lar orbitals of the ionized molecule are those of the parent molecule. Electronic relaxation (*i.e.*, change of orbitals) in the ionized molecule or a difference in correlation energies (not included in SCF–MO treatment) will invalidate Koopmans' theorem. Thus a difference in electronic relaxation energies for photoionization of the e_{2g} electron as compared to the a_{1g} electron or a difference in correlation energy differences is the probable cause of this disagreement.

It would be interesting to have photoelectron ionization data for other metallocenes. The ligand field treatment of ruthenocene[1] gave $\Delta\epsilon^{\mathrm{core}}(a_{1g}-e_{2g}) = -6600$ cm^{-1} and $B = 260$ cm^{-1}. In this case we would predict $\Delta\epsilon^{\mathrm{SCF}}(a_{1g}-e_{2g}) \cong +1400$ cm^{-1}, and, if the collapse of Koopmans' theorem is no more extensive in ruthenocene, the ionization potentials of the ruthenocene 4d a_{1g} and e_{2g} electrons should be closer in energy than those for the ferrocene 3d electrons.

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On the Exchange of Oxygen between Sulfate and Water

Sir:

A good deal of conflicting data on the rate and mechanism of oxygen exchange between sulfate and water has been reported;[1] for example, the exchange in 1 *N* NaOH at 100° has been reported to be as great as 85% in 26 hr[1a] and as little as <1% in 456 hr.[1d]

More recently, Hoering and Kennedy[2] reported some experiments on the acid-catalyzed exchange of oxygen between sulfuric acid and water. The results of these experiments, coupled with earlier reports (*e.g.*, ref 1a), suggest that there may be a change in the exchange mechanism from acid-catalyzed dehydration to, for example, nucleophilic displacement by H_2O and/or OH^- at higher pH values. We wish to report a reinvestigation of this question using ^{18}O-labeled sulfate (91.9 atom % excess obtained from Miles-Yeda Ltd.).

In these experiments solutions of 0.1 *M* $Na_2S^{18}O_4$ were incubated at 100° for 63 days in Teflon bombs, either with no additions of in the presence of 1 *N* NaOH. A 0.1-ml aliquot of the incubated solution was then introduced with a syringe into an evacuated 5-ml stoppered serum vial containing sufficient $NaHCO_3$ to produce 5 ml (at STP) of CO_2 upon acidification. An excess of 85% lactic acid (0.05 ml) was then added to release the CO_2. (The small dilution of ^{18}O label due to H_2O–lactic acid oxygen exchange was accounted for in the calculation of exchange rates.) After an equilibration time of 18 hr at room temperature (sufficient for complete isotopic equilibration[3]), the CO_2 was introduced into a modified CEC isotope ratio mass spectrometer through a syringe–needle inlet and the $^{18}O:^{16}O$ ratio of the CO_2 determined (at *m/e* 46 and 44). Preliminary experiments showed that, under the conditions used for equilibration with CO_2, no exchange of ^{18}O between the sulfate and water occurred. Therefore, it was not necessary to separate the water from the salt solutions before analyses.

Four readings were made on each of three replicates for each experimental condition. Measurements of "standard CO_2" (derived from $NaHCO_3$ in the same manner) were interspersed between experimental measurements to detect and correct for any drift in the mass spectrometer readings. Preliminary experiments using $H_2{}^{18}O$ indicated that we could reliably detect an exchange of 0.1% under the conditions employed.

These experiments showed that under neutral or alkaline conditions (1 *N* NaOH), no exchange (<0.1%) occurred at 100° in 63 days. This suggests that the second-order rate constant (k_2) is $<1 \times 10^{-11}$ M^{-1} sec^{-1} using H_2O as a nucleophile. Similarly, using OH^- as a nucleophile, the second-order rate constant (k_2) is $<8 \times 10^{-10}$ M^{-1} sec^{-1}. By way of comparison, we find $k_2 = 5.3 \times 10^{-5}$ M^{-1} sec^{-1} for the acid-catalyzed exchange reaction at 100°, a value in good agreement with the value calculated from the data in ref 2. It thus appears that sulfate oxygen does not undergo appreciable exchange with the oxygen of H_2O by any mechanism other than acid-catalyzed dehydration under these conditions.

