (5)
N—Cl(1^{iii})	3·599 (3)	3·614 (3)	3·976 (5)	3·989 (5)
N—Cl(2^{vi})	3·770 (3)	3·780 (3)	3·831 (6)	3·846 (6)
N—Cl(2^{xii})	4·128 (3)	4·142 (3)	4·008 (5)	4·022 (5)

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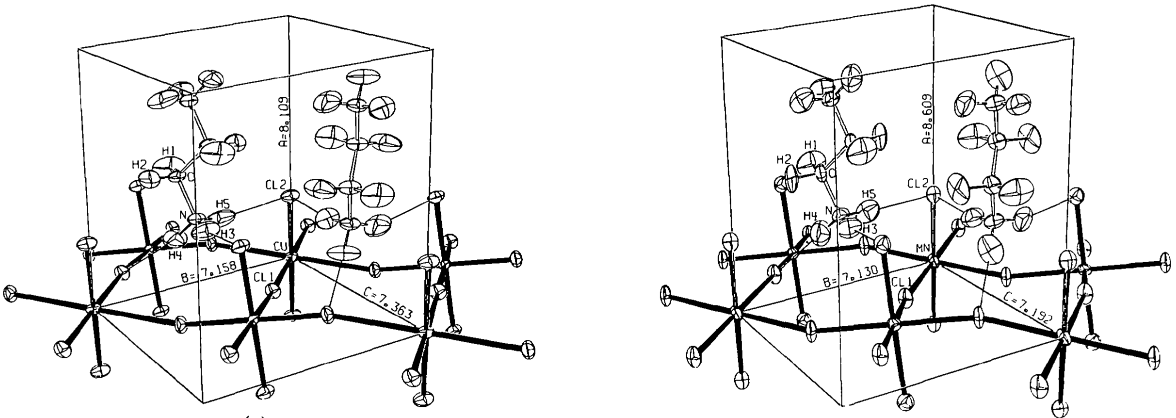
* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33656 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4 (*cont.*)

	$EDACuCl_4$		$EDAMnCl_4$	
	Uncorrected	Corrected	Uncorrected	Corrected
Hydrogen bonding				
N–H(3)	1·017 (8)	1·055 (9)	0·960 (14)	0·992 (16)
H(3)···Cl(2^{iii})	2·251 (7)	2·291 (6)	2·265 (12)	2·300 (11)
N···Cl(2^{iii})	3·247 (3)	3·265 (3)	3·204 (5)	3·221 (6)
N–H(3)···Cl(2^{iii})	166·0 (5)		165·9 (8)	
N–H(4)	1·005 (8)	1·056 (9)	0·973 (15)	1·027 (17)
H(4)···Cl(1^{v})	2·242 (7)	2·285 (7)	2·247 (13)	2·286 (12)
N···Cl(1^{v})	3·237 (3)	3·253 (3)	3·219 (5)	3·236 (5)
N–H(4)···Cl(1^{v})	170·2 (4)		177·7 (9)	
N–H(5)	0·961 (9)	1·024 (10)	1·009 (15)	1·047 (16)
H(5)···Cl(2)	2·512 (8)	2·541 (8)	2·339 (13)	2·376 (12)
N···Cl(2)	3·398 (3)	3·409 (3)	3·315 (6)	3·333 (6)
N–H(5)···Cl(2)	153·2 (5)		162·3 (8)	
Possible van der Waals H···Cl contacts				
H(5)···Cl(^{i})	2·772 (7)	2·806 (7)	2·968 (11)	2·997 (11)
N···Cl(1^{i})	3·348 (3)	3·361 (3)	3·515 (6)	3·531 (5)
N–H(5)···Cl(1^{i})	119·2 (5)		115·0 (8)	
H(5)···Cl(1)	2·869 (6)	2·905 (6)	3·033 (10)	3·058 (10)
N···Cl(1)	3·383 (3)	3·398 (3)	3·368 (5)	3·385 (5)
N–H(5)···Cl(1)	114·6 (5)		100·6 (7)	
Ammonium group				
N–H(3)	1·017 (8)	1·055 (9)	0·960 (14)	0·992 (16)
N–H(4)	1·005 (8)	1·056 (9)	0·973 (15)	1·027 (17)
N–H(5)	0·961 (9)	1·024 (10)	1·009 (15)	1·047 (16)
H(3)–H(4)	1·632 (8)	1·709 (9)	1·580 (14)	1·653 (15)
H(3)–H(5)	1·601 (9)	1·676 (10)	1·567 (16)	1·639 (16)
H(4)–H(5)	1·592 (10)	1·660 (10)	1·647 (16)	1·721 (16)
C–N–H(3)	111·3 (3)		111·6 (6)	
C–N–H(4)	109·7 (4)		108·8 (7)	
C–N–H(5)	111·9 (4)		108·9 (6)	
H(4)–H(3)–H(5)	59·0 (4)		63·1 (8)	
H(5)–H(4)–H(3)	59·5 (5)		58·1 (8)	
H(3)–H(5)–H(4)	61·5 (5)		58·8 (7)	
H(3)–N–H(4)	107·6 (5)		109·8 (9)	
H(3)–N–H(5)	108·1 (6)		105·5 (9)	
H(4)–N–H(5)	108·1 (5)		112·3 (9)	
Organic chain N–CH_2–CH_2–N				
C–C	1·503 (5)	1·557 (5)	1·497 (8)	1·555 (8)
C–N	1·483 (3)	1·538 (3)	1·485 (6)	1·544 (6)
C–H(1)	1·101 (7)	1·164 (8)	1·044 (12)	1·109 (14)
C–H(2)	1·004 (8)	1·067 (9)	1·101 (12)	1·152 (13)
H(1)–H(2)	1·689 (9)	1·756 (10)	1·731 (16)	1·806 (16)
N–C–C	110·7 (3)		110·9 (5)	
H(1)–C–H(2)	106·6 (6)		107·5 (9)	
N–C–H(1)	105·8 (3)		107·1 (7)	
N–C–H(2)	108·0 (3)		104·0 (6)	
C–C–H(1)	111·6 (4)		114·6 (7)	
C–C–H(2)	113·6 (4)		112·2 (7)	

