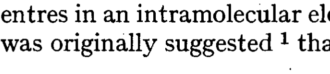
Crystal Structure of μ-Pyrazine-bis(penta-ammineruthenium) Penta-(Bromide Chloride)–Water (1/4)

By **James K. Beattie,** Department of Inorganic Chemistry, and **Noel S. Hush,** and **Peter R. Taylor,** Department of Theoretical Chemistry, University of Sydney, Sydney, New South Wales 2006
Colin L. Raston and **Allan H. White,*** School of Chemistry, University of Western Australia, Nedlands, Western Australia 6009

The crystal structure of the title compound, $[(NH_3)_5Ru\cdot N(CH)_4N\cdot Ru(NH_3)_5]Br_{10/3}Cl_{5/3}\cdot 4H_2O$, has been determined from *X*-ray diffractometer data by direct methods and refined by full-matrix least squares to *R* 0.062 for 2 951 observed reflections. Crystals are orthorhombic, probable space group *Pnnm*, $a = 17.790(4)$, $b = 11.590(2)$, $c = 7.096(1)$ Å, $Z = 2$. The cation has exact crystallographic symmetry of at least 2, and approximate *mmm* symmetry; Ru–N(pyrazine) is 2.006(6), Ru–NH_3(*trans*) 2.127(7), and Ru–NH_3(*cis*) 2.098(5) and 2.122(5) Å. The anions, together with the water molecules, are highly disordered.

THE μ-pyrazine-bis(penta-ammineruthenium)(5+) ion (I), which can formally be described as an Ru^{II}/Ru^{III} mixed-valence complex, was first described by Creutz and Taube,[1] who isolated the *p*-tolylsulphonate; a bromide and a perchlorate were also later prepared.



(I)

Complex ions of this type are of much interest from the point of view of electron-transfer theory, as it is possible that the ion has either a symmetrical delocalized electronic ground-state, or alternatively an unsymmetrical 'trapped-valence' electronic ground-state, in which an electron (or hole) is rapidly exchanged between the two Ru centres in an intramolecular electron-transfer process. It was originally suggested [1] that the ion (I) is of the latter type: a 'weak-interaction' complex in the terminology of Allen and Hush.[2] By application of the theory of intervalence transfer absorption to analysis of the near-i.r. absorption spectrum,[3,4] it was concluded that the rate of internal electron exchange was *ca.* 3×10^9 s^{-1} at 300 K.

Subsequent measurements of ^1H n.m.r.,[5] Mössbauer,[6] and Raman [7] spectra have not yielded unequivocal evidence for either structure. The Ru $3d_{5/2}$ *X*-ray photoelectron spectrum of the *p*-tolylsulphonate of (I) has been interpreted [8] as providing direct evidence for a localized structure, but it has subsequently been pointed out [9] that, when electron–phonon coupling is taken into account, a delocalized structure can give rise to a similar ESCA binding-energy pattern. In the most recent discussion, it was reported [10] that new i.r. (vibrational) measurements and a new theoretical analysis

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[1] C. Creutz and H. Taube, *J. Amer. Chem. Soc.*, 1969, 3988.
[2] G. Allen and N. S. Hush, *Progr. Inorg. Chem.*, 1967, **8**, 357.
[3] N. S. Hush, *Progr. Inorg. Chem.*, 1967, **8**, 391.
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[7] T. C. Strekas and T. G. Spiro, *Inorg. Chem.*, 1976, **15**, 974.
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[10] J. K. Beattie, N. S. Hush, and P. R. Taylor, *Inorg. Chem.*, 1976, **15**, 992.

of the i.r. electronic band suggest that the structure of (I) is in fact delocalized both in solution and in the solid state.

For a fuller understanding of the structure of this ion and its classification[11] it is necessary to know the detailed geometry. We have therefore prepared crystals of a mixed bromide chloride of (I) and examined their structure by *X*-ray diffraction.

EXPERIMENTAL

Preparation.—An aqueous solution containing the chloride of the ion (I), prepared by the method of ref. 12, was strongly acidified with hydrogen bromide and set aside for 48 h. Crystals were then filtered off and dried under vacuum. The visible–i.r. absorption spectrum of aqueous solutions of these was in good agreement with the data of ref. 1. The formula assumed here for these bromide chloride crystals is based on chemical analysis (Found: C, 5.95; H, 5.00; Br, 32.60; Cl, 7.17; N, 19.8; Ru, 21.50. $C_4H_{42}Br_{10/3}Cl_{5/3}N_{12}O_4Ru_2$ requires C, 5.65; H, 4.94; Br, 31.3; Cl, 6.95; N, 19.80; Ru, 23.8%).

