

# Möbius aromaticity in bipyramidal rhodium-centered bismuth clusters

R. Bruce King

Department of Chemistry, University of Georgia, Athens, Georgia 30602, USA

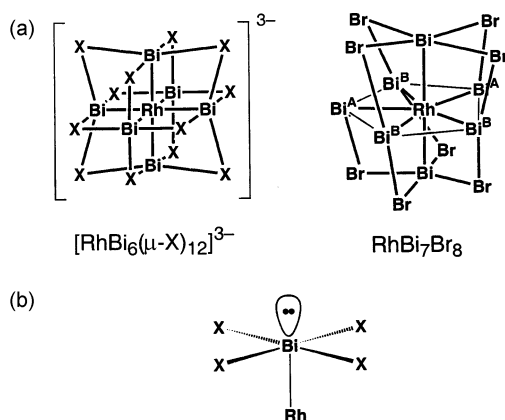
Received 19th November 2002, Accepted 3rd December 2002

First published as an Advance Article on the web 8th January 2003

The chemical bonding topologies in the mixed rhodium–bismuth clusters  $[\text{RhBi}_6(\mu\text{-X})_{12}]^{3-}$  ( $\text{X} = \text{Br}, \text{I}$ ) and  $\text{RhBi}_7\text{Br}_8$  are compared. The octahedral cluster  $[\text{RhBi}_6(\mu\text{-X})_{12}]^{3-}$  can be considered as a  $d^6$  Rh(III) complex containing six equivalent  $\text{BiX}_2^-$  ligands with interligand halogen bridging but no Bi–Bi bonding. However, the pentagonal bipyramidal cluster  $\text{RhBi}_7\text{Br}_8$  has only two similar  $\text{BiBr}_2^-$  ligands in the axial positions. The five equatorial bismuth atoms in  $\text{RhBi}_7\text{Br}_8$  form a bonding pentagon, which is an example of a five-atom Möbius aromatic system with a five-center four-electron bond. This unusual bond involves  $\sigma$ -type overlap between p orbitals in the plane of the pentagon with the single phase change required for Möbius aromaticity.

## 1. Introduction

The study of clusters of bismuth (the “wonder metal” of metal cluster chemistry)<sup>1</sup> dates back to 1963 when Hershaft and Corbett<sup>2</sup> found by X-ray diffraction the tricapped trigonal prismatic ion  $\text{Bi}_9^{5+}$  in material previously assumed to be “ $\text{BiCl}$ ” but actually found to be  $[\text{Bi}_9^{5+}]_4[\text{BiCl}_5^{2-}]_8[\text{Bi}_2\text{Cl}_8^{2-}]_2$  ( $= \text{Bi}_6\text{Cl}_7$ ). Subsequent work by Corbett and co-workers<sup>3</sup> led to the identification of anionic bismuth cluster Zintl ions, notably the cyclobutadiene analogue<sup>4</sup>  $\text{Bi}_4^{2-}$ . Much more recent work by Ruck and co-workers<sup>5</sup> has led to a great expansion of the scope of bismuth halide cluster chemistry through the isolation of ternary species containing bismuth, a transition metal, and a halogen. While most of the phases discovered by Ruck and co-workers were found to have infinite one- or two-dimensional networks of bismuth atoms,<sup>5</sup> two distinct types of discrete molecular ternary bismuth rhodium halide clusters were also isolated and characterized (Fig. 1a). The first type consisted of



**Fig. 1** (a) The structures of  $[\text{RhBi}_6(\mu\text{-X})_{12}]^{3-}$  ( $\text{X} = \text{Br}, \text{I}$ ) and  $\text{RhBi}_7\text{Br}_8$ . (b) The square pyramidal environment of all of the bismuth atoms in  $[\text{RhBi}_6(\mu\text{-X})_{12}]^{3-}$  and of the two axial bismuth atoms in  $\text{RhBi}_7\text{Br}_8$ .