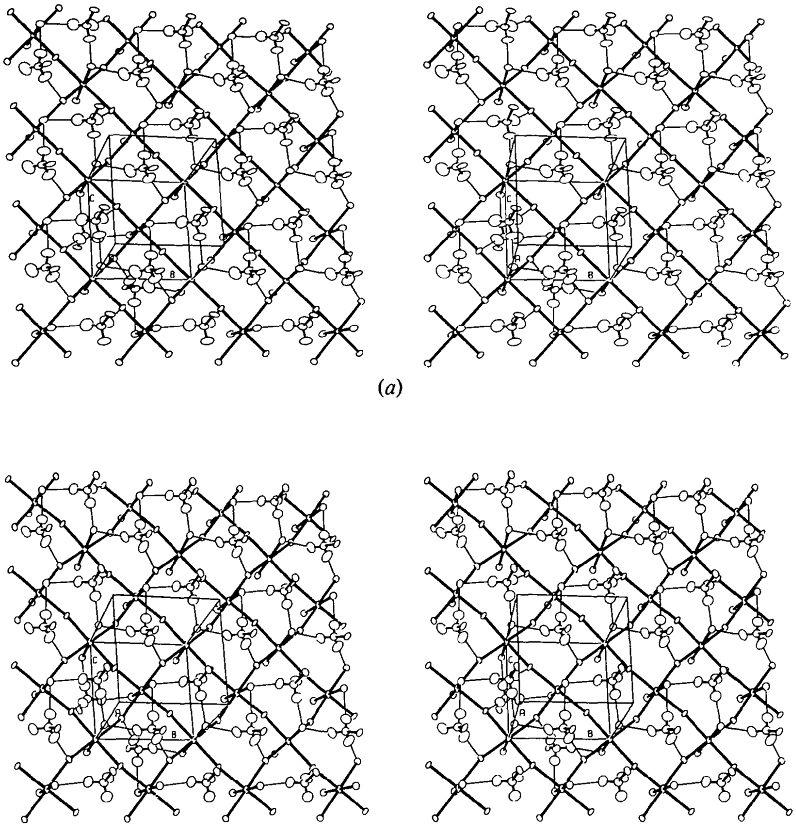
right angles to one another and an 'in-plane' Cl(1) atom from a neighbouring ion thus comes close to the metal atom giving rise to the octahedral coordination around the metal (see Fig. 2). The in-plane Cl(1) atoms are displaced alternately below and above the plane defined by the metal atoms [0·283 (1)‖0·278 (3) Å] and the corner-sharing metal–Cl_6 octahedra are alternately tilted backwards and forwards in the direction of the *c* axis. This puckering of the two-dimensional perovskite-layer is illustrated in Fig. 3. The angles of puckering, 162·5 (1)‖162·4 (2)°, are identical in the structures within experimental error, although the angles metal–Cl(1)–metal differ significantly: 166·46 (06)‖161·04 (12)°. This is explained by a larger displacement of Cl(1) atoms from the least-squares plane fitted through metal and Cl(2) atoms in the [011] direction, 0·111‖0·325 Å (see Fig. 2).

The environments of the metal atoms in the structures are different. The $[CuCl_4]^{2-}$ ion is nearly square with an in-plane Cu–Cl(1) bond 2·308 (2) Å



(a) (b)

Fig. 1. View (drawn with *ORTEP* II, Johnson, 1971) of the unit-cell content showing the embedding of ammonium groups into cavities in the metal–tetrachloride layer of (*a*) EDACuCl$_4$, (*b*) EDAMnCl$_4$. Thermal ellipsoids enclose 50% probability, hydrogen bonds are shown as light lines.



(a)

(b)

Fig. 2. Stereograms of hydrogen-bonding schemes with thermal ellipsoids scaled at 50% probability. (*a*) EDACuCl$_4$, (*b*) EDAMnCl$_4$. –C–NH$_3$ groups of molecules above the metal–tetrachloride layer and only two groups of molecules below the layer (near the *a* axis) are drawn.

