Bimetallic Ruthenium(II)−Ruthenium(III) Complexes. A Molecular Orbital View

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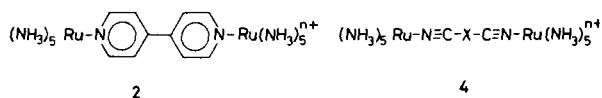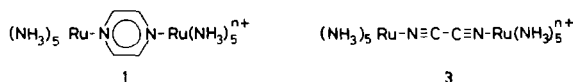
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The structures of bimetallic ruthenium(II)–ruthenium(III) ions with a variety of bridging ligands are considered using molecular orbital methods. These ions may by symmetrical with equivalent metal centers or may be distorted with nonequivalent sites, which in the extreme can be identified as Ru(II) and Ru(III). Certain ions with ligands such as 4,4′-bipyridine or nonconjugated dicyano species would have degenerate ground states if they were symmetrical and are thus distorted. In other ions the odd electron will be located in a coupled orbital and there will be less of a tendency toward distortion. The original Creutz and Taube pyrazine bridged complex is of this type.

Introduction

The bimetallic ruthenium pyrazine [1, 2] and 4,4′-bipyridine complexes [2–4], **1b** and **2b**, reported several years ago by Creutz and Taube were the first of many similar species prepared since then [4–9]. There have been numerous spectroscopic and

$(NH_3)_5$ Ru–N⟨⟩N–Ru$(NH_3)_5^{n+}$ $(NH_3)_5$ Ru–N≡C–C≡N–Ru$(NH_3)_5^{n+}$

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$(NH_3)_5$ Ru–N⟨⟩–⟨⟩N–Ru$(NH_3)_5^{n+}$ $(NH_3)_5$ Ru–N≡C–X–C≡N–Ru$(NH_3)_5^{n+}$

2   **4**

1a − 4a, n = 4.   1b − 4b, n = 5.   1c − 4c, n = 6.

chemical studies of these interesting complexes, with much discussion devoted to the question as to whether the complexes have discrete 'localized' Ru(II) and Ru(III) centers or alternatively have a 'delocalized' electronic structure with equivalent metal centers [1–14]. Theoretical treatments of these ions have relied primarily upon the theory of Hush [15] and the classifications of Robin and Day [16], although numerous authors have made contributions [17–18]. Molecular orbital analyses of individual molecules have been offered, but they are in general incomplete,

sometimes incorrect, and often contradictory with one another. We report here a systematic molecular orbital analysis of these interesting complexes.

Results and Discussion

The molecular orbitals of a square pyramidal Ru(NH_3)$_5^{+2}$ fragment are well known, **5**. The b_1 and a_1 orbitals are strongly antibonding due to sigma

b_1 —— x^2-y^2

a_1 —— z^2

e ⫩ xz,yz
b_1 ⫪ xy

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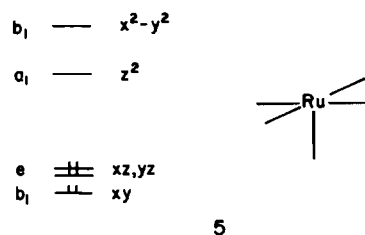
bonding while the e and b_2 orbitals are essentially nonbonding and correspond to the 't$_{2g}$' set of orbitals found for a completed octahedron. The addition of a sixth ligand such as a pyridine or other nitrogen heterocycle leads to the classical octahedral splitting but with one difference. One d orbital (the d_{xz} in our coordinate system) is of proper symmetry to interact with the π system of the ligand, **6**. Such ligands have both filled and empty π orbitals; filled π orbitals tend