transition metal-centered octahedral bismuth cluster anions of the type  $[\text{MBi}_6(\mu\text{-X})_{12}]^{3-}$  ( $\text{M} = \text{Rh}, \text{Ir}; \text{X} = \text{I}$ ) isolated as “salts” of the rather unusual bicapped square antiprismatic  $\text{Bi}_8\text{Si}_2^{3+}$  cation.<sup>6</sup> The second species of interest was the neutral molecular pentagonal bipyramidal ternary halide<sup>7</sup>  $\text{RhBi}_7\text{Br}_8$  interpreted to exhibit unusual five-center four-electron ( $5c\text{-}4e$ ) bonding.<sup>8</sup>

This paper discusses the chemical bonding in these two types of ternary bismuth halide clusters using the rhodium derivatives as examples. The cluster  $[\text{RhBi}_6(\mu\text{-X})_{12}]^{3-}$  is shown to be a rather unusual type of octahedral  $d^6$  Rh(III) complex with six

$\text{BiX}_2^-$  groups as ligands and non-bonding  $\text{Bi} \cdots \text{Bi}$  distances. However, the pentagonal bipyramidal  $\text{RhBi}_7\text{Br}_8$  has shorter Bi–Bi distances in the  $\text{Bi}_5$  equatorial pentagon. The  $5c\text{-}4e$  bonding in this equatorial pentagon<sup>8</sup> can be interpreted as a manifestation of Möbius aromaticity, a concept first suggested by Heilbronner<sup>9</sup> in 1964 and subsequently developed in further detail by Zimmerman.<sup>10–12</sup> In fact,  $\text{RhBi}_7\text{Br}_8$  appears to be the first unambiguous example of Möbius aromaticity in a purely inorganic compound.

## 2. Octahedral $[\text{RhBi}_6(\mu\text{-Br})_{12}]^{3-}$

The octahedral  $[\text{RhBi}_6(\mu\text{-I})_{12}]^{3-}$  anion (Fig. 1a) is found in the “salt”  $[\text{Bi}_8\text{Si}_2]^{3+}[\text{RhBi}_6(\mu\text{-I})_{12}]^{3-}$  obtained by reaction of a mixture of bismuth, rhodium, and iodine at high temperatures in a sealed evacuated quartz ampule in the presence of niobium.<sup>6</sup> Remarkably the silicon atoms in the cation arise from the silicon in the quartz ampule. The structure of the  $[\text{RhBi}_6(\mu\text{-I})_{12}]^{3-}$  anion may be described as a  $\text{Bi}_6$  octahedron with a rhodium atom in the center. The Rh–Bi distances of 2.71 Å are clearly bonding whereas the  $\text{Bi} \cdots \text{Bi}$  distances of 3.83 Å are essentially non-bonding. An iodine atom bridges each of the 12 edges of the octahedron. A closely related  $\text{RuBi}_6(\mu\text{-Br})_{12}$  structural unit is found in the phase  $\text{Ru}_3\text{Bi}_{24}\text{Br}_{20}$  in addition to discrete  $\text{BiBr}_4^-$  groups and  $\text{Ru}_2\text{Bi}_{17}\text{Br}_4$  stacks.<sup>13</sup>

The six bismuth atoms in  $[\text{RhBi}_6(\mu\text{-I})_{12}]^{3-}$  are equivalent and exhibit square pyramidal coordination (Fig. 1b), which can be regarded as a Bi(III) pseudooctahedron with the lone electron pair required for Bi(III) *trans* to the Rh atom. These bismuth atoms can be considered to form uninegative  $\text{BiI}_2^-$  ligands. However, the bismuth coordination number in these ligands is increased from three to five by dative bonding from iodine atoms in two adjacent  $\text{BiI}_2$  units. The rhodium atom may be regarded as  $d^6$  octahedral Rh(III) with three lone pairs. Excluding the lone pairs on the bismuth atoms and the two lone pairs on each iodine atom but not the three lone pairs on the central rhodium atom, the  $[\text{RhBi}_6(\mu\text{-I})_{12}]^{3-}$  anion is seen to have 66 “skeletal” electrons as follows:

6 Bi atoms: $6 \times 3 =$	18 electrons
1 Rh atom: $1 \times 9 =$	9 electrons
12 $\mu\text{-I}$ atoms: $12 \times 3 =$	36 electrons
$-3$ negative charge	<u>3 electrons</u>
Total available “skeletal” electrons:	66 electrons

These 66 “skeletal” electrons can be allocated to the 30 two-center two-electron bonds and the three lone pairs on the  $d^6$  Rh(III) atom as follows:

24 2c-2e Bi-I bonds: $24 \times 2 =$	48 electrons
6 2c-2e Bi-Rh bonds: $6 \times 2 =$	12 electrons
3 Rh lone pairs: $3 \times 2 =$	<u>6 electrons</u>
Total "skeletal" electrons required:	66 electrons

The cluster  $[\text{RhBi}_6(\mu\text{-I})_{12}]^{3-}$  is thus electron-precise for a localized skeletal bonding scheme using only 2c–2e bonds.

### 3. Pentagonal bipyramidal $\text{RhBi}_7\text{Br}_8$

The black air-stable neutral pentagonal bipyramidal Rh-centered bismuth cluster  $\text{RhBi}_7\text{Br}_8$  (Fig. 1a) is obtained by heating a mixture of bismuth, rhodium, and bromine in a 7 : 1 : 8 mole ratio to 1270 K in an evacuated quartz ampule.<sup>7</sup> The two axial bismuth atoms in the structure of  $\text{RhBi}_7\text{Br}_8$  have the same square pyramidal environment as all six bismuth atoms in the octahedral cluster discussed above (Fig. 1b). This means that only four bromine atoms are available to bridge axial–equatorial edges in the  $\text{Bi}_7$  pentagonal bipyramid so that one edge from each axial bismuth atom to the equatorial bismuth atoms does not have a bromine bridge.

The environments of the five equatorial bismuth atoms in  $\text{RhBi}_7\text{Br}_8$  are quite different from those of the axial bismuth atoms. More specifically, a comparison of the equatorial pentagon in  $\text{RhBi}_7\text{Br}_8$  with the equatorial square in  $[\text{RhBi}_6(\mu\text{-I})_{12}]^{3-}$  is quite informative. Thus whereas the Bi ··· Bi distances in the equatorial square of  $[\text{RhBi}_6(\mu\text{-I})_{12}]^{3-}$  are clearly non-bonding at 3.83 Å, the Bi–Bi distances in the equatorial pentagon of  $\text{RhBi}_7\text{Br}_8$  are only 3.2 to 3.3 Å suggesting some bonding in the  $\text{Bi}_5$  equatorial pentagon. However, the five equatorial bismuth atoms are not equivalent since three are bonded to two bromine atoms from the axial bismuth atoms ( $\text{Bi}^{\text{B}}$  in Fig. 1a) whereas the other two are only bonded to single bromine atoms from the axial bismuth atoms ( $\text{Bi}^{\text{A}}$  in Fig. 1a). The three equatorial  $\text{Bi}^{\text{B}}$  atoms (Fig. 1a) form a total of three bonds (two to Br and one to Rh) so that they may be considered to be trigonally  $\text{sp}^2$ -hybridized with an empty p orbital. The remaining two equatorial  $\text{Bi}^{\text{A}}$  atoms (Fig. 1a) are only two-coordinate forming one Bi–Rh and one Bi–Br bond and thus have two lone pairs in their  $\text{sp}^3$  bonding manifolds. One of these lone pairs is the external lone pair found in all of the bismuth atoms in both  $\text{RhBi}_7\text{Br}_8$  and  $[\text{RhBi}_6(\mu\text{-I})_{12}]^{3-}$ . The other lone pairs in the two equatorial  $\text{Bi}^{\text{A}}$  atoms of  $\text{RhBi}_7\text{Br}_8$  are available for bonding in the  $\text{Bi}_5$  equatorial pentagon. The four electrons from these two lone pairs become the four electrons in the "unusual five-center, four-electron bonding" (5c–4e bonding) proposed by Xu and Lin<sup>8</sup> on the basis of Hartree–Fock and B3LYP computations.