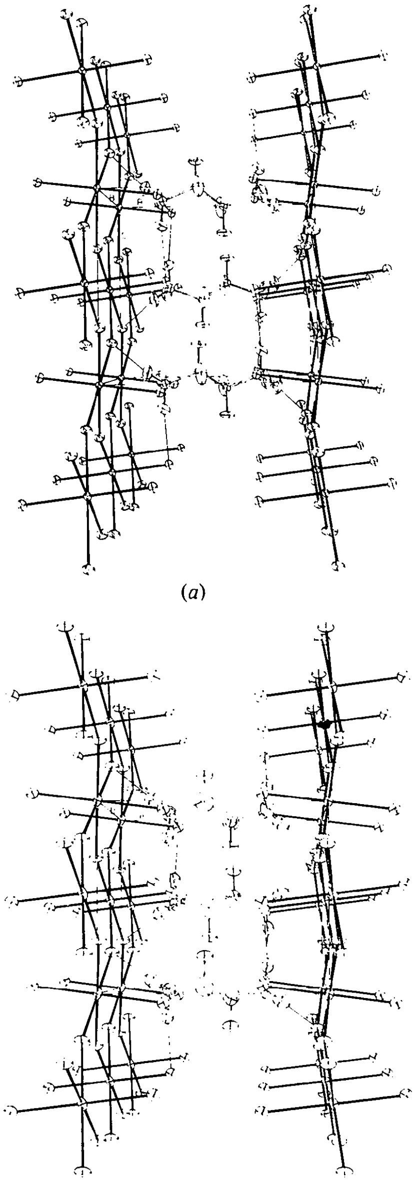


Fig. 3. Structure viewed nearly along the *b* axis showing the puckering of the metal–tetrachloride layer. Hydrogen bonds are shown by single lines, ellipsoids of thermal vibrations include 33% probability. (*a*) $EDACuCl_4$, (*b*) $EDAMnCl_4$.

and an out-of-plane Cu–Cl(2) bond 2·316 (2) Å and with an angle Cl(1)–Cu–Cl(2) = 90·01 (6)°. The distance of Cu to the in-plane Cl from the next $[CuCl_4]^{2-}$ ion is 2·896 (2) Å and is significantly larger than the distances 2·308 and 2·316 Å ('4 + 2' coordination of Cu). The distortion of the coordination octahedron $CuCl_6$ is thus much larger than that of $MnCl_6$ in $EDAMnCl_4$, which is nearly regular with the distances: in-plane Mn–Cl(1) = 2·579 (3) Å, out-of-plane Mn–Cl(2) = 2·508 (4) Å and 2·600 (3) Å to the next neighbour Cl atom. The angle Cl(1)–Mn–Cl(2) is 90·40 (10)°.

Bond distances and angles (in Tables 4 and 5) are consistent with those of the $CuCl_6$ and $MnCl_6$ octahedra in similar compounds, *e.g.* $(C_2H_5NH_3)_2CuCl_4$ (Steadman & Willett, 1970), $[(NH_3C_2H_4)_2NH_2]Cl(CuCl_4)$ (Ferguson & Zaslow, 1971), $(C_6H_5NH_3)_2CuCl_4$ (Larsen, 1974), $(CH_3C_2H_4NH_3)_2MnCl_4$ (Peterson & Willett, 1972; Depmeier, 1976), $NH_3(CH_2)_3NH_3MnCl_4$ (Willett & Riedel, 1975), and $(CH_3NH_3)_2MnCl_4$ (Heger, Mullen & Knorr, 1976).

(*b*) *Organic chain* $NH_3–CH_2–CH_2–NH_3$

Organic chains $N–CH_2–CH_2–N$ are almost identical in both structures. The skeleton N–C–C–N is planar, the planarity being imposed by the centre of symmetry in the middle of the C–C bond. The ammonium H(4) atom lies nearest to the N–C–C–N plane and continues its zig-zag line. The other two H atoms, H(3) and H(5), lie nearly symmetrically on both sides of the plane. The organic chains are completely isolated from one another as there are no contacts shorter than 3·0 Å between neighbouring chains (including CH_2 H atoms) and enough space between chains makes their large thermal vibrations physically reasonable (apparent in Figs. 1 and 3). Uncorrected values of C–N and C–C bonds are in a good agreement with bond lengths for $NH_3(CH_2)_3NH_3MCl_4$, M = Mn, Fe, reported by Willett & Riedel (1975). The bond lengths and angles summarized in Table 4 and dihedral angles between planes defined by different segments of the organic ion (in Table 5) have no unexpected values and indicate that there is no deformation of the ethylenediammonium ions due to their insertion between metal–tetrachloride sheets.