xz,yz ⫩ b_1,b_2 —— ⫩ b_2 —— b_1 π^*

xy ⫪ a_2 —— ⫪ a_2

⫪ b_1

—Ru⟨   ⫪ b_1 π

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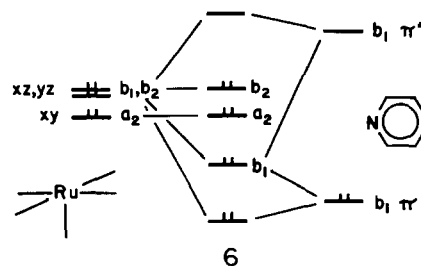
to destabilize the d_{xz}, while empty π^* orbitals tend to stabilize the same orbital. Accepted theory and experiments suggest that the interaction with the lowest π^* orbital is the most important and that the d_{xz} orbital is stabilized relative to the others by this

back bonding mechanism. In most treatments of such ions the interactions with the filled π orbitals are neglected since conventional π back bonding is the dominant effect.

Pyrazine and 4,4'-Bipyridine Bridged Ion

When a pyrazine molecule bridges two $Ru(NH_3)_5^{2+}$ fragments the situation is different. The symmetry of the ion is higher, D_{2h}, and the lowest π^* orbital is of a symmetry other than that of the highest π orbital with nitrogen coefficients. As shown in Fig. 1 this π^* orbital will overlap and stabilize the b_{3u} combination of metal orbitals $(xz_1 - xz_2)$. The π orbital is of b_{2g} symmetry and overlaps with and destabilizes the opposite combination $(xz_1 + xz_2)$. In nonbridged complexes these π and π^* orbitals are of the same symmetry and there is net ligand to metal back-bonding. In the dimer these interactions are separated by symmetry and the pyrazine π bonds in an amphoteric manner. One combination of metal orbitals is destabilized by the ligand π while the second combination is stabilized by the π^*. This results in a significant splitting or coupling of the two d_{xz} orbitals. The remaining four d orbitals remain
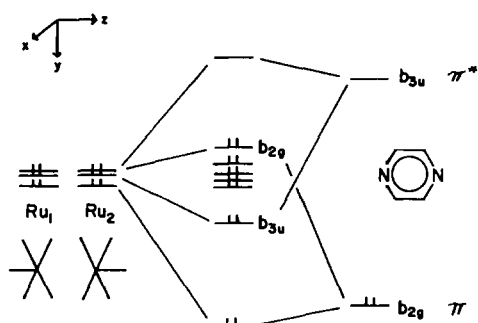

Fig. 1. An interaction diagram for the pyrazine bridged Ru(II)–Ru(II) ion, 1a. The Ru orbitals are shown on the left and the relevant pyrazine π orbitals are shown on the right. More details can be found in Table I.

Fig. 2. An interaction diagram for the bipyridine bridged Ru(II)–Ru(II) ion, 2a. The Ru orbitals are shown on the left and the relevant bipyridine π orbitals are shown on the right. More details can be found in Table I.
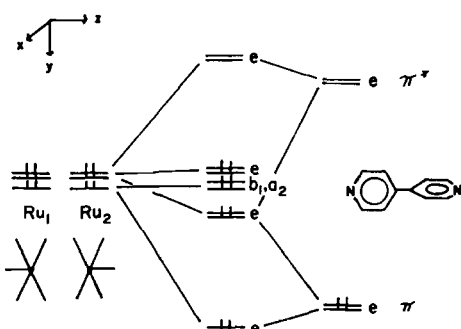
essentially nonbonding although there are smaller destabilizations due to the nonbonded repulsions with the sigma systems of the ligands.

When 4,4'-bipyridine bridges two $Ru(NH_3)_5^{2+}$ fragments the assumed symmetry is D_{2d} and the interactions shown in Fig. 2 take place [19]. Significantly the appropriate π and π^* orbitals are of the same symmetry in this case and thus overlap with the same combination of metal orbitals in a manner similar to a nonbridged complex. The π^* interaction is dominant and as a result there is a low lying stabilized e set of metal orbitals.

