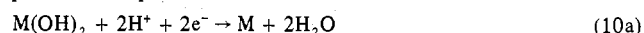
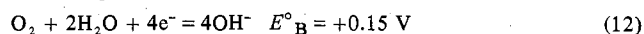


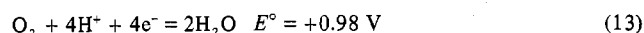
1. In contrast, the reduction of oxygen at freshly preoxidized electrodes is pH dependent, yields negligible amounts of hydrogen peroxide, and occurs at the same potential as that for the metal oxide of the electrode material.<sup>13,14</sup> The previously proposed mechanism<sup>13,14</sup> continues to provide a plausible explanation for these observations



In this mechanism, fresh metal oxide,  $M(OH)_2$ , is electrochemically reduced and re-formed by oxygen in solution. The scheme satisfies the requirement that the reduction potential and rate of reaction be dependent on the electrode material,  $M$ , and pH. The net reaction is



or



and does not involve formation of peroxide. Representative experimental reduction potentials at platinum are +0.30 and -0.32 V at pH 2 and pH 13, respectively.<sup>13</sup> Although eq 10 clearly represents the rate-determining step in the reduction of oxygen on preoxidized electrodes, some oxygen may react directly at freshly reduced electrode sites (scheme 1) to form trace amounts of peroxide.

In summary, there is no experimental or mechanistic basis for two-electron or four-electron processes in the direct electrochemical reduction of molecular oxygen. On the basis of the body of experimental data in support of mechanistic scheme 1, the one-electron-transfer process for reduction of molecular oxygen is concluded to be reversible and independent of electrode materials and solution conditions. The belief that the electrode surface is catalytic for the electron-transfer process is unjustified and not supported by the experimental data. Hence, the search for electron-transfer catalysts for oxygen reduction is a futile enterprise; the effective potential is limited to -0.2 V. Prechemical atom-transfer catalysts (eq 10 and 11 of scheme 2) can yield higher potentials that correspond to the reduction of the metal oxide.

The proposition of a one-electron mechanism for the electron-transfer reduction of oxygen and the associated conclusions present significant ramifications relative to the development of improved fuel cells and metal-air batteries. To date the practical forms of such systems have used strongly acidic or basic electrolytes. Such solution conditions normally cause scheme 2 to be the dominant reduction process for molecular oxygen at metal electrodes. Hence, the search for effective catalytic materials should be in this context rather than in terms of a one-electron-transfer process.

Finally, the concept of a one-electron mechanism for the electrochemical reduction of molecular oxygen is compatible with the current understanding of the biological electron-transfer reduction of oxygen and in accord with the mechanistic importance of superoxide ion.<sup>19-21</sup>

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## Mode of Bonding of Dinitrogen Oxide (Nitrous Oxide) in (Dinitrogen oxide)pentaammineruthenium

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Sir:

(Dinitrogen oxide)pentaammineruthenium,  $[Ru(NH_3)_5N_2O]^{2+}$ , is at present the only known complex containing coordinated  $N_2O$ . In order to characterize the properties of  $N_2O$  as a ligand molecule, it is important to establish the mode of bonding of  $N_2O$ . In earlier work<sup>1,2</sup> some evidence was presented which indicated that  $N_2O$  was bonded to the ruthenium via the terminal N atom (i.e., Ru-N-N-O). Recently Diamantis and Sparrow and collaborators<sup>3,4</sup> stated that force constant calculations show the  $N_2O$  to be bonded via the O atom (i.e., Ru-O-N-N). We wish to comment on their result, and on the bonding of  $N_2O$  in  $[Ru(NH_3)_5N_2O]^{2+}$ .