(*c*) *Hydrogen-bonding scheme*

The ammonium groups in $EDACuCl_4$ enter 0·049 (5) Å further into the cavities lined by eight Cl atoms in the metal–halogen framework than those of $EDAMnCl_4$ [the Cartesian *x* coordinates of N are 2·173 (2)‖2·416 (4) Å and those of Cl(2) are 2·272 (1)‖2·466 (3) Å]. A possible reason for this could be the larger size of the cavity, ~5·13‖~5·06 Å. Although the N atom is in the environment of eight Cl atoms (distances 3·22 to 4·14 Å) which may act as acceptors for ammonium H atoms to build –N–H···Cl bonds, ammonium H atoms occupy non-disordered positions (this was verified by the difference Fourier synthesis) between the N atom, two out-of-plane Cl(2) atoms and one in-plane Cl(1) atom. In $EDAMnCl_4$ these three hydrogen-bonded Cl atoms are nearest to the N, but in $EDACuCl_4$ there are two N···Cl distances shorter than the longest hydrogen bond. This affects the geometry of the hydrogen bonds.

The shortest two bonds $-$N$-$H(4)$\cdots$Cl(1^{v}) and $-$N$-$H(3)$\cdots$Cl(2^{iii}) are almost identical in both structures; their lengths are 2·285 (7)‖2·286 (12) and 2·291 (6)‖2·300 (11) Å, respectively, and their angles, 170·2 (4)‖177·7 (9) and 166·0 (5)‖165·9 (8)°, are not far from 180°. (For the difinition of the Roman superscripts refer to Table 4.) Furthermore, H(3) and H(4) have no contact shorter than 3·0 Å to any other Cl atom. In the bonding of the ammonium H(5) atom the two structures differ. H(5) forms the longest and least-

Table 5. *Selected least-squares planes, dihedral angles and other structural features*

X,Y,Z refer to the 'reference system of coordinates' defined in Table 6. For superscripts see explanation to Table 4.

	EDACuCl$_4$	EDAMnCl$_4$
(*a*) Plane equations		
Plane (1)	$0·9991X + 0·0413Y + 0·0000Z + 0·0000 = 0$	$0·9989X + 0·0468Y + 0·0000Z + 0·0000 = 0$
Plane (2)	$0·0000X + 0·0000Y + 1·0000Z + 0·0000 = 0$	$0·0000X + 0·0000Y + 1·0000Z + 0·0000 = 0$
Plane (3)	$-0·1294X - 0·0053Y + 0·9916Z + 0·0000 = 0$	$-0·1265X - 0·0059Y + 0·9919Z + 0·0000 = 0$
Plane (4)	$0·9875X + 0·0409Y + 0·1521Z + 0·0000 = 0$	$0·9871X + 0·0463Y + 0·1528Z + 0·0000 = 0$
Plane (5)	$0·9859X + 0·0653Y + 0·1538Z + 0·0000 = 0$	$0·9864X + 0·0659Y + 0·1504Z + 0·0000 = 0$
Plane (6)	$-0·0572X - 0·7294Y - 0·6817Z + 2·8319 = 0$	$-0·0029X - 0·7451Y - 0·6670Z + 2·6654 = 0$
Plane (7)	$0·9951X - 0·0975Y + 0·0137Z - 2·9634 = 0$	$0·9995X - 0·0147Y + 0·0295Z - 3·5274 = 0$
Plane (8)	$-0·9137X - 0·2422Y + 0·3263Z + 2·3186 = 0$	$-0·9127X - 0·2835Y + 0·2944Z + 2·6902 = 0$
Plane (9)	$0·0651X - 0·7147Y + 0·6964Z + 0·0000 = 0$	$0·0553X - 0·7084Y + 0·7037Z + 0·0000 = 0$
(*b*) Deviations of atoms (Å) from planes (starred atoms not used to define plane)		
Plane (1) = *bc* plane	Cu 0·000; Cu^{vi} 0·000; Cu^{x} 0·000; Cl(1)* −0·283;	Mn 0·000; Mn^{vi} 0·000; Mn^{x} 0·000; Cl(1)* −0·278;
Plane (2) = *ab* plane	Cu 0·000; Cu^{xi} 0·000; Cu^{vi} 0·000;	Mn 0·000; Mn^{xi} 0·000; Mn^{vi} 0·000;
Plane (3) = Cu$-$Cl(2) along *b* axis	Cu 0·000; Cl(2) 0·000; Cu^{vi} 0·000;	Mn 0·000; Cl(2) 0·000; Mn^{vi} 0·000;
Plane (4) = infinite chain of Cu$-$[Cl(1)]$_4$ on the *b* axis	Cu 0·000; Cl(1)−0·043; Cl(1^{iii}) 0·043; Cl(1^{iv}) 0·043; Cl(1^{ii}) −0·043; Cu^{vi} 0·000; Cl(1^{vi}) −0·043; Cl(1^{viii}) 0·043; Cl(1^{v}) 0·043; Cl(1^{vii}) −0·043;	Mn 0·000; Cl(1) −0·036; Cl(1^{iii}) 0·036; Cl (1^{iv}) 0·036; Cl(1^{ii}) −0·036; Mn^{vi} 0·000; Cl(1^{vi}) −0·036; Cl(1^{viii}) 0·036; Cl(1^{v}) 0·036; Cl(1^{vii}) −0·036;
Plane (5) = one Cu$-$[Cl(1)]$_4$ unit on the *b* axis	Cu 0·000; Cl(1) 0·000; Cl(1^{iii}) 0·000; Cl(1^{iv}) 0·000; Cl(1^{ii}) 0·000;	Mn 0·000; Cl(1) 0·000; Cl(1^{viii}) 0·000; Cl(1^{iv}) 0·000; Cl(1^{ii}) 0·000;
Plane (6) = N$-$C$-$C$-$N chain	C 0·000; N 0·000; C^{ix} 0·000; N^{ix} 0·000; H(1)* 0·907; H(2)* −0·782; H(3)* −0·811; H(4)* −0·035; H(5)* 0·788;	C 0·000; N 0·000; C^{ix} 0·000; N^{ix} 0·000; H(1)* 0·812; H(2)* −0·916; H(3)* −0·758; H(4)* −0·009; H(5)* 0·809;
Plane (7) = CH$_2$ group	C 0·000; H(1) 0·000; H(2) 0·000;	C 0·000; H(1) 0·000; H(2) 0·000;
Plane (8) = triangle through H(3), H(4), H(5)	H(3) 0·000; H(4) 0·000; H(5) 0·000; N* −0·356;	H(3) 0·000; H(4) 0·000; H(5) 0·000; N* −0·331;
Plane (9) = infinite chain of Cu$-$[Cl(2)]$_2$ units in the direction [011]	Cu 0·000; Cl(2) 0·207; Cl(2^{iv}) −0·207; Cu^{ii} 0·000; Cl(2^{ii}) 0·207; Cl(2^{iii}) −0·207; Cl(1)* −0·111; Cl(1^{iv})* 0·111;	Mn 0·000; Cl(2) 0·222; Cl(2^{iv}) −0·222; Mn^{ii} 0·000; Cl(2^{ii}) 0·222; Cl(2^{iii}) −0·222; Cl(1)* −0·325; Cl(1^{iv})* 0·325;
(*c*) Dihedral angle or distance between two planes		
Plane (1)$-$Plane (3)	82·56 (04)°	82·72 (08)°
Plane (1)$-$Plane (4)	8·75 (05)	8·79 (10)
Plane (4)$-$Plane (5)	1·41 (07)	1·13 (14)
Plane (6)$-$Plane (7)	89·73 (26)	89·33 (56)
Plane (6)$-$Plane (8)	89·62 (26)	89·00 (54)
Plane (1)$-$Plane (6)	84·99 (08)	87·83 (16)
Plane (2)$-$Plane (6)	47·02 (08)	48·17 (16)
Plane (7) and nearest Plane (7) of the same chain	1·15 Å	1·11 Å
(*d*) Angle between plane and bond (°)		
Plane (6)$-$bond C$-$H(1)	34·54 (30)	39·00 (70)
Plane (6)$-$bond C$-$H(2)	38·85 (30)	33·51 (72)
Plane (8)$-$bond N$-$C	88·91 (20)	88·51 (50)
Plane (7)$-$bond N$-$C	60·76 (24)	62·96 (58)
Plane (7)$-$bond C$-$C^{ix}	49·94 (24)	47·90 (58)
Plane (1)$-$bond Cu$-$Cl(2)	82·08 (06)	–
Plane (1)$-$bond Mn$-$Cl(2)	–	82·53 (13)