Crystallography.—A needle section 0.18 × 0.18 × 0.33 mm (*a*, *b* as section diagonals) was used. The unit cell was calibrated by a least-squares fit of the angular parameters of 15 reflections (2θ *ca.* 25°) centred in the counter aperture of a Syntex $P\bar{1}$ four-circle diffractometer. A unique data set in the range $2\theta < 65°$ was gathered by a conventional 2θ—θ scan yielding 3 461 independent reflections, which were corrected for absorption. Cell symmetry was checked initially using film methods on a number of independent crystals.

Crystal Data.—$[(NH_3)_5Ru{\cdot}N(CH)_4N{\cdot}Ru(NH_3)_5]Br_{10/3}Cl_{5/3}{\cdot}4H_2O$, $C_4H_{42}Br_{10/3}Cl_{5/3}N_{12}O_4Ru_2$, $M = 850.0$, Orthorhombic, $a = 17.790(4)$, $b = 11.590(2)$, $c = 7.096(1)$ Å, $U = 1\,463.2(5)$ Å^3, $D_m = 1.97(1)$, $Z = 2$, $D_c = 1.929$, $F(000) = 830$. Probable space group *Pnnm* (No. 58, D_{2h}^{12}). Monochromated Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 60.1$ cm^{-1}. Neutral atom scattering factors, those for Ru, Br, and Cl being corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).[13-15]

Intensity statistics suggested a centric lattice-symmetry and the structure was solved by direct methods in the space group *Pnnm*, the ruthenium, pyrazine, and bromine Br(1) being located in an *E* map; a subsequent difference map yielded the positions of the nitrogen atoms of the ammonia ligands and the second bromine Br(2). In space group *Pnnm*, the solution comprised a dimeric $[(NH_3)_5\text{-}Ru{\cdot}N(CH)_4N{\cdot}Ru(NH_3)_5]$ cation with overall $2m$ crystallographic symmetry, the approximate point symmetry being *mmm*. With the exception of ammonia nitrogens N(3) and N(4), all atoms occupied special positions of point symmetry *m*. Refinement of the structure was commenced by use of 9 × 9 block-diagonal least squares and anisotropic thermal parameters of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} \ldots + 2U_{23}klb^*c^*)]$. A further difference map showed several abnormal features: the thermal ellipsoid of bromine Br(2) (located 0.3921, 0.9408, 0), was very elongated in *z* (but with no dumb-bell structure), and above and below Br(2) at $z = \frac{1}{2}$ were found two regions of lower electron density, Br(21) and Br(22), separated in the *xy* plane by *ca.* 1.9 Å. These were designated as partially occupied bromide sites, it being presumed that Br(2) was disordered, primarily in *z*; this was further suggested by a negative density at the site of Br(2). A similar negative region was found at Br(1). A further anomaly was found in the region separating the pyrazine rings which lie in the plane $z = 0$. Between the parallel rings in adjacent cells in *z*, a series of regions of electron density was found at $z = \frac{1}{2}$, approximately 'ghosting' the pyrazine ring, and about the size of oxygen atoms. The likelihood of the three sites being occupied each by a water molecule was regarded as small, however, in view of their proximity; accordingly they, together with all other possible anion sites, were treated as being occupied by suitably populated bromine fragments [Br(31)—(33)]. In an attempt to locate the position of the chlorine and water-oxygen atoms, difference maps were computed using inner- and outer-data shells, since the bromide is a high-angle scatterer relative to the remainder; the result suggested partial occupancy of the site of Br(1) by chlorine. (A complete data set was preserved to this stage for this purpose.)