Figures 1 and 2 represent the situation for symmetric Ru(II)–Ru(II) ions. When one electron is removed by oxidation mixed valence Ru(II)–Ru(III) ions result. Such species may be symmetrical with equivalent Ru centers or they may distort yielding nonequivalent Ru centers, which in an extreme could be identified as Ru(II) and Ru(III) sites. To investigate such possible distortions we have performed extended Hückel calculations [20–21] upon these ions with both symmetrical and nonsymmetrical structures. For the pyrazine complex the symmetrical structure was taken directly from the known crystal geometry [13, 22]. The bipyridine complex was given similar Ru structural parameters and an idealized bipyridine geometry with perpendicular rings. The distorted geometries were modeled by small deviations of the Ru–NH$_3$ bond distances. The distances about one Ru center were made 0.02 Å shorter while the distances about the second metal center were made 0.02 Å longer. The resulting differences of 0.04 Å are equal to the differences found for Ru(II) and Ru(III) hexammine ions [23]. The distances to the bridging ligand were equal in all cases, 2.0 Å.

Table I shows the energies and more importantly the electron occupancies of each Ru atom for the six metal centered orbitals of each ion. The left side of the table shows the values found for the symmetrical ions, while the right side shows the values for the unsymmetrical ions. The orbitals of the symmetrical ions correspond directly to the orbitals shown in Figs. 1 and 2. They contain equal contributions from each metal atom. When the ions distort the symmetry is lowered, from D_{2h} to C_{2v} for the pyrazine ion and from D_{2d} to C_{2v} for the bipyridine ion. The highest and lowest orbitals of the pyrazine ion $(xz_1 + xz_2)$ and $(xz_1 - xz_2)$ are strongly coupled and upon distortion there is relatively little change in electron occupancy. The remaining four orbitals are combinations of yz and xy orbitals and are essentially degenerate in the symmetric case with no significant coupling. The distortion splits the degeneracies and leads to a completely localized occupancy. In the bipyridine ion the lowest e set of orbitals is stabilized by π bonding and changes little upon distortion, while the higher four orbitals are once again nearly

TABLE I. Energies and Electron Occupancies for Symmetric and Distorted[a] Ru(II)–Ru(II) Bridged Ions.

1. $(NH_3)_5Ru-N\langle\bigcirc\rangle N\text{-}Ru(NH_3)_5^{+4}$

Symmetrical					Distorted[a]				
Orbital		Ru_1	Ru_2	Energy	Orbital		Ru_1	Ru_2	Energy
b_{2g}	$xz_1 + xz_2$	0.82e	0.82e	−11.65 eV	b_1	$xz_1 + xz_2$	0.90e	0.76e	−11.65 eV
b_{2u}	$yz_1 - yz_2$	0.90	0.90	−11.76	b_2	$yz_1 - yz_2$	1.72	0.07	−11.73
b_{3g}	$yz_1 + yz_2$	0.90	0.90	−11.77	b_2	$yz_1 + yz_2$	0.07	1.74	−11.79
a_g	$(x^2 - y^2)_1 + (x^2 - y^2)_2$	0.91	0.91	−11.89	a_1	$(x^2 - y^2)_1 + (x^2 - y^2)_2$	1.81	0.01	−11.85
a_u	$(x^2 - y^2)_1 - (x^2 - y^2)_2$	0.92	0.92	−11.90	a_1	$(x^2 - y^2)_1 - (x^2 - y^2)_2$	0.01	1.83	−11.92
b_{3u}	$xz_1 - xz_2$	0.76	0.76	−12.13	b_1	$xz_1 - xz_2$	0.68	0.84	−12.13

2. $(NH_3)_5Ru-N\langle\bigcirc\rangle\langle\bigcirc\rangle N\text{-}Ru(NH_3)_5^{+4}$

