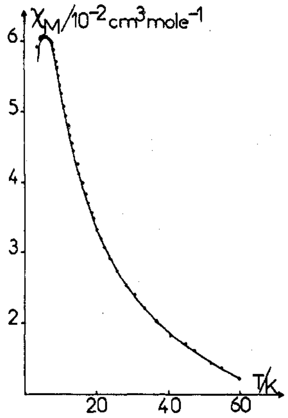

Figure 2. Temperature dependence of the molar magnetic susceptibility of $[Cu(NH_2CH_3)_2OH]_2SO_4{\cdot}H_2O$. The experimental points are noted as black dots and the best-fitting calculated curve is a continuous line.

This structure IV was somewhat idealized with regards to the actual structure of $[Cu(CH_3NH_2)_2OH]_2^{2+}$ by assuming the existence of a mirror plane containing the two hydroxo groups. The extended Hückel calculation of the energy gap $\Delta = \epsilon_A - \epsilon_S$ for the hypothetical dimer III carried out with the previously used parametrization[1] leads to almost exactly the same large value as for the hypothetical dimer I, 0.264 and 0.269 eV, respectively. Therefore, the coupling in III is expected to be strongly antiferromagnetic. In Figure 1 are given the variations of ϵ_A and ϵ_S vs. D. A crossover is obtained for $D = 130°$. Thus, for the actual value of the dihedral angle, $D = 132.9°$, one might expect a very small antiferromagnetic coupling or a ferromagnetic coupling. Indeed, in $[Cu(CH_3NH_2)_2OH]_2SO_4{\cdot}H_2O$ the J value was found equal to -7.9 ± 0.5 cm^{-1}. This result illustrates in a very satisfying manner the influence of the bending on the exchange interaction in copper(II) dimers with –OH bridges. In this correspondence, as in the previous paper,[1] we focused on the variation of the antiferromagnetic contribution J_{AF} vs. the dihedral angle. For completeness, it would be necessary to examine how the ferromagnetic contribution J_F varies when the Cu_2O_2 network is bent. We intend to approach this problem in our next paper.

Experimental Section

$[Cu(CH_3NH_2)_2OH]_2SO_4{\cdot}H_2O$ was prepared according to reference.[3] The magnetic measurements were carried out in the temperature range 4–300 K with a previously described magnetometer[1] on samples prepared by picking up needle-shaped crystals under a binocular lens. The diamagnetism was estimated as -204×10^{-6} cm^3 mol^{-1}. Three different samples of about 10 mg coming from different preparations were studied. The chemical analysis of each sample was performed after the magnetic study. As already noticed by Shimizu et al., the results of the chemical analyses were not excellent because of the instability of the compound which tends to lose its methylamine. The best analysis follows. Anal. Calcd for $Cu_2C_4H_{24}N_4O_7S$: Cu, 31.82; C, 12.03; H, 6.06; N, 14.03; S, 8.03. Found: Cu, 31.4; C, 11.58; H, 6.38; N, 13.22; S, 8.41. For absolute assurance that the studied compound had the structure described by Shimizu et al., the X-ray powder spectrum of the sample leading to the chemical analysis given above was recorded on a photographic film and the observed lines were compared to the lines computed from the published unit cell parameters. For the first 15 lines, the agreement was excellent. In addition to the lines corresponding to the expected compound, the spectrum exhibited three extremely weak lines corresponding most likely to the small amount of impurity. We checked that these three unexpected lines were undetectable in the X-ray powder spectra of freshly prepared samples. The magnetic data were fitted with the expression

$$\chi_M = \frac{2N\beta^2g^2}{kT}\left[3 + \exp\left(-\frac{J}{kT}\right)\right]^{-1}(1-\rho) + \frac{N\beta^2g^2}{2kT}\rho + 2N\alpha$$

in which we took into account the presence of a proportion ρ of monomeric impurity, the molecular weight of which was assumed to be half that of the studied dimer. J, g, and ρ were taken as adjustable parameters and the TIP. $2N\alpha$ was fixed to -120×10^{-6} cm^3 mol^{-1}. Least-squares fitting led to $J = -7.9$ cm^{-1}, $g = 2.15$, and $\rho = 0.124$ for the sample having the best chemical analysis. The agreement factor defined as

$$\frac{\sum(\chi_M^{obsd} - \chi_M^{calcd})^2}{\sum(\chi_M^{obsd})^2}$$

is then equal to 0.74×10^{-4}. Experimental data and theoretical curve in the range 4–60 K are compared in Figure 2. Above 60 K, χ_M closely follows a Curie law. For the two other samples, least-squares fitting led to the same value of J within 0.3 cm^{-1} and of g within 0.004 but, as expected, to larger values of ρ. The rather large proportion ρ of monomeric impurity in all the samples must be related to the instability of the complex and the impossibility of obtaining a perfect chemical analysis. It would be rewarding to assert that J in $[Cu(CH_3NH_2)_2OH]_2SO_4{\cdot}H_2O$ was determined with a very small uncertainty. In fact, we must recognize that the actual uncertainty is probably of the order of 0.5 cm^{-1}. Owing to the care taken in this study, it seems difficult to expect a significantly better accuracy.

Registry No. $[Cu(CH_3NH_2)_2OH]_2SO_4$, 59888-85-6.