An electron counting scheme for  $\text{RhBi}_7\text{Br}_8$  similar to that used above for  $[\text{RhBi}_6(\mu\text{-I})_{12}]^{3-}$  supports the idea of 5c–4e bonding in the  $\text{Bi}_5$  equatorial plane. The central Rh atom in  $\text{RhBi}_7\text{Br}_8$  is seven coordinate by forming 2c–2e bonds with each of the bismuth atoms in the pentagonal bipyramid so that it requires two lone pairs to attain the favored 18-electron configuration in its nine-orbital  $\text{sp}^3\text{d}^5$  valence orbital manifold. Excluding the external lone pairs on the bismuth and bromine atoms but not the lone pairs on the central rhodium atom,  $\text{RhBi}_7\text{Br}_8$  has 54 "skeletal" electrons as follows:

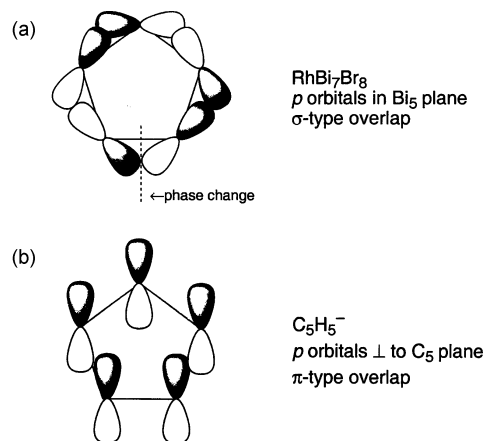
7 Bi atoms: $7 \times 3 =$	21 electrons
1 Rh atom: $1 \times 9 =$	9 electrons
8 $\mu\text{-Br}$ atoms: $8 \times 3 =$	<u>24 electrons</u>
Total available "skeletal" electrons:	54 electrons

These 54 "skeletal" electrons can be allocated as follows:

16 2c-2e Bi-I bonds: $16 \times 2 =$	32 electrons
7 2c-2e Bi-Rh bonds: $7 \times 2 =$	14 electrons
2 Rh lone pairs: $2 \times 2 =$	4 electrons
5c-4e bond in the $\text{Bi}_5$ equatorial pentagon: $1 \times 4 =$	<u>4 electrons</u>
Total "skeletal" electrons required:	54 electrons

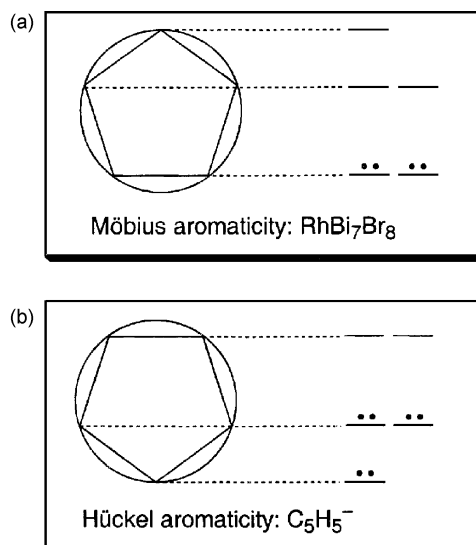
The cluster  $\text{RhBi}_7\text{Br}_8$  is thus electron-precise for a skeletal bonding scheme with 2c–2e Bi–Br and Bi–Rh bonds and a 5c–4e bond in the  $\text{Bi}_5$  equatorial pentagon.

What then is the nature of the 5c–4e bond in the  $\text{Bi}_5$  equatorial pentagon of  $\text{RhBi}_7\text{Br}_8$ ? Each of the equatorial bismuth atoms has a p orbital available to overlap with the adjacent bismuth atoms in the equatorial pentagon (Fig. 2a).