Examination of Table II of ref 3 shows a very large variation in some of the force constants as the negative ions are changed. Thus the Ru-N stretching constants for the Ru-N-N-O model and the Ru-O stretching constant for the Ru-O-N-N model change by more than a factor of 2 while the frequencies assigned to the Ru-N or Ru-O mode are in the range 300-340  $cm^{-1}$ . The stretching constants for the central bond of each model also change over a comparable range. These improbably large variations prompted us to recalculate the frequencies using the force constants of Diamantis and Sparrow. The frequencies obtained<sup>5</sup> by us differed from the observed by as much as 300  $cm^{-1}$ . We therefore suspected the vibrational

**Table I.** Calculated Force Constants<sup>a</sup> for [Ru(NH<sub>3</sub>)<sub>5</sub>N<sub>2</sub>O]X<sub>2</sub> (N m<sup>-1</sup>)

a. Assuming a Model with Ru-O-N-N Bonding				
X	$k_{\text{Ru-O}}$	$k_{\text{N-N}}$	$k_{\text{N-O}}$	Error, <sup>b</sup> cm <sup>-1</sup>
Br	234	1923	766	5.2
I	209	1925	814	3.4
BF <sub>4</sub>	196	1932	877	2.9
PF <sub>6</sub>	189	1936	906	2.1
b. Assuming a Model with Ru-N-N-O Bonding				
X	$k_{\text{Ru-N}}$	$k_{\text{N-N}}$	$k_{\text{N-O}}$	Error, <sup>b</sup> cm <sup>-1</sup>
Br	223	1850	838	5.1
I	202	1860	876	3.5
BF <sub>4</sub>	191	1872	933	3.2
PF <sub>6</sub>	184	1879	960	2.3

<sup>a</sup> In all cases  $k_{\text{N-N}^*\text{N-O}} = 80 \text{ N m}^{-1}$  and other interaction constants are zero. The maximum standard deviation of the force constants is  $\pm 4 \text{ N m}^{-1}$ ; this makes no allowance for experimental or model errors. <sup>b</sup> Error is the maximum difference between observed and calculated frequencies. The root-mean-square errors are less than  $2.8 \text{ cm}^{-1}$  in all cases.

analysis of Diamantis and Sparrow was in error, and using the same models and the seven observed frequencies of each substance<sup>4</sup> we recalculated the best values of the three stretching constants.<sup>6</sup> We also tried slightly different models, taking the heavy-atom mass as 101 (Ru alone) instead of 187 for Ru(NH<sub>3</sub>)<sub>5</sub> and changing the N-N, N-O interaction constant. These changes do affect the final force constant values but the essential results remain unaltered. We favor using the Ru atom mass (101) since the NH<sub>3</sub> groups are probably not strongly coupled to the Ru-N<sub>2</sub>O vibrations, and the value of  $80 \text{ N m}^{-1}$  for the interaction constant is close to the best value for gaseous N<sub>2</sub>O;<sup>7</sup> the force constants for these choices are given in Table I. As checks we also calculated the frequencies of [Ru(NH<sub>3</sub>)<sub>5</sub>N<sub>2</sub>O]Cl<sub>2</sub><sup>8</sup> using the Br salt force constants, and we set  $k_{\text{Ru-N}}$  or  $k_{\text{Ru-O}}$  to zero which reduces the model to the gaseous N<sub>2</sub>O case. Both checks gave good agreement with the observed or calculated data.

Examination of the table shows a satisfactory consistency in the force constants, and these constants reproduce the observed frequencies within  $\pm 5 \text{ cm}^{-1}$  or less. The Ru-O-N-N model has a marginally better fit between observed and calculated frequencies and the Ru-N-N-O model gives a slightly more consistent set of force constants, but neither of these differences is large enough to be significant. Thus our normal-coordinate analysis gives *no* basis for favoring one orientation of the N<sub>2</sub>O ligand over the other. In principle the question of N or O bonding could be settled by a complete vibrational analysis of the complexes. However, because of their instability and the great difficulty in obtaining pure samples the bands in the lower frequency region of the spectrum are broad, and assignments are correspondingly uncertain.

