

and  $\Psi^{\circ}_2$ .<sup>16,17</sup> As an example of this effect, we note that if  $S$  is allowed to be as large as 0.2 the calculated value of  $\rho$  for the *trans*-(3-F-py)(NH<sub>3</sub>)<sub>4</sub>Ru<sup>II</sup>pyzRu<sup>III</sup>(NH<sub>3</sub>)<sub>5</sub><sup>5+</sup> dimer changes from 0.91 to 0.96.<sup>18</sup> The result that the values of  $\rho$  obtained at the narrow  $\Delta\nu_{1/2}$  end of the first series are essentially equal to 1 supports a class III electronic structure for the Creutz-Taube ion.  $\rho$  values of the more perturbed end of the series are closer to 0.9 and indicate a transition toward a localized description. This is in agreement with the trend evidenced by the spectral data. In the class II molecules comprising the second series, it is found that  $\rho$  drops substantially to values more on the order of 0.4-0.5. This is also in accord with expectations based on the spectral observations.

It is interesting that  $m$  and  $\rho$  are as large as they are over the entire first series even though the  $\Delta\nu_{1/2}$  values point toward a substantial class III to class II transition in electronic structure. Relevant to this point, investigation of the solvent dependence of  $E_{IT}$  for some of the members of this series as well as further investigation of symmetrically substituted species is under way. Other work in progress includes precise determination of intervalence-transfer band extinction coefficients for the dimers reported here, extension of this approach to other bridging ligands such as 4-cyanopyridine and 4,4'-bipyridine, a comparison of the effects of *cis* vs. *trans* substitution at the directly perturbed metal center, and electrochemical investigation of various rhodium-ruthenium analogues.

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**Supplementary Material Available:** Detailed derivation of eq 5, a figure showing potential curves for an asymmetric, predominantly localized system, and a listing of microanalytical data (7 pages). Ordering information is given on any current masthead page.

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### A Novel $\mu$ -Terephthalato Copper(II) Dimer with Unexpected Strong Antiferromagnetic Exchange Interaction

*Sir:*

In our laboratory a research project aimed at investigating the factors affecting the superexchange interactions propagated by multiautom bridges is under way.<sup>1,2</sup> Within this framework a series of new  $\mu$ -terephthalato copper(II) binuclear complexes has been chosen and thoroughly investigated by using both experimental and theoretical approaches. Most of these new  $d^9$ - $d^9$  magnetic systems exhibited negligible intramolecular exchange interactions but showed weak intermolecular antiferromagnetic interactions

( $2J$  values in the range  $-1.00$  to  $-5.06$  cm<sup>-1</sup>), depending on the transition-metal ground state. Similar results were reported recently by Kahn et al.<sup>3</sup> for three analogous compounds. The magnetic behavior of all these compounds was also predicted by EHMO calculations performed on a series of model compounds exhibiting a variety of transition-metal ground states.<sup>2,4</sup> Contrary to our quantum-chemical predictions, the dimer ( $\mu$ -terephthalato)bis[(2,2'-bipyridine)aquocopper(II)] dication, in its salt form with perchlorate anions, [Cu<sub>2</sub>( $\mu$ -TPHA)(bpy)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**1**) (where TPHA = terephthalato and bpy = 2,2'-bipyridine), exhibited an unexpected stronger antiferromagnetic interaction ( $2J$  value of  $-51.8$  cm<sup>-1</sup>).

In this communication the experimental and theoretical data available accounting for this stronger antiferromagnetic interaction of complex **1** are presented. It proves to be intermolecular in nature.

Complex **1** was prepared by adding a solution of 0.336 g (1 mmol) of piperidinium terephthalate and 0.312 g (2 mmol) of 2,2'-bipyridine in methanol (10 mL) to a solution of 0.74 g (2 mmol) of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O in the same solvent (6 mL), at room temperature. The blue microcrystalline product formed gave satisfactory elemental analysis corresponding to the formula [Cu<sub>2</sub>( $\mu$ -TPHA)(bpy)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>. Numerous attempts in our laboratory to grow single crystals suitable for a structural investigation have been unsuccessful so far.