**Fig. 2** (a) The  $\sigma$ -type overlap of the five in-plane p orbitals of the bismuth atoms in the  $\text{Bi}_5$  pentagon of  $\text{RhBi}_7\text{Br}_8$ . (b) The  $\pi$ -type overlap of the five perpendicular p orbitals of the carbon atoms in  $\text{C}_5\text{H}_5^-$ .

The topology of this bonding is that of a pentagon like that in the cyclopentadienide anion,  $\text{C}_5\text{H}_5^-$ . However, the relevant p orbitals are oriented in the plane of the equatorial  $\text{Bi}_5$  pentagon (Fig. 2a) whereas the p orbitals involved in the delocalized bonding of  $\text{C}_5\text{H}_5^-$  are oriented perpendicular to the plane of the  $\text{C}_5$  pentagon (Fig. 2b). Consequently, the overlap between the p orbitals on the adjacent bismuth atoms in the equatorial  $\text{Bi}_5$  pentagon is of  $\sigma$ -type necessarily with a single phase change whereas that between the p orbitals on the adjacent carbon atoms in  $\text{C}_5\text{H}_5^-$  is of  $\pi$ -type with no phase changes (Fig. 2). Thus the bonding in the equatorial  $\text{Bi}_5$  pentagon in  $\text{RhBi}_7\text{Br}_8$



**Fig. 3** (a) Möbius aromaticity in the equatorial pentagon of  $\text{RhBi}_7\text{Br}_8$ . (b) Hückel aromaticity in  $\text{C}_5\text{H}_5^-$ . In both cases the Frost–Musulin mnemonic<sup>14</sup> for the relevant molecular orbital energies is shown.

meets the requirement for a Möbius aromatic system<sup>9-11</sup> with  $2k$  molecular orbitals and  $4k$  bonding electrons where  $k$  is 1 (Fig. 3a). This contrasts with  $C_5H_5^-$ , which is a Hückel aromatic system with  $2k + 1$  molecular orbitals and  $4k + 2$  bonding electrons where  $k$  again is 1 (Fig. 3b). The cluster  $RhBi_7Br_8$  appears to be the first example of a metal cluster with a cyclic substructure in which the geometry, available metal orbitals, and available skeletal electrons provide such a compelling case for Möbius aromaticity.

### Acknowledgements

I am indebted to the National Science Foundation for partial support of this work under Grant CHE-0209857.

### References

- 1 J. D. Corbett, *Prog. Inorg. Chem.*, 1976, **21**, 140.
- 2 A. Hershaft and J. D. Corbett, *Inorg. Chem.*, 1963, **2**, 979.
- 3 J. D. Corbett, *Chem. Rev.*, 1985, **85**, 383.
- 4 A. Cisar and J. D. Corbett, *Inorg. Chem.*, 1977, **16**, 2482.
- 5 M. Ruck, *Angew. Chem., Int. Ed.*, 2001, **40**, 1182.
- 6 M. Ruck, *Z. Anorg. Allg. Chem.*, 2000, **626**, 14.
- 7 M. Ruck, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1971.
- 8 Z. Xu and Z. Lin, *Angew. Chem., Int. Ed.*, 1998, **37**, 1686.
- 9 E. Heilbronner, *Tetrahedron Lett.*, 1964, 1923.
- 10 H. E. Zimmerman, *J. Am. Chem. Soc.*, 1966, **88**, 1564.
- 11 H. E. Zimmerman, *Acc. Chem. Res.*, 1971, **4**, 272.
- 12 H. E. Zimmerman, *Tetrahedron*, 1982, **38**, 753.
- 13 M. Ruck, *Z. Anorg. Allg. Chem.*, 1997, **623**, 1591.
- 14 A. Frost and B. Musulin, *J. Chem. Phys.*, 1953, **21**, 572.