Pergamon

0277–5387(95)00248–0

Polyhedron Vol. 15, No. 2, pp. 225–232, 1996
Elsevier Science Ltd
Printed in Great Britain
0277–5387/96 $9.50+0.00

THE X-RAY CRYSTAL STRUCTURES OF DOUBLE SALTS OF HEXAHALORHODATE(III) AND HALIDE WITH THE ETHANE-1,2-DIAMMONIUM CATION†

R. D. GILLARD,‡ DAVID E. HIBBS, CAROLYN HOLLAND,
MICHAEL B. HURSTHOUSE,‡ K. M. ABDUL MALIK
and GEORGIA SYKARA

Department of Chemistry, University of Wales Cardiff, P.O. Box 912,
Cardiff CF1 3TB, U.K.

(*Received* 23 *March* 1995; *accepted* 17 *May* 1995)

Abstract—The compounds precipitated on adding 1,2-diaminoethane (en) to hexachlororhodate(III) and hexabromorhodate(III) solutions in hydrochloric and hydrobromic acids, although classically described as anhydrous, are actually the hydrated $[enH_2]_2[RhCl_6][Cl]\cdot H_2O$ and $[enH_2]_2[RhBr_6][Br]\cdot H_2O$. The X-ray crystal structures of both compounds are reported. In each case, the cations adopt a *trans* conformation and the complex anion closely approximates to O_h symmetry. However, the crystals are not isostructural, but closely related. The *c* axis of the chloride is approximately double that of the bromide. Some spectroscopic and chemical properties of the double salts are given.

Complex compounds obtained from rhodium(III) chloride and 1,2-diaminoethane (en) have attracted much interest.[2] Many contain bonds from nitrogen to rhodium: these include salts of $[(en)RhCl_4]^-$, *cis*- and *trans*-$[Rh(en)_2Cl_2]^+$ and $[Rh(en)_3]^{3+}$.

Quite apart from these is the carmine-red compound obtained by mixing solutions in aqueous hydrochloric acid of 1,2-diaminoethane and rhodium(III) chloride. The square plates may readily be recrystallized unchanged from dilute hydrochloric acid. A dark red–brown compound is also obtained by mixing solutions in aqueous HBr of 1,2-diaminoethane and of rhodium(III)bromide. The crystals may be recrystallized from hydrobromic acid. The stoichiometry was until now taken as $[enH_2]_2[RhX_7]$, where X is Cl or Br, and the apparently seven-coordinated rhodium centre was discussed by Werner.[3] Its nature was studied by Gutbier,[4] with several chlororhodates, including $[N(CH_3)_4][RhCl_7]$ and (apparently independently) by Meyer.[5,6] Meyer and Kienitz concluded,[5] on the basis of an early application of visible spectra, that the compound probably contained the $[RhCl_6]^{3-}$ ion.

The $[enH_2]_2[RhBr_7]$ compound was originally made by Meyer and Hoehne[7] along with the chlorine analogue and other compounds, but to the best of our knowledge neither compound has been studied since.

The present study was undertaken to clarify the exact coordination geometry around rhodium and the nature of interactions with cations in the solid state.

EXPERIMENTAL

$[enH_2]_2[RhCl_6][Cl]\cdot H_2O$ (A)

(i) $RhCl_3\cdot nH_2O$ (1.89 m mol, 0.5 g) was added to concentrated HCl (10 cm^3) and the mixture was warmed (hotplate) until the $RhCl_3\cdot nH_2O$ dissolved. The solution was deep red: its electronic spectrum confirmed that the hexachlororhodate(III) ion $[RhCl_6]^{3-}$ was present. When ethylenediamine (0.3 cm^3) in concentrated HCl (3 cm^3) was added, a brick red precipitate formed immediately. This was collected by filtration and recrystallized from 4 M

---

† See ref. 1.

‡ Authors to whom correspondence should be addressed

hydrochloric acid. The carmine-red crystals were dried *in vacuo*. In accord with earlier descriptions[4,5] they were tetragonal prisms with right-angled corners and highly reflective. The yield of the recrystallized product was 51%.

(ii) The above preparation was repeated with all quantities doubled. The electronic spectrum of the initial rhodium solution confirmed the presence of the $[RhCl_6]^{3-}$ ion. For determination of $[RhCl_6]^{3-}$, the molar extinction coefficient (105.0) of $K_3[RhCl_6]$ for the visible band at 519.8 was determined after extrapolating back to time 0, and used to analyse solutions of the compound, again extrapolated to time 0. The yield of the recrystallized product was 1.14 g. Found: C, 9.7; H, 4.4; N, 11.0; $[RhCl_6]^{3-}$, 64.8%. Calc. for $[enH_2]_2[RhCl_6][Cl]\cdot H_2O$ ($C_4H_{22}N_4Cl_7ORh$): C, 9.7; H, 4.5; N, 11.3; $[RhCl_6]^{3-}$, 64.0%.