Orbital		Ru_1	Ru_2	Energy	Orbital		Ru_1	Ru_2	Energy
e	yz_1	1.79	–	−11.76	b_1	$xz_1 - xz_2$	0.01	1.80	−11.74
	xz_2	–	1.79		b_2	$yz_1 - yz_2$	1.80	0.01	−11.77
a_2	$(x^2 - y^2)_1 + (x^2 - y^2)_2$	0.88	0.88	−11.88	a_1	$(x^2 - y^2)_1 + (x^2 - y^2)_2$	1.80	0.00	−11.87
b_1	$(x^2 - y^2)_1 - (x^2 - y^2)_2$	0.92	0.92	−11.89	a_1	$(x^2 - y^2)_1 - (x^2 - y^2)_2$	0.00	1.80	−11.89
e	xz_1	1.48	–	−11.98	b_1	$xz_1 + xz_2$	1.12	0.29	−11.97
	yz_2	–	1.48		b_2	$yz_1 + yz_2$	0.36	1.10	−11.98

3. $(NH_3)_5Ru-NCCN-Ru(NH_3)_5^{+4}$

Orbital		Ru_1	Ru_2	Energy	Orbital		Ru_1	Ru_2	Energy
e_g	$xz_1 + xz_2$ / $yz_1 + yz_2$	0.84	0.84	−11.69	e	$xz_1 + xz_2$ / $yz_1 + yz_2$	0.94	0.74	−11.69
b_{1g}	$(x^2 - y^2)_1 + (x^2 - y^2)_2$	0.92	0.92	−11.91	b_1	$(x^2 - y^2)_1 + (x^2 - y^2)_2$	1.83	0.00	−11.86
b_{2u}	$(x^2 - y^2)_1 - (x^2 - y^2)_2$	0.92	0.92	−11.91	b_1	$(x^2 - y^2)_1 - (x^2 - y^2)_2$	0.00	1.83	−11.94
e_u	$xz_1 - xz_2$ / $yz_1 - yz_2$	0.67	0.67	−12.13	e	$xz_1 - xz_2$ / $yz_1 - yz_2$	0.67	0.87	−12.13

[a]The Ru_1–NH_3 distances are 0.04 Å shorter than the Ru_2–NH_3 distances. See the text for details.

degenerate in the symmetric case and thus localized upon distortion.

These electron occupancies are the key to an understanding of the relative tendencies of mixed valence ions to distort. If one electron is removed by oxidation of the Ru(II)–Ru(II) pyrazine ion, **1a**, it will come from the b_{2g} ($xz_1 + xz_2$) orbital which is highly coupled and relatively insensitive to distortion. If one electron is removed from the bipyridine complex, **2a**, it will come from a degenerate set of orbitals which are essentially nonbonding and sensitive to distortion. This Jahn–Teller distortion will split the ground state degeneracy giving a lower energy and a 'localized' electron structure to the ion. Our methods are not suitable for evaluating the exact electronic structure of any of these ions, so no absolute energy differences can be given. There is little doubt, however, that the bipyridine Ru(II)–Ru(III) ion will readily distort and that the corresponding pyrazine will be relatively stable with a symmetric geometry.

It should be noted that our model predicts that the relative coupling may be greater for the Ru(II)–Ru(III) pyrazine ion, **1b**, than it is for the Ru(II)–Ru(II) ion, **1a**, since the electron comes from an antibonding orbital. This is supported by the observation that the metal to ligand charge transfer band, $b_{2g} \rightarrow b_{3u}(\pi^*)$, which occurs at 547 nm for **1a**, moves to a *lower* energy, 565 nm, upon oxidation to **1b** [1]. Simple considerations of charge would predict an opposite shift. The absorption found in the near infrared at 1530 nm is assigned to the fully allowed transition between the two highly coupled metal orbitals, $b_{3u} \rightarrow b_{2g}$ [1]. The metal to ligand charge transfer peak for the bipyridine ion, **2a**, occurs at 521 nm and does not shift upon oxidation [4]. The near infrared absorbance found for **2b** would be a true intervalence transition following the Hush model.

Meyer [4–7] has reported a series of mixed valence pyrazine bridged complexes which have 2,2'-bipyridine nonbridging ligands. These ions appear to have localized nonsymmetrical structures. As Meyer

has pointed out, the presence of nonbridging π back-bonding ligands will decrease the coupling caused by the bridging ligand. Evidently in these ions the normal coupling is disrupted sufficiently such that the localized structures become more stable.