Further improvements to the model were tried, including attempted refinement in the acentric space group *Pnn*2 (No. 34) but proved fruitless. The model finally adopted for full-matrix refinement comprised an anion distribution as follows: Br(1) was refined with a variable population parameter, and Cl(1) was constrained to the same site, with a population restricted so that the total population of the site was one anion, as suggested by difference maps. Br(2) was refined over three sites, Br(2), Br(21), and Br(22), with the population of Br(21) and Br(22) fixed from difference maps, and Br(2) considered variable, with isotropic thermal parameters for Br(2) and Br(22); the sum of these at convergence was slightly greater than one anion, but it was not possible to refine all three sites with variable populations constrained to a total of unity. The regions between the pyrazine rings were refined as bromides Br(31)—(33) with variable populations. Hydrogen atoms were located on all expected ligand sites, except ammonia N(2) on the cation axis. N(2) is in the proximity of the regions of disorder and it is likely that the hydrogens themselves are disordered; the hydrogen atoms were included as invariants in the refinement with isotropic *U* 0.05 Å^2, after attempts to refine their positional parameters failed. The final data set used in refinement was truncated to include only reflections with $I > 2\sigma(I)$; a complete data set was used up to this point to assist in the definition of bromide/chloride/water populations but, in fact, the considerable number of weaker reflections contained considerable 'noise.' This left 2 951 of the original 3 461 reflections as the data set. Refinement converged at *R* 0.062, R' $[= (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{\frac{1}{2}}]$ being 0.072; a weighting scheme of the form $w = [\sigma^2(F_o) + n \times 10^{-4}(F_o)^2]^{-1}$ was found appropriate for $n = 6$. Parameter shifts in the final least-squares cycle were less than 0.01σ. In summary, considerable doubt exists as to the identity of the disordered non-cationic species observed in the crystal structure. Clearly the bromide ions are primarily confined to sites Br(1) and Br(2), the total population being 1.71 in quite good agreement with that of 1.67 expected from chemical analysis; however, in view of the nature of the disorder and the large U_{33} component of the thermal tensor, it

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would not be surprising to find bromide occupancy of sites Br(21) and Br(22) also to be significant. The chloride ion appears to be primarily associated with partial occupancy of the Br(1) site; the considerable electron-density at Br(31) suggests considerable anion occupancy also. Although the interplanar spacing of the pyrazine rings is compatible with either Br or Cl occupancy, it seems more reasonable to suppose that the entity is likely to be *ca.* 0.5 Cl rather than 0.24 Br, and this, together with Cl(1), gives a total chloride population of *ca.* 0.75 which approaches the expected value of 0.83 given by chemical analysis. Water analyses by difference (as in the present case) have been shown by *X*-ray structure determination to be notoriously inaccurate. However, if we assume the presence of two waters of crystallization in the asymmetric unit, it would seem reasonable for these to be distributed over sites Br(32), Br(33) and over Br(2), Br(21), and Br(22). [We note, however, that the proximity of a number of the disordered sites precludes their simultaneous occupation by the suggested species.]

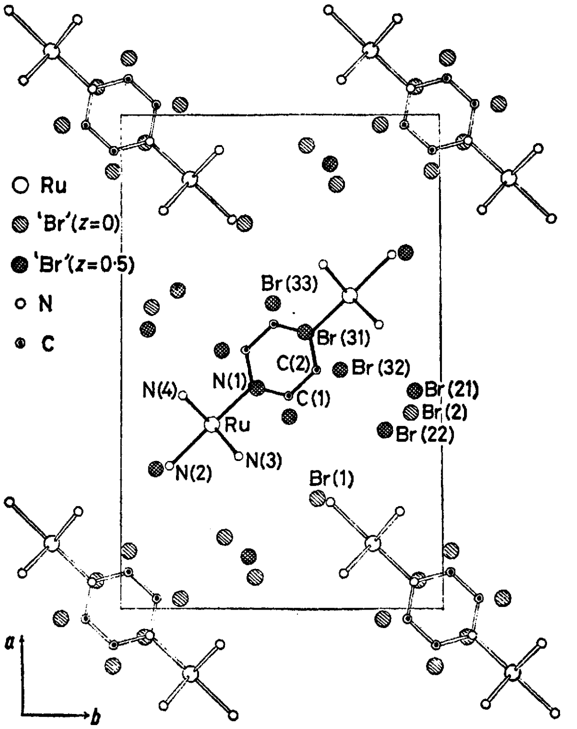

FIGURE 1 Unit-cell contents projected down c; the cation with solid bonds is in the plane $z = 0$, others are at $z = \frac{1}{2}$

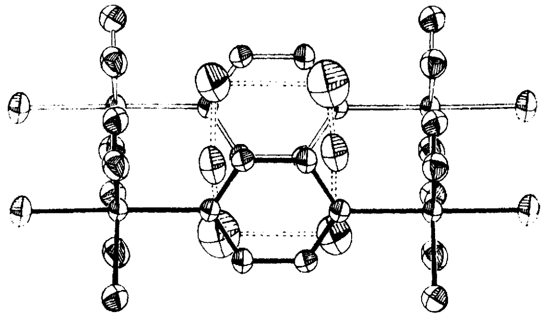

FIGURE 2 Projection of the cations showing 50% thermal ellipsoids, and the interleaving disordered anions, Br(3n)

TABLE 1

Atomic fractional cell * and thermal parameters ($\times$ 10^3 Å^2) with least-squares estimated standard deviations in parentheses; p is the population