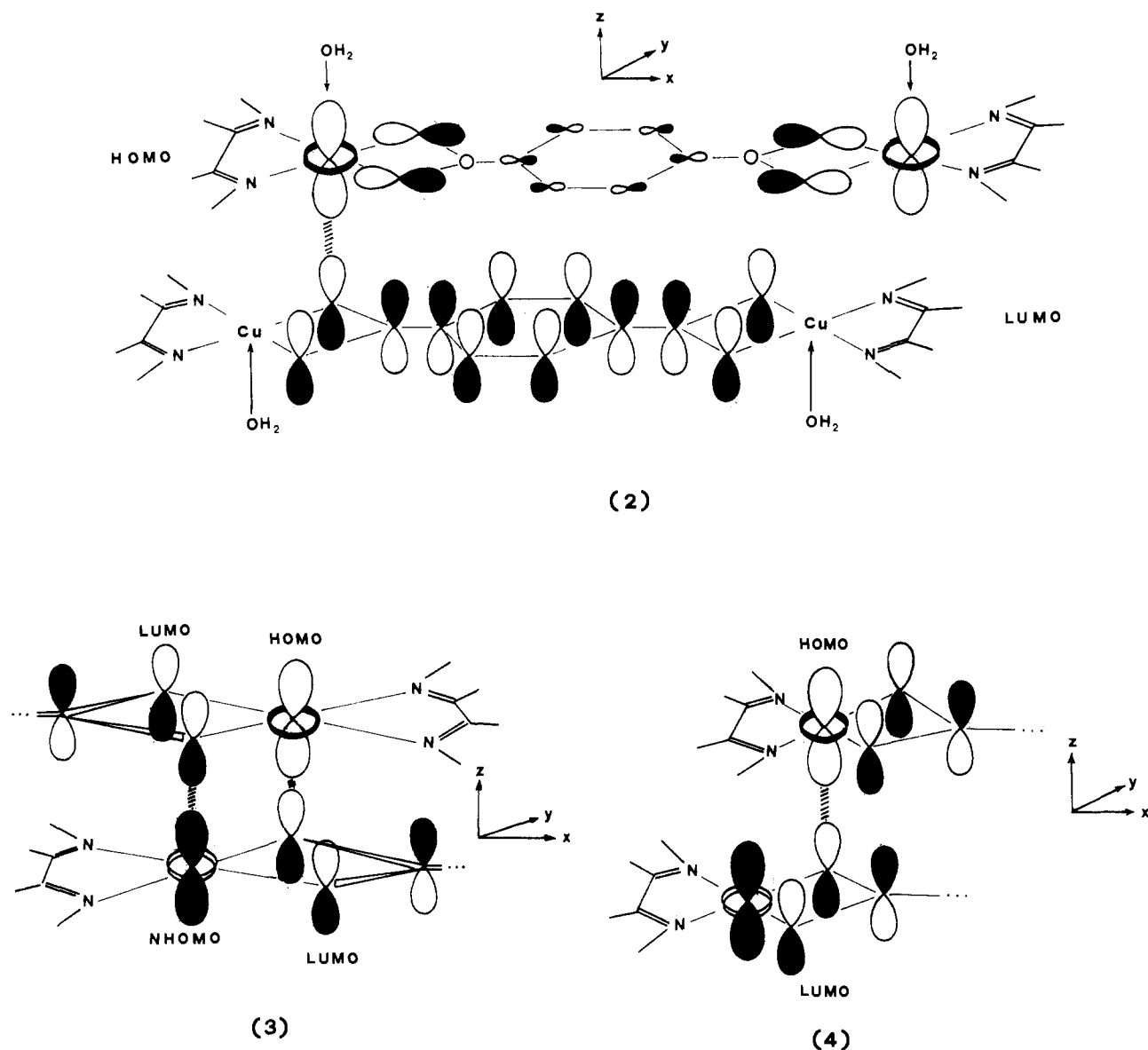
The IR spectrum of **1** exhibited the  $\nu_{as}(\text{CO}_2)$  and  $\nu_s(\text{CO}_2)$  strong absorption bands due to the terephthalato ligand, along with the characteristic bands of the noncoordinated perchlorate anions.<sup>5</sup> The absence of any splitting of the  $\nu_{as}(\text{CO}_2)$  and  $\nu_s(\text{CO}_2)$  bands strongly suggests the end-to-end linking of the terephthalato ligand in an equivalent way at both sites. Furthermore, the observed  $\nu_{as}(\text{CO}_2)$ - $\nu_s(\text{CO}_2)$  value of 182 cm<sup>-1</sup> calls for an ambidentate bonding mode<sup>6</sup> of the carboxylato groups.