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RECEIVED OCTOBER 4, 1971

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[1] (a) S. C. Datta, J. N. E. Day, and C. K. Ingold, *J. Chem. Soc.*, 1968 (1937); (b) G. A. Mills, *J. Amer. Chem. Soc.*, **62**, 2833 (1940); (c) N. F. Hall and O. R. Alexander, *ibid.*, **62**, 3455 (1940); (d) E. R. S. Winter, M. Carlton, and H. V. A. Briscoe, *J. Chem. Soc.*, 131 (1940); (e) E. R. S. Winter and H. V. A. Briscoe, *ibid.*, 631 (1942).

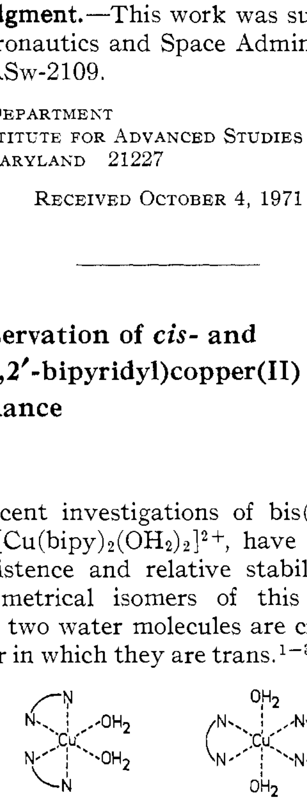
[2] T. C. Hoering and J. W. Kennedy, *J. Amer. Chem. Soc.*, **79**, 56 (1957).

[3] M. Cohn and H. C. Urey, *ibid.*, **60**, 679 (1938).

On the Observation of *cis*- and *trans*-Bis(2,2′-bipyridyl)copper(II) by Electron Spin Resonance

Sir:

Several recent investigations of bis(2,2′-bipyridyl)copper(II), $[Cu(bipy)_2(OH_2)_2]^{2+}$, have been concerned with the existence and relative stability of the two possible geometrical isomers of this complex: one in which the two water molecules are cis to each other and the other in which they are trans.[1-3]



cis trans

Among these investigations is the comprehensive nmr and esr study of Noack and Gordon[1] of the Cu^{2+}–

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[1] M. Noack and G. Gordon, *J. Chem. Phys.*, **48**, 2689 (1968).

[2] C. K. Jørgenson, *Acta Chem. Scand.*, **9**, 1362 (1955).

[3] Y. I. Skurlatov and A. P. Purmal, *Russ. J. Phys. Chem.*, **43**, 880 (1969).

bipy system. From nmr data they were able to show that $[Cu(bipy)_2(OH_2)_2]^{2+}$ exists predominantly in the cis form in aqueous solution at room temperature. They also concluded, from esr spectra of ethanol–water glasses at 77°K, that the cis and trans forms existed in comparable concentrations under these conditions of low temperature and mixed solvents. This conclusion was based upon the existence of two sets of parallel lines in the esr spectra of solutions containing $Cu(NO_3)_2$ and bipyridyl in a 1:2 ratio. One set of lines had its lowest field peak at approximately 2610 G, while the second set appeared to have its lowest field peak at approximately 2720 G; the two sets of lines had similar splittings. The g values calculated from these two sets of parallel lines were thus quite different: $g_{\parallel} = 2.285$ for the former and 2.227 for the latter. Although the 2.285 value was fairly similar to the value of $g_{\parallel}$ for the 1:3 complex (2.271), the $g_{\parallel}$ value for the other species (2.227) was quite different from any other $g_{\parallel}$ value in this system. On this basis, Noack and Gordon[1] concluded that the two species were *cis*-$[Cu(bipy)_2(OH_2)_2]^{2+}$ ($g_{\parallel} = 2.227$) and *trans*-$[Cu(bipy)_2(OH_2)_2]^{2+}$ ($g_{\parallel} = 2.285$).

We have repeated several of the experiments of Noack and Gordon[1] in the course of an investigation of ternary complexes which contain Cu^{2+}, bipy, and one of several bidentate ligands with oxygen as donor atom[4] and have discovered new evidence which suggests that the two species observed by Noack and Gordon[1] were actually the disproportionation products $[Cu(bipy)(OH_2)_4]^{2+}$ and $[Cu(bipy)_3]^{2+}$.