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	p
Ru	36 912(3)	28 383(5)	0	24.6(2)	21.8(2)	32.8(3)	−3.3(2)			1
Pyrazine										
N(1)	4 461(3)	4 103(5)	0	25(3)	22(3)	33(3)	−2(2)			1
C(1)	4 268(4)	5 227(7)	0	26(3)	25(3)	47(5)	−4(3)			1
C(2)	5 206(4)	3 895(6)	0	26(3)	23(3)	40(4)	2(3)			1
Ammine										
N(2)	2 862(4)	1 517(6)	0	41(4)	31(4)	46(4)	−13(3)			1
N(3)	3 054(3)	3 675(4)	2 128(7)	37(2)	35(2)	39(3)	−2(2)	4(2)	−3(2)	1
N(4)	4 282(3)	1 927(4)	2 081(8)	35(2)	40(3)	51(3)	−2(2)	−2(2)	11(2)	1
Anions										
Br(1)	22 105(8)	6 128(1)	0	53(2)	45(3)	47(2)	18(2)			0.748 (5)
Cl(1)				18(7)	51(18)	14(7)	17(8)			0.252
Br(2)	39 214(9)	9 048(1)	0	67(9)	41(8)	229(27)	16(6)			0.963 (5)
Br(21)	435(4)	917(6)	5 000	105(18) †						0.03
Br(22)	358(2)	820(3)	5 000	92(8) †						0.06
Br(31)	5 570(2)	5 751(4)	5 000	49(3)	62(3)	42(2)	−19(2)			0.243 (4)
Br(32)	4 801(7)	6 851(12)	5 000	63(8)	75(9)	95(10)	−6(6)			0.105 (4)
Br(33)	6 148(8)	4 748(14)	5 000	100(10)	123(14)	108(11)	−19(9)			0.135 (5)

* Cell parameters $\times 10^4$, except Ru, Br(1), Br(2) $\times 10^5$, Br(21), Br(22) $\times 10^3$. † Isotropic.

Structure amplitudes, hydrogen atom parameters, and C–H and N–H distances are deposited as Supplementary Publication No. SUP 21978 (17 pp., 1 microfiche).* Atom positional and thermal parameters are listed in Table 1, and distances and angles in Table 2. Computation was carried out on a CDC 6200 at the University of Western Australia, by use of a local variant of the '*X*-Ray '72' system.[16] Atom numbering is shown in Figure 1 and a projection of the cations in Figure 2.

DISCUSSION

As already described, the crystal lattice is comprised of binuclear $[(NH_3)_5Ru{\cdot}N(CH)_4N{\cdot}Ru(NH_3)_5]$ cations accompanied by disordered anions. The symmetry of the cation closely approximates to *mmm*. In space

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue.

[16] '*X*-Ray' Program System, Technical Report TR 192, Computer Science Center, University of Maryland, U.S.A., 1972.

group *Pnnm* an exact crystallographic symmetry of 2*m* is imposed, the two-fold axis being normal to the Ru ··· Ru axis in the plane of the pyrazine ring which also contains the mirror plane. In space group *Pnn*2, the crystallographic symmetry of the cation falls to 2; it seems unlikely that the space group is other than one of these and it therefore follows that the cation symmetry must be at least 2, *i.e.* the ruthenium atoms must be equivalent, as are their environments. There can thus be no difference in the ruthenium–pyrazine nitrogen distances which are 2.006(6) Å, considerably shorter than the ammine–ruthenium distances; if the system contained completely localized ruthenium(II) and ruthenium(III) species, these distances would be expected to differ, as also would the ruthenium–ammine distances. If the cation (I) were of the 'weak-interaction' type, intramolecular electron hopping with a relaxation time of *ca.* 3 × 10^{-10} s at 300 K would be expected.[1] Although we cannot easily distinguish by *X*-ray diffraction such a structure from one in which the ground state is completely delocalized and electronically stable, we note that the rapid dynamic motion might be reflected in unusually high thermal motion and anisotropy of the ruthenium and its environs; however, the cation is very well defined, considering the disorder of the remainder of the structure and its thermal motion quite low by comparison. The relative rigidity of the cation system, in fact, seems to be the reason for the quite extensive data set.