The IR spectrum of a single crystal measured using an FTIR microscope showed absorptions (in cm^{-1}) at: 3587 (m), 3530 (m), 3237 (vb, vs), 1848 (b, w), 1575 (b, s), 1545 (sh), 1510 (sh), 1500 (s), (CH_2 scissors), 1460 (sh), 1324 (m), *1020 (vb, s) and *760 (b, w). In mull spectra, the bands marked * had much more clearly resolved structure at: 1060 (sh), 1030 (w), 1008 (s), (CN str), 1002 (m), 971 (m), 806 (w), 791 (w) (CH_2 rock), 749 (m). A weak band at 1160 cm^{-1} becomes well defined in mull spectra. The IR spectrum in a KBr disc showed absorptions at 455 (m) and 330 cm^{-1}.

Potassium hexachlororhodate (III)

$RhCl_3\cdot nH_2O$ (0.5 g, 1.9 mmol) and KCl (0.5 g, 6.7 mmol) were added to concentrated HCl (50 cm^3). The red–brown solution was heated (hotplate) and stirred for 30 min. The electronic spectrum confirmed that the $[RhCl_6]^{3-}$ ion had been obtained. The deep-red solution was evaporated to 30 cm^3 and left to cool. The crystals obtained were collected and dried *in vacuo*. Yield 0.21 g. The filtrate evaporated to 10 cm^3 and left to cool gave a second crop (0.19 g).

cis-*Dichlorobis*-1,2-*diaminoethanerhodium*(III) *chloride*

The double salt (**A** above; 0.1 g) was added to dilute sodium hydroxide solution (10 cm^3) and the whole set to reflux for 30 min. A preliminary experiment had shown that, in the absence of the condenser, less than one-tenth of the amine distilled out. The contents of the reflux flask were centrifuged, removing a small amount of black solid. The filtrate had maximal absorption at 365 nm, and after neutralization with dilute hydrochloric acid and heating, this shifted to 347 nm: cf.[2] *cis*-Cl_2, (350, ε 195) vs *trans*-Cl_2 (406 ε 75). The cation could be precipitated using nitrate or perchlorate.

$[enH_2]_2[RhBr_6][Br]\cdot H_2O$ (**B**)

(i) *Preparation of* $RhBr_3\cdot nH_2O$. $RhCl_3$ (1.0 g) was dissolved in H_2O (13 cm^3). KOH was added dropwise to the solution until a yellow–red precipitate was formed. This was collected and dissolved in concentrated HBr. The solution was dark red. The same procedure was repeated twice more in order to obtain pure $RhBr_3$ in the red solution.

(ii) *Preparation of* $(enH_2)_2[RhBr_6][Br]\cdot H_2O$. $RhBr_3\cdot H_2O$ (6 cm^3) was added to concentrated HBr (8 cm^3) and the mixture warmed until the solution was bright red; this was then left for a while and some dark red crystals of unknown identity were formed. Those were removed. Ethylenediamine (0.3 cm^3) in concentrated HBr (3 cm^3) was added to the intense-red filtrate and a precipitate was formed. This was collected by filtration and recrystallized from dilute HBr. The dark red–brown crystals were dried *in vacuo*. In agreement with an earlier description,[7] they were shiny right-angled prisms and leaflets. Found: C, 6.1; H, 3.0; N, 7.3. Calc. for $[enH_2]_2[RhBr_6][Br]\cdot H_2O$ ($C_4H_{22}N_4Br_7ORh$): C, 6.0; H, 2.8; N, 7.0%.

The IR spectrum of a single crystal using the FTIR microscope showed absorptions (cm^{-1}) at: 3581 (m), 3523(w), 3225–2711 (broad), 2622(w), 2521(m), 2400(m), 2267(w), 2229(w), 1822(s), 1594(s), 1486(s), 1359(s), 1321(s), 1048(s), 997(s), 775(s). The IR spectrum in a KBr disc showed absorption at 260(s) cm^{-1}.

X-ray structure determination of $[enH_2]_2[RhCl_6][Cl]\cdot H_2O$ (**A**) *and* $[enH_2]_2[RhBr_6][Br]\cdot H_2O$ (**B**)

X-ray structure determinations of compounds **A** and **B** were undertaken to determine unambiguously their exact stoichiometry and nature of bonding interactions. Table 1 shows the crystal data and details of data collection and refinement for **A** and **B**.