Since earlier work<sup>1,2,8-10</sup> has not explicitly considered the point, it is worth summarizing here the available evidence on the mode of bonding of N<sub>2</sub>O in [Ru(NH<sub>3</sub>)<sub>5</sub>N<sub>2</sub>O]<sup>2+</sup>. The physical and chemical properties of [Ru(NH<sub>3</sub>)<sub>5</sub>N<sub>2</sub>O]<sup>2+</sup> prepared by different methods<sup>1,4,8,10</sup> are identical, and therefore linkage isomerism is (as yet) not a problem.

1. The x-ray powder results<sup>1,4</sup> clearly indicate the Ru(N<sub>2</sub>O) moiety is linear within close limits. Although it might well be possible to produce a molecular orbital model having a linear Ru-O-N-N, the most attractive explanation of the linearity is that the N<sub>2</sub>O is N bonded with the valence bond structure Ru-N≡N-O predominating.

2. The relative shifts in infrared frequencies and force constants for N<sub>2</sub>O (see Table I and ref 1 and 4) are also

consistent with a model in which the linear Ru-N≡N-O predominates.<sup>11</sup>

3. The observation that the relative intensities of the infrared bands of N<sub>2</sub>O change drastically on coordination in the sense  $\nu_3 > \nu_1 > \nu_2$  (uncoordinated) to  $\nu_1 \gg \nu_3$  (coordinated); the assignment of  $\nu_2$  in the complex is uncertain<sup>1,4</sup> is consistent with the Ru-N-N-O model but not with Ru-O-N-N.

4. Armor and Taube prepared [Ru(NH<sub>3</sub>)<sub>5</sub><sup>15</sup>N<sup>14</sup>N]<sup>2+</sup> and [Ru(NH<sub>3</sub>)<sub>5</sub><sup>14</sup>N<sup>15</sup>N]<sup>2+</sup> from <sup>15</sup>N<sup>14</sup>NO and <sup>14</sup>N<sup>15</sup>NO, respectively.<sup>2</sup> The infrared spectra of the labeled N<sub>2</sub> complexes are consistent with the Ru-N-N-O model, and the band assignments have been supported by later work.<sup>13</sup>

5. A mechanism for formation of [Ru(NH<sub>3</sub>)<sub>5</sub>N<sub>2</sub>O]<sup>2+</sup> from [Ru(NH<sub>3</sub>)<sub>5</sub>NO]<sup>3+</sup> and NH<sub>2</sub>OH has been proposed<sup>1</sup> and has received support from work on related systems.<sup>14</sup> The mechanism requires that the N atom of the NO group in [Ru(NH<sub>3</sub>)<sub>5</sub>NO]<sup>3+</sup> remains attached to the ruthenium throughout reaction and becomes the terminal N of N<sub>2</sub>O. We are unable to postulate a chemically reasonable mechanism which produces Ru-O-N-N. A completely intermolecular rearrangement after N<sub>2</sub>O formation is excluded because of the known instability of [Ru(NH<sub>3</sub>)<sub>5</sub>N<sub>2</sub>O]<sup>2+</sup> toward substitution in aqueous solution.<sup>1,4,9</sup>

6. The electronic spectrum of [Ru(NH<sub>3</sub>)<sub>5</sub>N<sub>2</sub>O]<sup>2+</sup> is very similar to that of [Ru(NH<sub>3</sub>)<sub>5</sub>N<sub>2</sub>]<sup>2+</sup>.<sup>1,4,9</sup>

It is clear from the above that there is no definitive evidence for either mode of bonding, but the circumstantial evidence is heavily in favor of bonding through N, i.e., Ru-N-N-O, and the infrared spectra and force constants are consistent with this model.

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**Registry No.** [Ru(NH<sub>3</sub>)<sub>5</sub>N<sub>2</sub>O]<sup>2+</sup>, 25069-25-4.

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