TABLE 2

Interatomic distances (Å) and angles (°), with least-squares estimated standard deviations in parentheses

(*a*) Intra-cation geometry			
Ru–N(1)	2.006(6)	C(2$^{\mathrm{I}}$)–C(1)–N(1)	122.6(7)
N(1)–C(1)	1.349(9)	C(1$^{\mathrm{I}}$)–C(2)–N(1)	122.4(7)
N(1)–C(2)	1.347(9)	C(1)–N(1)–C(2)	115.0(6)
C(1)–C(2$^{\mathrm{I}}$)	1.382(10)	C(1)–N(1)–Ru	122.2(5)
Ru–N(2)	2.127(7)	C(2)–N(1)–Ru	122.8(5)
Ru–N(3)	2.122(5)	N(1)–Ru–N(2)	179.1(3)
Ru–N(4)	2.098(5)	N(1)–Ru–N(3)	91.8(2)
N(3)–*Ru*–*N*(4)	89.8(2)	N(1)–Ru–N(4)	91.5(2)
N(2)–Ru–N(3)	87.6(2)	N(3)–Ru–N(3$^{\mathrm{II}}$)	90.7(2)
N(2)–Ru–N(4)	89.1(2)	N(4)–Ru–N(4$^{\mathrm{II}}$)	89.5(2)
(*b*) Distances and angles between anion fragments			
Br(2) ··· Br(21)	3.634(9)		
Br(2) ··· Br(22)	3.728(8)		
Br(31) ··· Br(32)	1.87(1)		
Br(31) ··· Br(33)	1.55(2)		
Br(32) ··· Br(33$^{\mathrm{I}}$)	2.51(2)		
Br(21) ··· Br(22)	1.77(5)		
Br(32) ··· Br(33) ··· Br(31$^{\mathrm{I}}$)	96.2(7)		
Br(33) ··· Br(31) ··· Br(32)	174.5(8)		
Br(31) ··· Br(32) ··· Br(33$^{\mathrm{I}}$)	89.4(7)		
(*c*) Anion–cation contacts			
N(1) ··· Br(31)	3.552 5(7)	C(2) ··· Br(32)	3.652 (4)
C(1) ··· Br(33)	3.624 (3)		

Atoms with superscripts are at: I 1 − *x*, 1 − *y*, *z*; II, *x*, *y*, *z*.

We further note that the U_{ii} range from 0.022 to 0.051 Å^2, corresponding to root-mean-square amplitudes of 0.15—0.23 Å. From the reference data (see later) for Ru–ammine distances, one might expect a difference of *ca.* 0.04 Å for supposed $\mathrm{Ru^{II}}$–pyrazine and $\mathrm{R^{III}}$–pyrazine distances. The rapid dynamic motion for the 'weak-interaction' type of bonding would thus correspond to a smearing amplitude of the order of 0.04 Å, which is much smaller than the overall amplitudes of 0.15 — 0.23 Å. Disorder with domains asymmetric by this magnitude would also not be detected. It is clear therefore that the *X*-ray crystallographic results do not give a definite answer to the bonding problems posed.

The ruthenium–ammine geometries are of considerable interest. Three independent Ru–N distances are observed, two being very similar [2.122(5) and 2.127(7) Å], the third rather shorter [2.098(5) Å]. Accurate estimates of Ru–N distances in the ruthenium hexa-ammine derivatives[17] put Ru–N at 2.144(4) in $[\mathrm{Ru^{II}(NH_3)_6}]^{2+}$ and 2.104(4) Å in $[\mathrm{Ru^{III}(NH_3)_6}]^{3+}$; in the present case, the ammine distance *trans* to the pyrazine may be influenced by a *trans*-effect, but *cis*-effects are usually considerably less, and the *cis*-Ru–N distances can be regarded as being biased relatively little by the presence of the pyrazine. Consideration of these factors suggests that the impression that the Ru–N distances lie midway between the values for the ruthenium-(II) and -(III) ammines is a real one; all three structures are quite accurate in respect of these distances and have been refined by full-matrix least-squares. All N(1)–Ru–*cis*-ammine-N angles in the present structure are greater than 90° as might be expected. The geometry of the pyrazine ring is unexceptional.

With the exception of the *cis*-ammine ligands, and the hydrogen atoms of the *trans*-ammonia ligand, all other atoms in the structure lie in the planes $z = 0,\frac{1}{2}$ in space group *Pnnm*; the result is the formation of columns of alternate pyrazine rings and Br(3*n*) fragments up the *c* axis, and of columns of Br(2*n*) fragments also parallel to *c*. The spacing of the planes $z = 0,\frac{1}{2}$ is $0.5c = 3.55$ Å. The van der Waals radii estimates for bromine and nitrogen are 1.95 and 1.50 Å respectively. The large thermal anisotropy of Br(21), together with the curious six-fold multiplicity of Br(3), suggests that Br(2) may be mobile between the three potential minima assigned to it, while Br(3) may also be mobile and involved in a charge transfer interaction with the pyrazine ring.

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[6/1763 *Received, 20th September,* 1976]

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