All crystallographic measurements were made using a Delft Instruments FAST TV area-detector diffractometer positioned at the window of rotating anode generator with Mo-K_α radiation by following previously described procedures.[8]

The structures were solved by the heavy atom procedure[9] and refined on F^2 using full-matrix least squares.[10] All non-hydrogen atoms were anisotropic. The hydrogen atoms in the structure of compound **A** were located from a difference map and

Table 1

	Complex **A**	Complex **B**
Formula	$(C_4H_{20}N_4)[RhCl_6][Cl] \cdot H_2O$	$(C_4H_{20}N_4)[RhBr_6][Br] \cdot H_2O$
M. wt	493.32	804.54
Crystal system	Monoclinic	Monoclinic
a (Å)	8.062(2)	8.296(4)
b (Å)	10.003(1)	10.190(5)
c (Å)	20.701(4)	10.794(3)
α (°)	90.0	90.0
β (°)	90.83(1)	90.68(4)
γ (°)	90.0	90.0
V (Å^3)	1669.2(4)	912.4(7)
Space group	$P2_1/c$	$P2_1/m$
Z	4	2
D_c (g cm^{-3})	1.963	2.928
F(000)	984	744
μ(Mo-K_α) (cm^{-1})	21.32	162.56
T (K)	293	120(2)
Crystal size (mm)	$0.20 \times 0.08 \times 0.06$	$0.18 \times 0.10 \times 0.08$
θ range for data (°)	3.1–29.7	1.89–25.09
h_{min}, h_{max}	−10, 4	−9, 9
k_{min}, k_{max}	−13, 13	−12, 12
l_{min}, l_{max}	−26, 28	−10, 12
Total data measured	5312	4012
Total unique	2359	1505
R_{int}	0.063	0.0692
Total observed	1745	1204
No. of parameters	154	94
ρ_{min}, ρ_{max} (e Å^{-3})	−0.55, 0.60	−1.184, 1.767
$(\Delta/\sigma)_{max}$	0.004	0.001
Weighting scheme	$w = 1/\sigma^2[F_o^2]$	$w = 1/\sigma^2[F_o^2]$
$R^a[I > 2\sigma(I)]$	0.0346	0.0341
$wR_2[2\sigma(I)]$	0.1007	0.0877
R^a (all data)	0.0431	0.0443
wR_2 (all data)	0.1134	0.0896

[a] $R = \Sigma(\Delta F)/\Sigma(F_o)$; $wR_2 = [\Sigma\{w(\Delta F^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$.

included in the calculation of F_c with a fixed $U_{iso} = 0.05$ Å, whereas in the structure of compound **B** the hydrogen atoms were placed in idealized positions and included in the calculation of F_c with a U_{iso} tied to the U_{eq} of the parents. No parameters of these atoms were refined. All calculations were performed on a 486DX2/66 personal computer. Sources of scattering factor data are given in ref. 10.

Important bond lengths and angles for both compounds **A** and **B** are given in Tables 2 and 3, respectively, and the dimensions of possible hydrogen bonds in Tables 4 and 5, respectively. Tables of fractional coordinates and anisotropic displacement parameters of the non-hydrogen atoms, hydrogen-atom parameters, and tables of structure factors have been deposited with the editor.

RESULTS AND DISCUSSION

Analytical results for the crystalline materials agreed well with the heptahalide monohydrate formulation. Thermogravimetric analysis for $[enH_2]_2[RhCl_6][Cl] \cdot H_2O$ showed a loss from 100 to 140°C, corresponding to about one water molecule, whereas the presence of one water molecule in $[enH_2]_2[RhBr_6][Br] \cdot H_2O$ was shown from the loss of mass at 95–120°C. The IR spectra of the two compounds from 4000 to 400 cm^{-1} were almost superimposable. The IR spectrum of $[enH_2]_2[RhCl_6][Cl] \cdot H_2O$ showed two sharp bands at 3587 and 3530 cm^{-1}, owing to symmetric–antisymmetric vibrations of the water of crystallization. This was in addition to the very strong and broad absorption centred at *ca* 3000 cm^{-1} with a width of

Table 2. Selected bond lengths (Å) and angles (°) for $[enH_2]_2[RhCl_6][Cl] \cdot H_2O$ (**A**)

Rh—Cl(1)	2.356(1)	Rh—Cl(2)	2.346(1)
Rh—Cl(3)	2.342(1)	Rh—Cl(4)	2.342(2)
Rh—Cl(5)	2.346(1)	Rh—Cl(6)	2.342(1)
N(1)—C(2)	1.489(8)	C(2)—C(3)	1.485(9)
C(3)—N(4)	1.480(8)	N(5)—C(6)	1.465(8)
C(6)—C(6^{i})*	1.468(13)	N(7)—C(8)	1.480(9)
C(8)—C(8^{ii})	1.475(11)		

Cl(2)—Rh—Cl(1)	90.31(5)	Cl(3)—Rh—Cl(1)	179.17(4)
Cl(4)—Rh—Cl(1)	89.94(6)	Cl(5)—Rh—Cl(1)	89.47(5)
Cl(6)—Rh—Cl(1)	90.72(6)	Cl(3)—Rh—Cl(2)	90.50(5)
Cl(4)—Rh—Cl(2)	89.37(6)	Cl(5)—Rh—Cl(2)	179.77(4)
Cl(6)—Rh—Cl(2)	89.40(5)	Cl(4)—Rh—Cl(3)	89.89(6)
Cl(6)—Rh—Cl(3)	89.46(6)	Cl(5)—Rh—Cl(3)	89.72(5)
Cl(5)—Rh—Cl(4)	90.55(6)	Cl(6)—Rh—Cl(4)	178.61(5)
Cl(6)—Rh—Cl(5)	90.68(6)		
C(3)—C(2)—N(1)	111.9(5)	N(4)—C(3)—C(2)	112.1(5)
N(5)—C(6)—C(6^{i})	113.3(7)	C(8^{ii})—C(8)—N(7)	112.6(7)

* Symmetry transformations used to generate equivalent atoms: (i) $1-x$, $1-y$, $1-z$; (ii) $1-x$, $-y$, $1-z$.