Figure 1 shows the esr spectrum of "$[Cu(bipy)_2(OH_2)_2]^{2+}$" obtained by dissolving, in the designated solvent mixture, solids which gave the chemical analyses[4] and polycrystalline esr spectra[4] consistent with the formulas $Cu(bipy)_2(ClO_4)_2$ or $Cu(bipy)_2(NO_3)_2$. The appearance of the spectrum quite clearly depends on both the composition of the solvent (compare a and b or c and d) and the anion (compare b and c or a and d). It also depends (not shown) on the amount of added salt ($NaClO_4$ or $NaNO_3$). Noack and Gordon[1] used the nitrate anion, and as solvent they used 40% ethanol–60% water. Although in our case the shape of the perpendicular region of the spectrum (*cf.* Figure 1c) is slightly different (probably due to the presence of a different concentration of NO_3^- in the solution), the parallel region of the spectrum is the same. That is, there is no *obvious* doubling of the lowest field parallel peak (~2610 G). However, in each of the other spectra (1a, b, d) an additional peak appears at lower field (~2575 G). With this in mind, careful reexamination of Figure 1c suggests that this additional peak may, in fact, be present here as well. The existence of this low-field peak means that the value of 2.227 for $g_{\parallel}$ for the "cis" complex reported by Noack and Gordon[1] is not correct. In fact, since *each* of the parallel lines of Figure 1 appears to be doubled, the two species present must have similar values of $g_{\parallel}$.

We have measured the esr spectra of the 1:1, "1:2," and 1:3 Cu^{2+}–bipy complexes under the same sets of conditions as those of Figure 1, except that we have used the pure isotope ^{63}Cu in the hope that the lines might be sharpened. Figure 2 shows a representative set of spectra of the "three" species (in this case in 67%

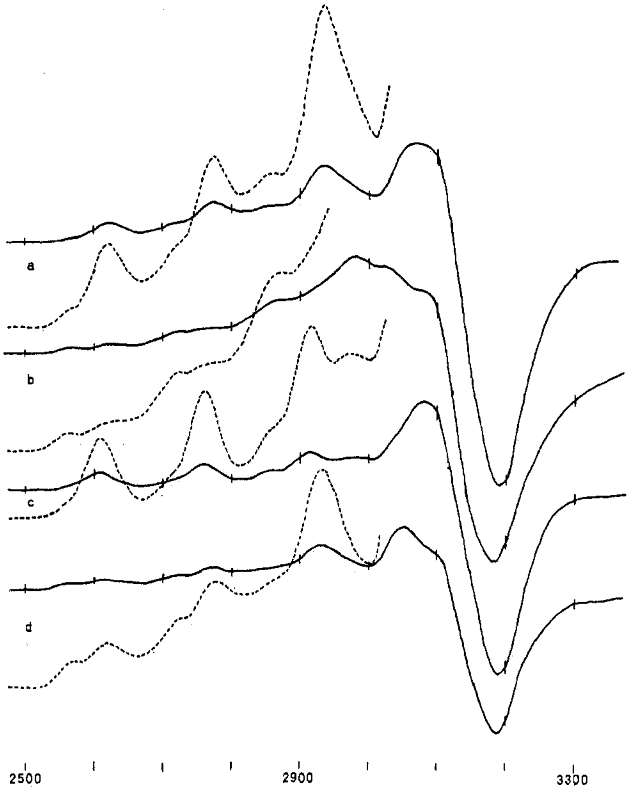

Figure 1.—Glassy esr spectra of "$[Cu(bipy)_2(OH_2)_2]^{2+}$" (natural mixture of isotopes): (a) $Cu(bipy)_2(ClO_4)_2$ in 40% ethylene glycol–60% water; (b) $Cu(bipy)_2(ClO_4)_2$ in 40% ethanol–60% water; (c) $Cu(bipy)_2(NO_3)_2$ in 40% ethanol–60% water; (d) $Cu(bipy)_2(NO_3)_2$ in 40% ethylene glycol–60% water. $[Cu^{2+}] \approx 5 \times 10^{-3}$ *M*. All spectra were recorded at 77°K. Dotted lines show the magnification of the low-field portion of each spectrum.