Table 6. *Principal axes of thermal motion*

Direction cosines of the principal axes are referred to the 'reference Cartesian system', where x is parallel to **a**, y is parallel to (**a** × **b**) × **a**, z is parallel to **a** × **b** (computed with *ORTEP* II, Johnson, 1971).

$EDACuCl_4$

	r.m.s. displacement	Row vectors, based on reference		
Cu	0·097017	0·7833746	0·2863013	0·5516845
	0·115854	−0·6215204	0·3521910	0·6997670
	0·152432	0·0060459	−0·8910629	0·4538396
Cl(1)	0·113698	−0·2361986	0·6847355	0·6894545
	0·161373	−0·4199458	0·5679154	−0·7078966
	0·181929	−0·8762738	−0·4567377	0·1534109
Cl(2)	0·122370	−0·9445586	−0·1215465	−0·3050171
	0·150582	−0·3209011	0·1450758	0·9359356
	0·201937	−0·0695091	0·9819264	−0·1760370
C	0·104723	−0·3000308	−0·2371416	0·9239834
	0·131058	−0·9508422	0·1522103	−0·2696873
	0·229067	−0·0766857	−0·9594769	−0·2711520
H(1)	0·111832	0·0441973	−0·0035639	−0·9990165
	0·234236	−0·9818287	0·1845753	−0·0440953
	0·389746	0·1845509	0·9828119	0·0046586
H(2)	0·170913	−0·9983974	0·0527974	0·0203709
	0·210804	−0·0441054	−0·9515034	0·3044601
	0·363918	0·0354577	0·3030737	0·9523072
N	0·120668	−0·9672604	0·0566306	0·2473870
	0·152211	0·2252938	−0·2571489	0·9397431
	0·207786	0·1168335	0·9647111	0·2359714
H(3)	0·158370	−0·4829902	0·0802204	0·8719433
	0·211035	−0·8706354	−0·1501593	−0·4684508
	0·295340	0·0933511	−0·9854019	0·1423682
H(4)	0·145382	−0·9231394	0·2248999	−0·3118232
	0·233144	−0·3842942	−0·5155654	0·7658396
	0·327244	0·0114720	0·8268086	0·5623664
H(5)	0·152635	−0·9550285	−0·2840862	0·0849452
	0·266295	−0·1056109	0·5935919	0·7978064
	0·329046	−0·2770685	0·7529566	−0·5968997