Table 3. Selected bond lengths (Å) and angles (°) for $[enH_2]_2[RhBr_6][Br] \cdot H_2O$ (**B**)

Rh—Br(1)	2.479(1)	Rh—Br(2)	2.474(2)
Rh—Br(3)	2.462(1)	Rh—Br(4)	2.485(1)
Rh—Br(5)	2.477(2)	C(2)—N(1)	1.473(9)
C(2)—C(2$'^{i}$)	1.490(14)	C(4)—N(3)	1.466(9)
C(4)—C(4$'^{ii}$)	1.495(14)		

Br(1)—Rh—Br(2)	90.49(6)	Br(1)—Rh—Br(3)	179.54(4)
Br(1)—Rh—Br(4)	90.55(2)	Br(1)—Rh—Br(5)	88.84(6)
Br(2)—Rh—Br(3)	89.97(6)	Br(2)—Rh—Br(4)	89.48(2)
Br(2)—Rh—Br(5)	179.33(4)	Br(3)—Rh—Br(4)	89.46(2)
Br(3)—Rh—Br(5)	90.70(6)	Br(4$'^{iii}$)—Rh—Br(4)	178.50(5)
Br(4)—Rh—Br(5)	90.52(2)	N(1)—C(2)—C(2$'^{i}$)	111.7(7)
N(3)—C(4)—C(4$'^{ii}$)	111.9(7)		

Symmetry transformations used to generate equivalent atoms: (i) $-x+1$, $-y$, $-z$; (ii) $-x+1$, $-y+1$, $-z+1$; (iii) x, $-y+1/2$, z.

ca 1000 cm^{-1}, characteristic of the RNH_3^+ unit. Finally, the IR spectrum (KBr disc) of the diamagnetic compound showed a very strong absorption at 330 cm^{-1}, which we assign to the Rh—Cl stretching mode, comparable with that at 330 and 310 cm^{-1} in $K_3[RhCl_6]$ and at 330 cm^{-1} in the salt[11] $[N(CH_2CH_2NH_3)_3(RhCl_6)]$. Slightly lower bands were shown in the IR spectrum of $[enH_2]_2[RhBr_6][Br] \cdot H_2O$, as the two bands of the water molecule were shown at 3581 and 3523 cm^{-1}. The characteristic broad peak of RNH_3^+ was shown at 3225 cm^{-1} downwards. In the IR spectra (KBr disc) a strong absorption at 260 cm^{-1} was shown corresponding to the Rh—Br stretching mode, slightly lower than Rh—Cl. The most notable feature of the IR spectrum is its relative simplicity. In a survey of the relationships between vibrations and conformations of en derivatives, Iwamoto and Shriver pointed out[12] the absence of absorption at 1260–1280 cm^{-1} in centrosymmetric en. The present salts show no sign of absorption there.

One chemical reaction merits mention. The salt $[enH_2]_2[RhCl_6][Cl] \cdot H_2O$ represents a simple but exact way of establishing the stoichiometry 2 : 1 for

Table 4. Dimensions of possible hydrogen bonds (distances in Å and angles in °) in $[\mathrm{enH_2}]_2[\mathrm{RhCl_6}][\mathrm{Cl}]\cdot\mathrm{H_2O}$ (**A**)

A—H···B	A—H	A···B	H···B	<AHB
N(1)—H(1A)···Cl(2$^{\mathrm{i}}$)	0.982	3.330	2.488	143.7
N(1)—H(1A)···Cl(6$^{\mathrm{i}}$)	0.982	3.481	2.807	126.5
N(1)—H(1C)···Cl(7$^{\mathrm{i}}$)	0.942	3.228	2.311	164.3
N(5)—H(5B)···O(1$^{\mathrm{i}}$)	0.919	2.907	2.126	142.2
N(7)—H(7C)···O(1$^{\mathrm{i}}$)	0.919	3.063	2.152	170.7
O(1)—H(1W)···Cl(7$^{\mathrm{i}}$)	1.031	3.034	2.144	143.3
N(1)—H(1B)···Cl(1$^{\mathrm{ii}}$)	0.934	3.398	2.566	148.6
N(1)—H(1B)···Cl(4$^{\mathrm{ii}}$)	0.934	3.239	2.565	129.4
N(5)—H(5C)···Cl(3$^{\mathrm{iii}}$)	0.900	3.228	2.630	124.7
N(5)—H(5C)···Cl(4$^{\mathrm{iii}}$)	0.900	3.377	2.539	155.3
N(4)—H(4B)···Cl(7$^{\mathrm{iii}}$)	1.087	3.174	2.136	158.8
N(4)—H(4A)···Cl(2$^{\mathrm{iii}}$)	0.962	3.308	2.391	159.1
N(4)—H(4C)···Cl(6$^{\mathrm{iv}}$)	0.935	3.298	2.653	126.7
N(4)—H(4C)···Cl(1$^{\mathrm{iv}}$)	0.935	3.329	2.486	149.9
N(5)—H(5A)···Cl(4$^{\mathrm{v}}$)	1.095	3.402	2.450	144.6
N(7)—H(7A)···Cl(5$^{\mathrm{v}}$)	0.820	3.296	2.494	166.3
N(7)—H(7B)···Cl(3$^{\mathrm{vi}}$)	0.921	3.173	2.374	145.1
N(7)—H(7B)···Cl(6$^{\mathrm{vi}}$)	0.921	3.450	2.767	131.8