Nitrile Bridged Ions

For further examples of both symmetric and distorted mixed valence ions we will consider various nitrile bridged complexes. We can consider two extremes, the known cyanogen bridged dimer [8], **3b**, and a model ion, **4b**, in which the bridging ligand has two cyano functionalities bound to a group X which allows no conjugation between the cyano groups. Cyanogen has two mutually perpendicular π systems each with nodal patterns similar to those of butadiene, **7**. The Ru(II)–Ru(II) ion, **3a**, would have an e_u orbital set stabilized by the lowest π^* orbitals

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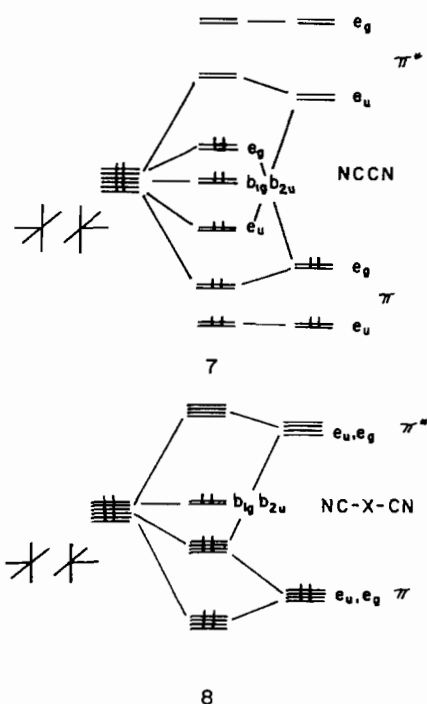
and an e_g set destabilized by the highest π set. This results in a strong coupling of orbitals. If one electron is removed by oxidation it comes from a degenerate orbital set, but distortion to a localized structure will not appreciably stabilize the ion. The orbitals involved, Table I, are those of a linear system and the Jahn–Teller theorem does not apply, since distortions along the axis do not split the degeneracy.

For the model ion, **4a**, the cyano groups are not conjugated meaning that there are four low lying π^* orbitals of e_g and e_u symmetries and four π orbitals of similar symmetries, **8**. Since the π and π^* orbitals are of the same symmetries they overlap with the same metal orbitals and the π^* dominates. This leaves the essentially degenerate b_{1g} and b_{2u} orbitals as the highest occupied orbitals. Removal of an electron from one of these orbitals would result in a ready distortion to a localized structure.

An examination of the known nitrile bridged Ru ions reveals examples of both extremes. The cyanogen bridged ion is a known species and is thought to be symmetrical [8]. Dialkyl malonitrile bridged ions are known and may be examples of the model **4b** complexes, since there would be little conjugation between the cyano groups. An intermediate case would be bridged complexes of dicyanobenzene. There is some conjugation between the cyano groups, but it is likely that the conjugation will not be great enough to stabilize a symmetric structure [23]. A final example is a Ru(II)–Ru(III) ion which has as the bridging ligand the anion of *tert*-butyl malonitrile [9]. This ligand has a high lying filled π orbital and should bond in a manner similar to pyrazine, Fig. 1, except the π donor interaction would be much more important. Since the odd electron is in a highly coupled orbital the symmetric ion is stable.

Conclusions

Bimetallic Ru(II)–Ru(III) ions may be symmetrical with equivalent ruthenium centers or may be distorted with nonequivalent metal sites, which in the extreme can be identified as Ru(II) and Ru(III). Certain ions with ligands such as 4,4'-bipyridine or nonconjugated dicyano species would have degenerate ground states if they were symmetrical and are thus distorted. In other species such as the cyanogen bridged complex the odd electron will be in a highly coupled orbital and the symmetric ion will be stable. The original Creutz and Taube pyrazine complex, **1b**, has the odd electron in a coupled orbital, unfortunately the coupling is not particularly strong and the true energy surface must be quite flat. The actual structure and electron transfer problem requires careful analyses of the vibronic states and the question of whether or not the ion is symmetrical may become a question of semantics.