$EDAMnCl_4$

	r.m.s. displacement	Row vectors, based on reference		
Mn	0·105613	−0·3229209	0·9234685	−0·2071907
	0·131694	0·8713966	0·3755344	0·3156610
	0·192475	0·3693102	−0·0786117	−0·9259752
Cl(1)	0·101815	0·0665494	−0·8539653	−0·5160566
	0·160647	−0·0198586	0·5159672	−0·8563781
	0·225030	0·9975855	0·0672396	0·0173788
Cl(2)	0·150082	−0·0310180	−0·9706907	0·2383223
	0·175954	−0·3999850	−0·2064579	−0·8929653
	0·184395	0·9159967	−0·1230234	−0·3818578
C	0·113782	0·1343835	−0·8890385	0·4376661
	0·187197	0·9414399	0·2523792	0·2235971
	0·196170	−0·3092443	0·3819885	0·8708919
H(1)	0·163318	0·0534901	−0·1761258	0·9829133
	0·266301	−0·9956785	−0·0842395	0·0390901
	0·352827	0·0759154	−0·9807565	−0·1798707
H(2)	0·091062	−0·0539458	−0·9912146	0·1207620
	0·285675	0·9140432	−0·0977079	−0·3936728
	0·330963	0·4020136	0·0891447	0·9112839
N	0·142578	−0·9448182	−0·3188708	0·0751005
	0·176677	0·2301524	−0·4829646	0·8448521
	0·196013	−0·2331277	0·8155162	0·5297026
H(3)	0·189345	−0·9503494	−0·2356111	−0·2032815
	0·230847	−0·2797054	0·3604558	0·8898520
	0·254007	−0·1363850	0·9025293	−0·4084606
H(4)	0·202419	0·1187392	0·7249122	−0·6785303
	0·239413	0·5176006	−0·6283600	−0·5807351
	0·309789	−0·8473433	−0·2822516	−0·4498260
H(5)	0·174532	0·5207863	0·7915414	0·3197559
	0·242767	0·6139758	−0·0870432	−0·7845108
	0·277965	−0·5931402	0·6048849	−0·5313182

straight hydrogen bond, –N–H(5)···Cl(2), in both structures, 2·541 (8)‖2·376 (12) Å and 153·2 (5)‖162·3 (8)°.

In $EDAMnCl_4$ its length does not differ too much (~7 e.s.d.'s) from the other two hydrogen bonds and the distances of H(5) to Cl(1^{I}) and Cl(1), which are next nearest to the N atom (after H-bonded Cl atoms), are 2·997 (11) and 3·058 (10) Å, respectively. Therefore, it may be stated that in $EDAMnCl_4$ the ammonium H atoms form pure hydrogen bonds to three nearest Cl atoms only.

In contrast, in $EDACuCl_4$, the third hydrogen bond is significantly longer (~36 e.s.d.'s) than two shorter bonds and the distances H(5) to Cl(1^{I}) and Cl(1) [which in this structure are nearer to the N atom than the third hydrogen-bonded Cl(2) atom] are 2·806 (7) and 2·905 (6) Å, respectively. These two distances can be classified as normal van der Waals H–Cl contacts, with the expected value of 2·8 Å (Koetzle, Lehmann, Verbist & Hamilton, 1972) and their weak interaction may explain why the –N–H(5)···Cl(2) bond is so bent.

Fig. 2 illustrates how adjacent ammonium groups are hydrogen bonded to the metal–halogen framework. Each out-of-plane Cl(2) atom is bonded to two H atoms belonging to two neighbouring ammonium groups, while each in-plane Cl(1) atom is linked to only one H atom, H(4). The shortest bond, Cl(1)···H(4), contributes to the lifting of Cl(1) and thus to the tilting of the metal–Cl_6 octahedron. The sequence of hydrogen bonds ···H(5^a)–N^a–H(3^a)···Cl(2^{I})···H(5^b)–N^b–H(3^b)···Cl(2^{II})··· runs across the crystal in a zig-zag line parallel to the b axis and the pair of bonds H(3^a)···Cl(2)···H(5^b) tilts the metal–Cl_6 octahedron in the same direction as it is already tilted by the lifting-up effect of the H(4)···Cl(1) bond.

(*d*) *Corrections for bond lengths and thermal motion*

For several reasons it seems to be justifiable to draw only qualitative conclusions about the thermal motion in both structures. First of all, there is considerable thermal motion of the organic chains with r.m.s. displacements as large as ~0·300 Å (compared with

Table 7. C—H *and* N—H *bond distances corrected for thermal motion*

u_H, u_X: total r.m.s. displacements of atoms H, X normal to the X—H bond, v_H, v_X: total r.m.s. displacements of atoms H, X in the direction of the X—H bond. The corrected bond length $d = d_o + w/2d_o$, where d_o is the uncorrected bond length and w is the correction: $w = (u_H - u_X)^2$ for minimum bond length; $w = (u_H + u_X)^2$ for maximum bond length; $w = u_H^2 - u_X^2$ for H atom riding on X atom; $w = u_H^2 + u_X^2$ for independent motion of H and X atoms. (See Busing, Martin & Levy, 1964; Busing & Levy, 1964; Johnson, 1969.)