Symmetry codes: (i) x, y, z; (ii) $-x, 1/2+y, 1/2-z$; (iii) $1-x, 1/2+y, 1/2-z$; (iv) $1+x, y, z$; (v) $1+x, 1/2-y, 1/2+z$; (vi) $1-x, -1/2+y, 1/2-z$.

Table 5. Dimensions of possible hydrogen bonds (distances in Å and angles in °) in $[\mathrm{enH_2}]_2[\mathrm{RhBr_6}][\mathrm{Br}]\cdot\mathrm{H_2O}$ (**B**)

A—H···B	A—H	A···B	H···B	<AHB
N(1)—H(1B)···Br(3$^{\mathrm{i}}$)	0.890	3.317	2.481	157
N(3)—H(3A)···Br(2$^{\mathrm{i}}$)	0.890	3.414	2.563	160
N(3)—H(3C)···Br(6$^{\mathrm{i}}$)	0.890	3.364	2.505	162
N(1)—H(1A)···Br(5$^{\mathrm{ii}}$)	0.890	3.416	2.768	131
N(1)—H(1C)···O(1$^{\mathrm{iii}}$)	0.890	2.883	2.009	167
N(3)—H(3B)···Br(1$^{\mathrm{iv}}$)	0.890	3.454	2.603	160
O(1)—H(1W)···Br(6$^{\mathrm{i}}$)	0.951	3.174	2.546	124
O(1)···Br(3$^{\mathrm{v}}$)		3.2655		

Symmetry codes: (i) x, y, z; (ii) $-x, -y, -z$; (iii) $-x+1, -y, -z+1$; (iv) $-x, -y+1, -z+1$; (v) $x+1, y, z+1$.

en : $\mathrm{RhCl_3}$, and on neutralizing the system with sodium hydroxide, bis-complexes may be made, essentially as in eq. (1).

$$[\mathrm{enH_2}]_2[\mathrm{RhCl_6}][\mathrm{Cl}]+6\mathrm{NaOH}\longrightarrow [(\mathrm{en})_2\mathrm{Rh(OH)_2}][\mathrm{Cl}]+6\mathrm{NaCl}+4\mathrm{H_2O} \quad (1)$$

The product gave, with an excess of hot dilute hydrochloric acid, the *cis*-isomer, eq. (2), suggesting that the product of eq. (1) is also the *cis*-isomer.

$$[(\mathrm{en})_2\mathrm{Rh(OH)_2}]^+ +2\mathrm{HCl}\longrightarrow cis\text{-}[\mathrm{Rh(en)_2Cl_2}]^+ +2\mathrm{H_2O} \quad (2)$$

The reactivity of the crystalline material $[\mathrm{enH_2}]_2[\mathrm{RhBr_6}][\mathrm{Br}]\cdot\mathrm{H_2O}$ has not been studied.

It is often the case that salts with such compositions as $\mathrm{C}_x\mathrm{A}_y$ (where C denotes a complex cation, organic or inorganic, and A a complex anion, and where $x \neq y$, particularly where x and y are 2 and 3) are not easily made by precipitation, and that more satisfactory packing (possibly in a kinetic rather than a thermodynamic sense) is obtained by the incorporation of a third component, B, in proportions which give such solids as $C_xA_xB_n$ or $C_xA_{2x}B_n$. Among well-known examples are Hassel's isomorphous trio $[Co(NH_3)_6](SO_4)I$ and $[Co(NH_3)_5(OH_2)](SO_4)X$, (X = Br or I) and the pair $\{[M(en)_3](+)$ tartrate$\}Cl \cdot nH_2O$, with M = Co or Rh. In the present examples, the highest formal charge is on the anions $[RhCl_6]^{3-}$ and $[RhBr_6]^{3-}$: this is probably also the case in Wilm's salt, $(NH_4)_4[RhCl_6] \cdot (NO_3)$. The salts formed here are $[enH_2]_2[RhCl_6][Cl] \cdot H_2O$ and $[enH_2]_2[RhBr_6][Br] \cdot H_2O$, of type $C_{2x}A_xB_1$ [eqs (3) and (4)], an interesting contrast with the C_xA_x possible for $[N(CH_2CH_2NH_3)_3][RhCl_6]$ and $[N(CH_2CH_2NH_3)_3][RhBr_6]$.[11] During attempts to characterize the present double salt $[enH_2]_2[RhCl_6][Cl] \cdot H_2O$, Meyer and Kienitz carried out reaction (5), removed silver chloride and reported obtaining colourless crystals of the presumably similar product, by concentration over sulphuric acid.