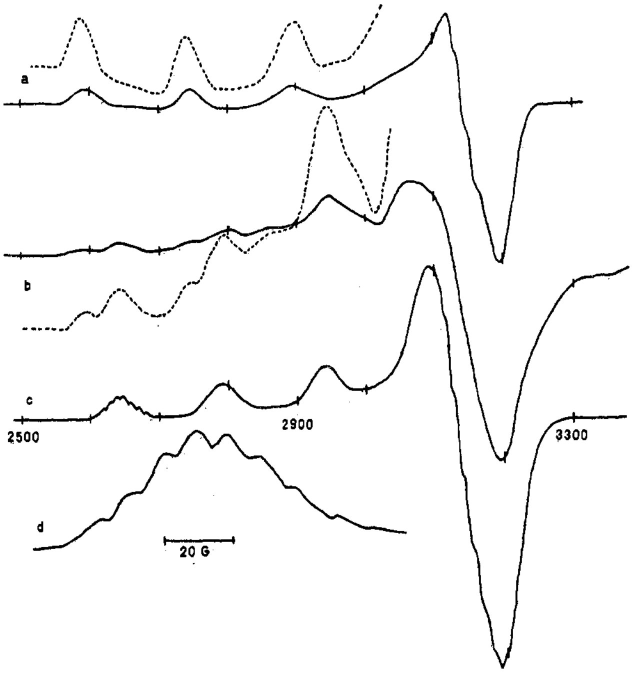

Figure 2.—Glassy esr spectra: (a) $[^{63}Cu(bipy)(OH_2)_4]^{2+}$ (Cu:bipy = 1:1); (b) "$[^{63}Cu(bipy)_2(OH_2)_2]^{2+}$" (Cu:bipy = 1:2); (c) $[^{63}Cu(bipy)_3]^{2+}$ (Cu:bipy = 1:4, or any ratio greater than 1:3); (d) low-field line of (c) under greater magnification. All samples are in 67% ethylene glycol–33% water at pH 5.2. $[Cu^{2+}] = 10^{-3}$ *M* in each case. Spectra were recorded at 77°K.

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(4) F. A. Walker, H. Sigel, and D. B. McCormick, submitted for publication.

TABLE I
ESR PARAMETERS FOR Cu^{2+}–bipy COMPLEXES

Complex	$g_\parallel$	$g_\perp$	$10^{-4}\lvert A_\parallel(Cu)\rvert$, cm^{-1}	$10^{-4}\lvert A_\perp(Cu)\rvert$, cm^{-1}	$10^{-4}\lvert A_\parallel(^{14}N)\rvert$, cm^{-1}	$10^{-4}\lvert A_\perp(^{14}N)\rvert$, cm^{-1}	Ref
$[^{63}Cu(bipy)(OH_2)_4]^{2+}$	2.308 ± 0.004	2.068 ± 0.004	166 ± 2	7 ± 2	*a*	*a*	*b*
$[^{63+65}Cu(bipy)(OH_2)_4]^{2+}$	2.315 ± 0.008	2.072	165.4 ± 2.0	8.0	*a*	*a*	*c*
$[^{63}Cu(bipy)_3]^{2+}$	2.266 ± 0.004	2.070 ± 0.004	161 ± 2	12.9 ± 1	16.1	9.7	*b*
$[^{63+65}Cu(bipy)_3]^{2+}$	2.271 ± 0.008	2.073	160.5 ± 2.0	8.0	*a*	*a*	*c*
$[^{63}Cu(bipy)_2(OH_2)_2]^{2+}$							
Species 1 (trans?)	2.269 ± 0.008	2.082	161 ± 4	*a*	*a*	*a*	*b*
Species 2 (cis?)	2.308 ± 0.008		165 ± 4	*a*	*a*	*a*	*b*
$[^{63+65}Cu(bipy)_2(OH_2)_2]^{2+}$							
Cis	2.227 ± 0.010	2.082	128.9 ± 2.0	*a*	*a*	*a*	*c*
Trans	2.285 ± 0.010	2.082	165.4 ± 2.0	*a*	*a*	*a*	*c*

[a] Not resolved. [b] This work. [c] Reference 1.