	C—H(1)	C—H(2)	Mean C—H	N—H(3)	N—H(4)	N—H(5)	Mean N—H
EDACuCl$_4$							
Total r.m.s. displacements (Å)							
v_X	0·144 (6)	0·226 (4)		0·160 (5)	0·150 (5)	0·207 (4)	
u_X	0·284 (4)	0·284 (4)		0·285 (3)	0·285 (3)	0·285 (3)	
v_H	0·139 (13)	0·238 (9)		0·169 (11)	0·169 (12)	0·272 (9)	
u_H	0·469 (7)	0·454 (7)		0·369 (7)	0·428 (7)	0·450 (8)	
Bond lengths (Å)							
uncorrected	1·101 (7)	1·004 (8)	1·053	1·017 (8)	1·005 (8)	0·961 (9)	0·994
minimum	1·117	1·019	1·068	1·023	1·016	0·975	1·005
riding motion	1·164 (8)	1·067 (9)	1·115	1·055 (9)	1·056 (9)	1·024 (10)	1·045
independent motion	1·238 (9)	1·147 (10)	1·192	1·134 (9)	1·137 (10)	1·108 (11)	1·126
maximum	1·358	1·276	1·317	1·245	1·258	1·242	1·248
EDAMnCl$_4$							
Total r.m.s. displacements (Å)							
v_X	0·190 (8)	0·146 (11)		0·186 (7)	0·172 (7)	0·186 (8)	
u_X	0·294 (6)	0·294 (6)		0·300 (5)	0·300 (5)	0·300 (5)	
v_H	0·195 (19)	0·122 (24)		0·232 (14)	0·263 (16)	0·207 (16)	
u_H	0·471 (11)	0·446 (11)		0·392 (10)	0·440 (11)	0·408 (11)	
Bond lengths (Å)							
uncorrected	1·044 (12)	1·101 (12)	1·073	0·959 (14)	0·973 (15)	1·009 (15)	0·980
minimum	1·059	1·112	1·085	0·963	0·983	1·015	0·987
riding motion	1·109 (14)	1·152 (13)	1·130	0·992 (16)	1·027 (17)	1·047 (16)	1·022
independent motion	1·191 (14)	1·231 (14)	1·211	1·086 (17)	1·119 (17)	1·136 (16)	1·114
maximum	1·324	1·350	1·337	1·208	1·255	1·257	1·240

Table 8. *Corrections for the thermal vibrations for* C—C *and* C—N *bonds*

For explanation of symbols see Table 7.

	EDACuCl$_4$		EDAMnCl$_4$	
	C—C	C—N	C—C	C—N
Total r.m.s. displacements (Å)				
v_X	0·140 (5)	0·130 (5)	0·152 (7)	0·145 (6)
u_X	0·284 (4)	0·285 (3)	0·294 (6)	0·300 (5)
v_C	0·140 (5)	0·127 (7)	0·152 (7)	0·185 (7)
u_C	0·284 (4)	0·284 (4)	0·294 (6)	0·294 (6)
Bond lengths (Å)				
uncorrected	1·503 (5)	1·483 (3)	1·497 (8)	1·485 (6)
minimum	1·503	1·483	1·497	1·485
riding motion	1·503 (5)	1·483 (3)	1·497 (8)	1·486 (6)
independent motion	1·557 (5)	1·538 (3)	1·555 (8)	1·544 (6)
maximum	1·611	1·592	1·612	1·604

~0·010 Å in e.s.d.'s of the bond lengths). Thus a correction of several hundredths of an ångström for a bond length may already contain a significant error (Cruickshank, 1969). Furthermore, the quality of the data from twinned samples is inherently lower than that from an untwinned single crystal, if collected with the same care. Therefore no detailed study of thermal motion is presented. In the absence of a detailed knowledge of the nature of atomic vibrations we confined our calculations to lower and upper limits of bond lengths (Busing & Levy, 1964) which are summarized in Tables 7 and 8. These limits are consistent with expected values of bond lengths. The riding model seems to be an adequate approximation for the correction of X—H bonds; for C—C and C—N bonds (riding correction not applicable) the correction for independent motion clearly overcorrects the bond lengths. Correction for independent motion was applied to interatomic distances in the metal—halogen framework and to H···Cl hydrogen bonds.

In both structures large anisotropic vibrations of organic chains are caused by a complete lack of contact between neighbouring chains. Although the ammonium group $-NH_3$ exhibits hindered rotation at room temperature (Kammer, 1976*a,b*),* the amplitudes of thermal vibrations of ammonium H atoms are smaller than those of H atoms in the CH_2 group.

Main axes of thermal ellipsoids and their direction cosines (computed with *ORTEP*, Johnson, 1971) are given in Table 6.