$$2en + 4HCl + (RhCl_3)_{aq} \longrightarrow [enH_2]_2[RhCl_6][Cl] \cdot H_2O \quad (3)$$

$$2en + 4HBr + (RhBr_3)_{aq} \longrightarrow [enH_2]_2[RhBr_6][Br] \cdot H_2O \quad (4)$$

$$2(enH_2)_2Cl_2 + Ag_3[Rh(NO_2)_6] \longrightarrow 3AgCl + [enH_2]_2[Rh(NO_2)_6]Cl \quad (5)$$

All the early work[4,5,6] on the nature of compound A is consistent with its true composition, although, in hindsight, silver nitrate titrations were misleading, Meyer, Kawczyk and Hoehne having found[6] four ionizable chloride ions in both the present compound and in $[H_3CNH_3]_4[RhCl_7]$. This led Sidgwick[13] to say that "the heptachlorides appear to include a curious ethylene diamine salt of the composition $RhCl_3(en,2HCl)_2$, of which there is a bromine analogue. This has been shown to be probably a crystal aggregate of the en hydrochloride and the non-ionized form of the trichloride".

The crystal structure of $[enH_2]_2[RhCl_6][Cl] \cdot H_2O$, projected along *a* is shown in Fig. 1. The full unit cell contains four $[RhCl_6]^{3-}$ and four Cl^- anions, eight $[enH_2]^{2+}$ cations, and four H_2O molecules of crystallization, all the species being held together in the crystal by an extensive network of hydrogen bonds and electrostatic interactions (Table 4). All the hydrogens on the H_3N^+-cations are acting as donors, all the seven Cl atoms of the anions are acting as acceptors and the water molecule is acting as both donor and acceptor. The $[RhCl_6]^{3-}$ ion is closely octahedral with Rh—Cl distances 2.342(1)–2.356(1) Å and Cl—Rh—Cl angles 89.37(6)–90.72(6)° (*cis*) and 178.61(5)–179.787(4)° (*trans*). Interestingly, the longest Rh—Cl bond [to Cl(1)] does not seem to be that most involved in hydrogen bonding, and the origin of the small differences in Rh—Cl bond lengths is not clear. One $[enH_2]^{2+}$ ion [containing the N(1) and N(4) atoms] is situated at a general position, whilst two $[enH_2]^{2+}$ ions [containing the unique N(5) and N(7) atoms, respectively] sit on two sets of centres of symmetry (1/2, 1/2, 1/2 and 1/2, 0, 1/2). All the cations have the same *trans* conformation. The bond lengths and angles in these cations are as expected, with the C—C and C—N bonds being equal to 1.468–1.485 and 1.465–1.489 Å.

The crystal structure of $[enH_2]_2[RhBr_6][Br] \cdot H_2O$, viewed along *a* is also shown in Fig. 1. The unit cell contains two $[RhBr_6]^{3-}$ and two Br^- anions, four $[enH_2]^{2+}$ cations, and two H_2O molecules of crystallization, with an extensive network of hydrogen bonding involving all the species. The geometry of the $[RhBr_6]^{3-}$ ion is close to octahedral with Rh—Br distances 2.4619(13)–2.4850(14) Å and Br—Rh—Br angles 88.85(6)–90.71(6)° (*cis*) and 178.50(5)–179.54(3)° (*trans*). All the $[enH_2]^{2+}$ ions are located on centres of symmetry (1, 0, 1/2 and 0, 0, 1), having the same *trans* conformation. The bond lengths and angles in these cations are as expected. The C—C and C—N bond lengths have values between 1.490(1)–1.496(14) and 1.466(9)–1.473(9), respectively.

The two crystal structures are strikingly similar, but they are not isostructural. Both the *a* and *b* axes are comparable, but the *c* axis in the chloro-compound is almost double that in the bromo-compound; both have monoclinic unit cells with a *β* angle very near to 90°, but the space groups are different. The difference lies mainly in the fact that the lattice halide and O(water) in the bromo-compound lie exactly on the crystallographic mirror plane at $y = 1/4$ and 3/4, whereas those in the chloro-compound are significantly displaced from this plane, causing the breakdown of the mirror symmetry. Thus, although the packing of the species have overall similarity, the differences are significant enough to result in different crystal symmetry. These differences are interesting and must be attributed to the sizes of chloride and bromide, and their charge fields.