ethylene glycol–33% water[5]) and demonstrates, by comparison with earlier work,[1] that more information is obtained from the spectra of $[Cu(bipy)(OH_2)_4]^{2+}$ and $[Cu(bipy)_3]^{2+}$ by using the pure isotope. In particular, the perpendicular branch of the spectrum is much better resolved in each of these cases. From more expanded sweeps of this portion it is possible to estimate $A_\perp(^{63}Cu)$ and $A_\parallel(^{14}N)$ and, from the lowest field parallel hyperfine line of this species, $A_\perp(^{14}N)$ (*cf.* Table I)[6] for $Cu(bipy)_3{}^{2+}$. The spectrum of "$[Cu(bipy)_2(OH_2)_2]^{2+}$" is not significantly improved in resolution when the pure isotope is used (*cf.* Figure 1a and 2b). Careful comparison of Figures 2a, b, and c suggests that Figure 2b, where Cu:bipy = 1:2, appears to be largely a mixture of $[Cu(bipy)(OH_2)_4]^{2+}$ and $[Cu(bipy)_3]^{2+}$. The data calculated from these spectra also bear this out (Table I).[7]

The absence of any ^{14}N superhyperfine structure on the "upfield set" of parallel lines of Figure 2b, which in our interpretation are the parallel lines of $[Cu(bipy)_3]^{2+}$, suggests that if some of the bis species does exist, in the presence of the mono and tris complexes, its predominant geometrical isomer (if any) may possibly have parallel esr parameters similar to, though not identical with, those of the tris complex.

In conclusion, it appears from the data presented that the esr spectrum observed in glasses where Cu^{2+}:bipy = 1:2 may be attributed mainly to the 1:1 and 1:3 disproportionation species and not to the presence of cis and trans isomers of $[Cu(bipy)_2(OH_2)_2]^{2+}$. Hence, the esr spectra of these latter species are either practically identical with, or obscured by, the spectra of the 1:1 and 1:3 complexes and thus remain unknown. This does not invalidate the main conclusions, derived from nmr results, of Noack and Gordon,[1] which indicate that the species $[Cu(bipy)_2(OH_2)_2]^{2+}$ exists mainly as the cis isomer at room temperature. It does, however, point out that esr data are not useful in substantiating this result.[8]

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(5) Ethylene glycol–water glasses produced better ^{14}N resolution on spectra of the 1:1 and 1:3 complexes than did ethanol–water glasses, although other features of the spectra were the same in either solvent mixture, except for the relative intensities of the two sets of parallel lines in Figure 2b.

(6) As has been pointed out by C. M. Guzy, J. B. Raynor, and M. C. R. Symons, *J. Chem. Soc. A*, 2299 (1969), the ^{14}N shfs observed around $g_\parallel$ in a square-planar Cu(II) system is actually $A_\perp(^{14}N)$, since the principal direction of the ^{14}N tensor is along the Cu–N bond perpendicular to the principal axis of the molecule. Likewise, ^{14}N shfs observed around $g_\perp$ in such a system is $^1/_2(A_\parallel + A_\perp)$, on the average. The spectrum of a six-coordinate Cu(II) complex should also be described in this manner, since the unpaired electron is in the $d_{x^2-y^2}$ orbital and thus exhibits little or no hyperfine coupling with the two axial nitrogens.

(7) Although all of the glassy esr work reported to date has been carried out in mixed solvents, this argument may be tentatively supported by the thermodynamic data determined by G. Anderegg, *Helv. Chim. Acta*, **46**, 2813 (1963), for aqueous solutions ($I = 0.1$, $NaNO_3$). The disproportionation constant, K_D, due to the equilibrium $2Cu(bipy)_2{}^{2+} \rightleftharpoons Cu(bipy)^{2+} + Cu(bipy)_3{}^{2+}$ is given by $K_D = K_{Cu(bipy)_3}{}^{Cu(bipy)_2}/K_{Cu(bipy)_2}{}^{Cu(bipy)}$. At 20° $K_D = 10^{3.48}/10^{5.60} = 7.6 \times 10^{-3}$; *i.e.*, the left side of the equilibrium is strongly favored. For −180° (usually the solutions are considerably subcooled before they solidify to a glass) the calculation gives $K_D = 10^{14.0}/10^{14.5} = 0.3$; *i.e.*, the three complex species are now present in comparable concentrations. The difference in solvent composition may shift the equilibrium in either direction; this would explain the apparently different ratios of species observed in Figure 1.

(8) Esr spectra were recorded on a Varian E-3 esr spectrometer in the Department of Biochemistry, Cornell University, Ithaca, N. Y., and on a Varian E-9 spectrometer at Varian Associates, Analytical Instruments Division, Palo Alto, Calif. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work (F. A. W.), and to the Schweizerischen Nationalfonds zur Förderung der wissenschaftlichen Forschung (H. S.).