Conclusions

Both structures were refined with H atoms and with anisotropic temperature factors; the structure of $EDACuCl_4$ reported by Birrell & Zaslow (1972) without H positions was essentially confirmed. The only difference is in the length of the *b* axis: 7·187 (6) Å in Birrell & Zaslow and our value is 7·158 (3)Å.

The differences in unit-cell dimensions of both structures can be explained in terms of the metal—Cl bonding. The dimension *a* consists of the length of the organic chain $N-CH_2-CH_2-N$ (which turned out to be identical in both structures) and twice the distance of N from the *bc* plane. This distance is 2·173 (2)‖ 2·416 (4)Å, and twice the difference 0·486 (5) Å, equals approximately the difference in the *a* parameter, *i.e.* 0·500 (3) Å. As we have seen in the preceding section, ammonium groups enter only 0·049 (5) Å more deeply into the cavities of the metal—halogen layer in $EDACuCl_4$ and therefore a major part of this difference is attributed to metal—Cl(2) bonds. The dimensions *b* and *c* are determined by metal—Cl(1) contacts only; they cannot be affected by organic chains as they completely lack any contact with their neighbours.

The hydrogen-bonding scheme in both structures is the same, but in $EDAMnCl_4$ we find only pure hydrogen bonding while in $EDACuCl_4$ one of the ammonium H atoms, H(5), has van der Waals contacts to the two nearest Cl atoms as well, which contribute to the strong bending of this hydrogen bond.

The puckering of metal—halogen layers (defined here as an angle subtended by adjacent planes fitted through the infinite chain of metal—$[Cl(1)]_4$ units in the direction of the *b* axis) is (within experimental error) equal in both structures, although the valence angles metal—Cl(1)—metal, 166·46 (06)‖161·04 (12)°, differ significantly. In $NH_3(CH_2)_3NH_3MnCl_4$, as reported by Willett & Riedel (1975), this angle is 167·7 (1) and we think therefore that the angle metal—Cl(1)—metal is not as good an indicator of the degree of puckering as the angle defined above.

Comparing these two structures with related room-temperature structures (Steadman & Willett, 1970; Ferguson & Zaslow, 1971; Larsen, 1974; Peterson & Willett, 1972; Willett & Riedel, 1975; Walpen, 1976), we can draw the following conclusions:

(*a*) The geometry of a metal—Cl_6 octahedron is determined predominantly by the nature of the metal atom and is only slightly affected (if at all) by hydrogen bonding.

(*b*) The puckering of the metal—halogen network is predominantly caused by forces of hydrogen bonding.

It has been demonstrated here that in the absence of a single-crystal sample suitable for neutron diffraction work, the presented method which uses neutron data collected from a twin is capable of the determination of H atom positions with far greater certainty and accuracy than an X-ray diffraction single-crystal study.

For a more detailed analysis of thermal motion the quality of the data could have been improved by a detailed knowledge of the distribution of twin volumes which would allow a more adequate treatment of absorption and extinction corrections. We think, however, that a great amount of the thermal motion at room temperature is genuine (*i.e.* that it was not artificially introduced by measuring the data on twins). If a greater accuracy in bond distances and angles were needed, a data collection at lower temperatures would be opportune.

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* Nuclear quadrupole resonance measurements on deuterium atoms of $EDACuCl_4$ with fully deuterated ND_3 groups indicate that the ND_3 groups rotate with a frequency substantially higher than a Larmor frequency of 14 MHz. At the temperature of 108 ± 5 K a discontinuous transition takes place and the rotation of ND_3 groups freezes.

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Comparison of Two Independent Determinations of the Structure of Calcium L-Ascorbate Dihydrate

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Two independent determinations of the crystal structure of calcium L-ascorbate dihydrate, $Ca^{2+}(C_6H_7O_6^-)_2.2H_2O$ [Hearn & Bugg (1974). *Acta Cryst.* B**30**, 2705–2711 and Hvoslef & Kjellevold (1974). *Acta Cryst.* B**30**, 2711–2716], are compared by use of normal probability plots. The two sets of measured structure factors give a normal probability plot that is largely linear, with a slope of 2·7 and nearly zero intercept. Both sets are hence drawn from essentially similar populations that differ only slightly in systematic error distribution, with pooled standard deviations underestimated by a factor of nearly three. Difficulties in comparing the original atomic position and thermal parameters and standard deviations were obviated by additional least-squares refinement of both sets under identical conditions. A half-normal probability plot based on the refined parameters is nearly linear with a slope of 1·7 and zero intercept. The ascorbate ion is shown, from the anomalous scattering contribution to both sets of data, to be the L-enantiomer. The crystal structure of calcium L-ascorbate is best represented by the weighted mean of the two independent parameter sets.

Introduction

The chances that two or more independent determinations of a given crystal structure may be undertaken nearly simultaneously have greatly increased since automatic diffractometers and a more powerful methodology have become rather widely available. It is highly desirable in such cases to present a detailed comparison of the replicate structural information. Such information is valuable for several reasons. Should the differences between determinations be identified as primarily random, confidence in the meas-