The mixed bromo–chloro-complex anions $[MBr_nCl_{6-n}]^{x-}$ of some platinum group and other elements have been studied by Mootz and others, chiefly by anion exchange chromatography. Little is known of the rhodium(III) systems $[MBr_nCl_{6-n}]^{3-}$. In particular, selective effects of bromide against chloride have not deliberately been

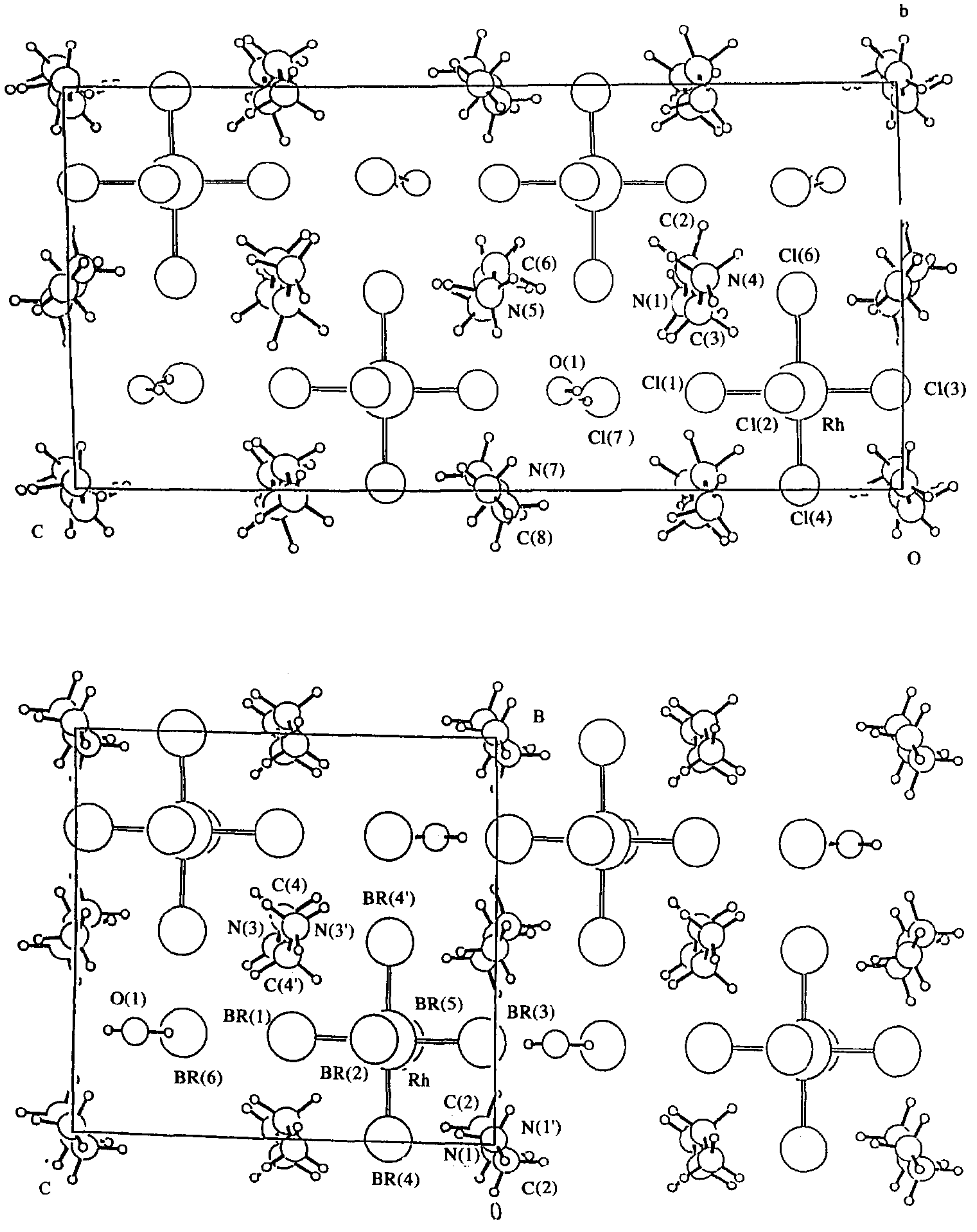

Fig. 1. Crystal structures of $[enH_2]_2[RhCl_6]Cl \cdot H_2O$ (top) and $[enH_2]_2[RhBr_6]Br \cdot H_2O$ (bottom), showing the atom labelling used.

studied, although there was one highly suggestive observation[14] in an examination of species distribution by ^{103}Rh NMR. For the isomeric pair $[MCl_3Br_3]^{3-}$ (*fac* and *mer*), the experimental intensities[14] suggested a distribution of 3 : 1, rather than the statistical[15] 3 : 2.

In view of the many structures known for chelated ligand en, there are surprisingly few available for protonated diaminoethane, although the carbocentric propane-1,2,3-triammonium cations, $[R\text{-}C(CH_2NH_3)_3]^{3+}$ ($R = CH_3$, C_2H_5), closely similar to $[N(CH_2NH_3)_3]^{3+}$, have been analysed[16] in some detail.