The electronic reflectance spectrum of the complex exhibited in the visible region a broad band envelope with a maximum at  $15.62 \times 10^3$  cm<sup>-1</sup> and two shoulders at  $17.00 \times 10^3$  and  $13.23 \times 10^3$  cm<sup>-1</sup>, respectively. According to the well-established electronic criteria of stereochemistry for Cu(II) compounds,<sup>7</sup> this spectrum is at first sight characteristic of five-coordinated Cu(II) chromophores with distorted square-pyramidal configuration. However, the appearance of the shoulder at  $17.00 \times 10^3$  cm<sup>-1</sup> provides evidence for the presence of six-coordinated chromophores with strongly distorted elongated octahedral configurations. The coexistence of both five- and six-coordinated chromophores in **1**, although prohibited by the stoichiometry and the bonding mode of the ligands in the binuclear complex, could be explained on the grounds of intermolecular solid-state interactions. Therefore, the formation of dimers or polymers in the solid state involving both types of coordination could not be excluded. These intermolecular solid-state interactions are accounted for by the nature and energies of the frontier MO's of **1** calculated on the basis of the EHMO method. It is obvious that the frontier MO's that would be responsible for the solid-state interactions of the isolated binuclear entities are only those exhibiting significant metal 3d<sub>z<sup>2</sup></sub> and ligand p<sub>z</sub> character. For **1** these MO's were the HOMO and LUMO with significant metal and ligand character, respectively. These HOMO-LUMO orbital interactions lead to the formation of a dimeric (**2**) or polymeric (**3**) structure (see Chart I) and account for the coexistence of both the five- and six-coordinated chromophores in the solid state. Moreover, the dimerization or polymerization of the binuclear moieties is also favored by their planarity due to the extensive conjugation encountered for both

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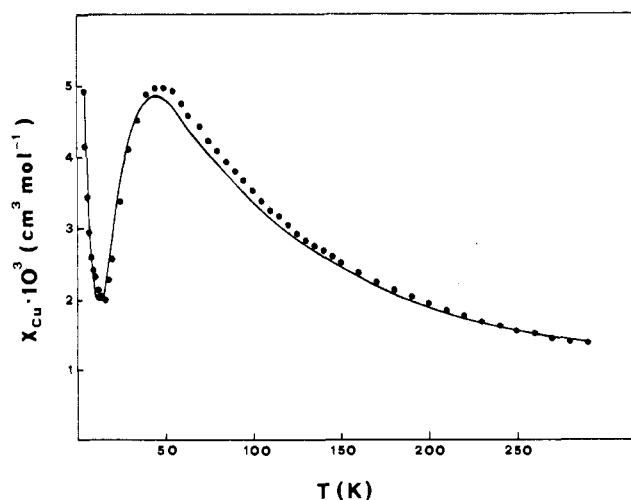
Chart I



the planar terephthalato bridging unit and the planar terminal 2,2'-bipyridine ligands. Such a structure should also be expected for the analogous compound with tmen (=N,N,N',N'-tetramethylethylenediamine) as terminal ligand, but the preparation of that complex has been unsuccessful.<sup>3</sup>