Acknowledgement

References

1 C. Creutz and H. Taube, *J. Am. Chem. Soc., 91,* 3988 (1969); *95,* 1086 (1973).
2 C. Creutz, *Ph. D. Thesis,* Stanford University, Stanford, Calif., July 1970.

3 D. K. Lavallee and E. B. Fleischer, *J. Am. Chem. Soc.*, *94*, 2583 (1962).

4 G. M. Tom, C. Creutz and H. Taube, *J. Am. Chem. Soc.*, *96*, 7827 (1974).

5 S. A. Adeyemi, J. N. Braddock, G. M. Brown, J. A. Ferguson, F. J. Miller and T. J. Meyer, *J. Am. Chem. Soc.*, *94*, 300 (1972); S. A. Adeyemi, E. C. Johnson, F. J. Miller and T. J. Meyer, *Inorg. Chem.*, *12*, 2371 (1973).

6 R. W. Callahan, G. M. Brown and T. J. Meyer, *Inorg. Chem.*, *14*, 1443 (1975).

7 R. W. Callahan, F. R. Keene, T. J. Meyer and D. J. Salmon, *J. Am. Chem. Soc.*, *99*, 1064 (1977).

8 G. M. Tom and H. Taube, *J. Am. Chem. Soc.*, *97*, 5310 (1975).

9 H. Krentzien and H. Taube, *J. Am. Chem. Soc.*, *98*, 6379 (1976).

10 P. Critin, *J. Am. Chem. Soc.*, *95*, 6472 (1973).

11 C. Creutz and H. Taube, *J. Am. Chem. Soc.*, *91*, 3988 (1969).

12 J. Beattie, N. Hush and P. Taylor, *Inorg. Chem.*, *15*, 992 (1976).

13 J. Beattie, C. Raston and A. White, *J. Chem. Soc. Dalton Trans.*, 1121 (1977).

14 B. C. Bunker, R. S. Drago, D. N. Hendrickson, R. M. Richman and S. L. Kessell, *J. Am. Chem. Soc.*, *100*, 3805 (1978).

15 N. Hush, *Prog. Inorg. Chem.*, *8*, 357, 391 (1967).

16 M. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, *10*, 248 (1967).

17 B. Mayoh and P. Day, *Inorg. Chem.*, *13*, 2273 (1974).

18 M. Ratner and M. J. Ondrechen, *Mol. Phys.*, *32*, 1233 (1976).

19 The D_{2d} geometry was assumed to simplify the argument, if D_2 or D_{2h} geometries are assumed the conclusions do not significantly change.

20 R. Hoffmann, *J. Chem. Phys.*, *39*, 1397 (1963); R. Hoffmann and W. N. Lipscomb, *ibid.*, *36*, 2179, 3489 (1962); *37*, 2872 (1962).

21 Ruthenium parameters used were: Ru 5s, $\zeta = 2.08$, $H_{ii} = -9$ eV; Ru 5p, $\zeta = 2.04$, $H_{ii} = -4.5$ eV; Ru 4d, $\zeta_1 = 5.3$, $\zeta_2 = 2.0$, $C_1 = 0.553$, $C_2 = 0.659$, $H_{ii} = -12.5$. Standard parameters were used for the remaining elements.

22 The pyrazine has a staggered geometry with respect to the remaining ligands. This *cis* NH_3 ligands have a 2.124 A bond distance and the *trans* ligand has a 2.098 A bond distance [13].

23 H. C. Stynes and J. A. Ibers, *Inorg. Chem.*, *10*, 2304 (1971).

24 The Ru(II)–Ru(II), 1,4-dicyanobenzene ion has been reported [25] but not the Ru(II)–Ru(III) ion.

25 C. P. Guengerich and K. Schug, *J. Am. Chem. Soc.*, *99*, 3298 (1977); P. C. Ford and R. E. Clarke, *Inorg. Chem.*, *9*, 495–499 (1970).