In the structures reported for the ethylenediammonium cation, the *trans* conformation seems to be dominant, although by no means exclusive.

The compound $[H_3NCH_2CH_2NH_3][Ni(OH_2)_6](SO_4)_2$, a variant on the standard Tutton salts, contains centrosymmetric organic cations, with the N—C—C—N framework planar and nitrogen atoms mutually *trans*.[17] In environments more akin to the present one, the ethylenediammonium cation is known in the isostructural pair $[enH_2][MX_6]$, for M = Sn or Te, X is Cl,[18] and for M = Pd, X is Br.[19] The $[MX_6]^{2-}$ anion is closely octahedral, and again, the centrosymmetric $[enH_2]^{2+}$ cation has a planar *trans* structure.

In a series of crystallographic studies of the products from aqueous solutions containing en, metal salts and phosphates, Averbuch-Pouchot and coauthors have observed several salts and double salts of the centrosymmetric $[enH_2]^{2+}$ cation, including $[enH_2][HXO_4][X = P, As]$[20] and $[Cu(OH_2)_6][enH_2]_3[P_4O_{12}]_2 \cdot 8H_2O$,[21] where $[enH_2]^{2+}$ is present in both centrosymmetric and non-centrosymmetric conformations.

Several salts of the $[enH_2]^{2+}$ cation involving only its *cis* configuration have been observed. Santhakumari and Vallabham[22] have reported the ethylenediammonium sulphate $[enH_2][SO_4]$, having the *cis*-NH_3^+ groups arranged in symmetrically equivalent positions in the lattice.

There are two other salts with compositions like these of our adducts here. These are reported as $(H_3CNH_3)_4[RhCl_7]$ and $RhBr_3 \cdot 2C_3H_6N_2H_6Br_2$.[7] They should presumably be formulated as containing hexahalorhodate(III) ions, and may be hydrated.

REFERENCES

1. This is part 16 of the series "*Adducts of Coordination Compounds*": Part 15 is R. D. Gillard, L. R. Hanton and S. H. Mitchell, *Polyhedron* 1990, **9**, 2127.
2. F. H. Jardine and P. S. Sheridan, in *Comprehensive Coordination Chemistry* (Edited by G. Wilkinson, R. D. Gillard and J. A. McCleverty), Vol. 823ff. Pergamon Press, Oxford (1987).
3. A. Werner, *Neuere Anschauungen in der Gebiet des Anorganischen Chemie*, p. 227, 3rd edn. F. Enke Verlag (1923).
4. A. Gutbier, *Z. Anorg. Chem.* 1923, **129**, 828.
5. J. Meyer and H. Kienitz, *Z. Anorg. Chem.* 1939, **242**, 281.
6. J. Meyer, M. Kawczyk and K. Hoehne, *Z. Anorg. Chem.* 1937, **232**, 410.
7. J. Meyer and K. Hoehne, *Z. Anorg. Chem.* 1937, **231**, 372.
8. J. A. Darr, S. R. Drake, M. B. Hursthouse and K. M. A. Malik, *Inorg. Chem.* 1993, **32**, 5704.
9. G. M. Sheldrick, *Acta Cryst.* 1990, **A46**, 467.
10. G. M. Sheldrick, SHELXL-93, Program for Crystal Structure Analysis. University of Göttingen, Germany (1993).
11. S. G. Zipp and S. K. Madan, *Inorg. Chim. Acta* 1975, **14**, 83.
12. T. Iwamoto and D. F. Shriver, *Inorg. Chem.* 1971, **10**, 2428.
13. N. V. Sidgwick, *Chemical Elements and their Compounds*, Vol. II, p. 1526. Oxford University Press (1950).
14. B. E. Mann and C. M. Spencer, *Inorg. Chim. Acta* 1982, **76**, L65.
15. P. S. Sheridan, in *Comprehensive Coordination Chemistry* (Edited by G. Wilkinson, R. D. Gillard and J. A. McCleverty), Vol. 4, p. 1058. Pergamon Press, Oxford (1987).
16. R. Cini, G. Giorgi, D. Masi, A. Sabatini and A. Vacca, *J. Chem. Soc., Perkin Trans. 2* 1991, 765.
17. P. C. Healy, J. M. Patrick and A. H. White, *Aust. J. Chem.* 1984, **37**, 1105.
18. W. Abriel, *Acta Cryst.* 1986, **B42**, 449.
19. H. M. Dawes and M. B. Hursthouse, *Polyhedron* 1988, **7**, 2611.
20. M. T. Averbuch-Pouchot, A. Durif and J. C. Guitel, *Acta Cryst.* 1987, **C43**, 1984.
21. M. T. Averbuch-Pouchot and A. Durif, *Acta Cryst.* 1989, **C45**, 46.
22. N. C. Santhakumari and C. P. G. Vallabhan, *J. Phys. Chem. Solids* 1992, **53**, 697.