The X-band powder EPR spectrum of **1** indicated only a single line and did not exhibit any sign of exchange interaction either at room temperature or at 173 K. The calculated *g* values were 2.122 and 2.123 at room temperature and 173 K (peak-to-peak line widths 195 and 188 G), respectively. These values are intermediate between those observed for elongated octahedral and square-pyramidal Cu(II) complexes<sup>7b</sup> with polyamine ligands. Furthermore, these values are consistent with the coexistence of both structures in the solid state of **1**. Although one should expect two lines in the EPR spectrum, corresponding to the two different environments of the magnetic centers in the solid state, the appearance of a single line could be the result of exchange averaging.<sup>10</sup>

The variable-temperature magnetic susceptibility data collected for **1** are given in Table I<sup>8</sup> and illustrated in Figure 1. Experimental magnetic susceptibility data, obtained on a powder specimen, have been found to fit the modified Bleaney-Bowers equation.<sup>9</sup> Least-squares fitting gave the exchange parameter



**Figure 1.** Plot of molar paramagnetic susceptibility per copper(II) ion,  $\chi_{\text{Cu}}$ , vs. temperature of  $[\text{Cu}(\mu\text{-TPHA})(\text{bpy})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$  (data obtained on a powder specimen). The solid line represents the least-squares fit of the data to the theoretical equation.

$J = -25.9 \text{ cm}^{-1}$  at EPR =  $1.06 \times 10^{-6}$  (the molecular percentage of the mononuclear impurities was 4.89%). The  $\mu_{\text{eff}}/\text{Cu(II)}$  values

(8) Supplementary material.

ranged from  $1.77 \mu_B$  at 290 K to  $0.41 \mu_B$  at 4.2 K. The molar magnetic susceptibility  $\chi_M$  follows the Curie-Weiss law from room temperature (290 K) down to 100 K with values of  $0.409 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  and  $-13 \text{ K}$  for the Curie and Weiss constants, respectively. The corrected molar magnetic susceptibility vs. temperature curve for **1** is indicative of antiferromagnetic exchange interaction with susceptibility maximum at 50 K. Furthermore, the increase in  $\chi_M$  at the lowest temperatures is due to mononuclear impurities.

On the basis of the relatively sharp susceptibility maximum observed, a polymeric form could be excluded<sup>10</sup> and therefore the dimeric form seems to be the most probable one for **1**. In fact, this structure accounts well for the magnetic exchange interactions observed, which are further substantiated by suitable pathways. These pathways involve the orbital interactions (structure 4) located on the Cu-O...Cu moieties, which actually favor the transmission of the electronic effects through intermolecular interactions. The contribution of intramolecular types of interactions to the overall magnetic behavior of **1**, if any, should be insignificant on the grounds of the EHMO calculations. Accordingly, the terephthalato bridging unit exhibits an unfavorable character to transmit the electronic effects over long distances owing to the very low electron density delocalization on the bridging unit of each magnetic orbital (structure 2).

Finally, considering the interference of the superexchange interactions, it is expected that the  $2J$  value of the Cu-O...Cu magnetic system will be about<sup>11</sup> one-fourth of the  $2J$  value for the



magnetic systems. In fact, the calculated  $2J$  value of  $-51.8 \text{ cm}^{-1}$  for **1** is in the range of  $-35$  to  $-95 \text{ cm}^{-1}$ , which corresponds to one-fourth of the  $2J$  values observed for a number of magnetic systems with two oxygen atom bridging units.<sup>12</sup>

**Supplementary Material Available:** Table I, listing experimental magnetic susceptibility data (2 pages). Ordering information is given on any current masthead page.

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### Reduction Potential of the Trinitrogen Radical As Determined by Chemical Kinetics: Novel Application of Spin Trapping

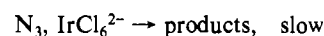
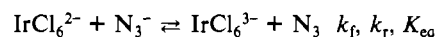
Sir:

Azide is easily oxidized in aqueous solution; its single-electron oxidation product, the trinitrogen radical (azidyl,  $N_3$ ) is frequently encountered in radiation chemistry and photochemistry. However, the relationships between these two species are somewhat uncertain. The assignment of the CTTS band in the UV spectrum of  $N_3^-$ , which should link the energies of the two species, is

controversial.<sup>1</sup> Photoelectron emission studies of  $N_3^-$  in solution have not really resolved the issue.<sup>1d,e</sup> The high-energy assignment of the CTTS band has been used to estimate the reduction potential of  $N_3$  (1.87 V) and thereby to interpret the rates of fluorescence quenching of aromatic molecules<sup>2</sup> and aromatic ketones.<sup>3</sup> Electron-transfer quenching by  $N_3^-$  of nitrofurans,<sup>4</sup> flavins,<sup>5</sup> thionine,<sup>5</sup> and a variety of organic molecules<sup>6</sup> has also been interpreted by use of the CTTS band. Other estimates of the reduction potential of  $N_3$  have ranged from 1.15<sup>7</sup> to 1.90 V.<sup>8</sup> Criteria to assign SET mechanisms to organic reactions of  $N_3^-$  rely on this poorly known potential.<sup>9</sup> In inorganic chemistry the radical has been implicated in photoredox studies of azido complexes<sup>8</sup> and in redox reactions of  $N_3^-$  with coordination complexes.<sup>10</sup> There appears to be only one report of simple kinetics for outer-sphere oxidation of  $N_3^-$ , and this used the strongly oxidizing species  $[\text{Ni}(\text{bpy})_3]^{3+}$ .<sup>11</sup> Weaker oxidants such as  $\text{IrCl}_6^{2-}$  gave complex and poorly understood kinetics.<sup>7</sup> This paper reports a reinvestigation of the reaction of  $\text{IrCl}_6^{2-}$  with  $N_3^-$ , which leads to an accurate evaluation of the reduction potential for the  $N_3/N_3^-$  couple.

Qualitative studies of the reaction of excess  $N_3^-$  with  $\text{IrCl}_6^{2-}$  (which yields  $N_2$  quantitatively as determined by Toepler pumping) rapidly established that the kinetics was far from pseudo first order, consistent with prior observations.<sup>7</sup> Also consistent with prior observations was the observation that  $\text{IrCl}_6^{3-}$  (the iridium-containing product)<sup>7</sup> strongly inhibited the kinetics. With excess  $N_3^-$  and  $\text{IrCl}_6^{3-}$  the kinetics was pseudo second order, but the dependence on  $[\text{IrCl}_6^{3-}]$  was complex. A detailed description of these observations and the overall mechanism will be presented later;<sup>12</sup> nevertheless, the first stages of the reaction can be represented by Scheme I.

#### Scheme I



Unusually complex kinetics arises because there is no efficient pathway for consumption of the azidyl radicals. Unlike in the oxidations of  $I^-$ ,  $\text{SCN}^-$ , and  $\text{S}_2\text{O}_3^{2-}$  where reaction of the free radical with the corresponding anion to form  $X_2^-$  is rapid and strongly driven,<sup>7,13</sup>  $N_3$  exhibits little such tendency.<sup>14</sup> Dimerization of  $N_3$  is diffusion-controlled,<sup>15</sup> but it is second order in  $[\text{N}_3]$ .  $\text{NO}_2$  likewise has no efficient decay pathway, but in the oxidation of  $\text{NO}_2^-$  this is not a severe problem because  $k_r$  is relatively slow.<sup>16</sup>

Spin traps react efficiently with  $N_3$ , and the spin adduct with PBN (*N-tert-butyl- $\alpha$ -phenylnitron*) has been observed by several research groups.<sup>17</sup> In the prior reports it was shown that PBN

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