Laboratoire de Spectrochimie des Elements de Transition
Equipe de Recherche Associée au CNRS No. 672
Université de Paris Sud
91405 Orsay Cedex, France

Marie France Charlot
Olivier Kahn*

Laboratoire de Chimie des Métaux de Transition
Equipe de Recherche Associée au CNRS No. 608
Université Pierre et Marie Curie
75231 Paris Cedex 05, France

Simone Jeannin
Yves Jeannin

Received August 2, 1979

Discriminating and Stability Increasing Properties of the Imidazole Moiety in Mixed-Ligand Complexes[1,2]

Sir:

It has already been recognized several years ago that the presence of an aromatic amine, i.e., a heteroaromatic N base, is crucial for a high stability of a ternary complex;[3] this observation was attributed to π back-bonding from the metal ion

(1) Part 34 of the series "Ternary Complexes in Solution". For Part 33, see: Orenberg, J. B.; Fischer, B. E.; Sigel, H. *J. Inorg. Nucl. Chem.*, in press. For Part 33, see: Orenberg, J. B.; Fischer, B. E.; Sigel, H. *J. Inorg. Nucl. Chem.* **1979**, in press. Part 32: Mitchell, P. R.; Prijs, B.; Sigel, H. *Helv. Chim. Acta* **1979**, *62*, 1723.

(2) Abbreviations: AMP, adenosine 5′-monophosphate; asp, aspartate; bpy, 2,2′-bipyridyl; en, ethylenediamine; gly, glycinate; ha, histamine; his, histidinate; im, imidazole; mal, malonate; nta, nitrilotriacetate; ox, oxalate; pyr, pyrocatecholate; 5-ssa, 5-sulfosalicylate.

(3) Sigel, H. *Chimia* **1967**, *21*, 489.

Table I. Comparison of the Stability of the Ternary Cu(im)(L) and $Cu(im)_2(L)$ Complexes, Studied by Abbott et al.,[18] Based on the Corresponding Values of $\Delta \log K_{Cu}$ (25 °C; $I = 0.2$, KNO_3)[a]

ligand (L)[2]	chelate ring size with L	$\Delta \log K_{Cu(1)}$[b]	$\Delta \log K_{Cu(2)}$[c]
bpy	5	−0.36	−0.98
ha	6	−0.84	−2.62
gly	5	−0.28	−0.76
asp	*d*	−0.35	−0.86
mal	6	−0.51	−1.40
5-ssa	6	−0.59	−1.48

[a] The data are those of Table III in ref 18. [b] $\Delta \log K_{Cu(1)} = \log K^{Cu(im)}_{Cu(im)(L)} - \log K^{Cu}_{CuL}$ (see eq 1). [c] $\Delta \log K_{Cu(2)} = \log K^{Cu(im)_2}_{Cu(im)_2(L)} - \log K^{Cu}_{Cu(L)}$. [d] See footnote 20.

to the aromatic amine.[4,5] For example, $Cu(bpy)^{2+}$ forms even more stable complexes than $Cu(aq)^{2+}$ with ligands containing anionic oxygen donors;[6] this result has often been confirmed,[3-5,7,8] and it is also valid for ternary surface silica complexes.[9] Moreover, $Cu(bpy)^{2+}$ exhibits discriminatory properties: it prefers to coordinate ligands with O donors rather than those with N donors.[3-5,10] On the basis of these results and those obtained with histamine[11] and imidazole[12] it was concluded[4,13] that the imidazole moiety, for several reasons[14,15] a versatile binding site in biological systems,[16] does impart similar discriminatory qualities to metal ions and that this is one of the tools of nature to achieve *selectivity*. In all these considerations the stability of the ternary complexes was quantified by eq 1–3.[3-5,17]

$$MA + MB \rightleftharpoons MAB + M \quad (1)$$

$$10^{\Delta \log K_M} = [MAB][M]/([MA][MB]) \quad (2)$$

$$\Delta \log K_M = \log \beta^M_{MAB} - (\log K^M_{MA} + \log K^M_{MB}) = \log K^{MA}_{MAB} - \log K^M_{MB} = \log K^{MB}_{MBA} - \log K^M_{MA} \quad (3)$$

On the basis of the results listed in Table I, Abbott et al.[18] have recently argued against the conclusions indicated in the second half of the preceding paragraph by, e.g., the following statements: (i) "For imidazole the $\Delta \log K$ values are negative for all systems. A significant astatistical mixed-ligand formation is not observed in any of the systems..." and (ii) "Imidazole, unlike bipyridyl, does not enhance the affinity of Cu(II) for the oxygen donor sites of anionic ligands. In the series of mixed complexes studied [Cu(im)(L) and $Cu(im)_2$-(L)] the order of stability for the ligand L is glycine > aspartic acid > bipyridyl > malonic acid > 5′-sulfosalicylic acid > histamine".

These statements, (i) and (ii), need to be put into perspective. To (i): the observation of negative values of $\Delta \log K_M$ does not exclude a stability increasing influence of imidazole; it should be noted that a *less* negative value may already indicate a "positive" effect. Statistical considerations are difficult to apply to Cu^{2+} (cf. ref 5) as the authors[18] conclude themselves (end of the Results in ref 18). A solid basis for comparisons can in such a case only be obtained by studying also the complexes of a ligand which does not have the π-accepting properties of imidazole, e.g., NH_3; then meaningful comparisons become possible. To (ii): a conclusion about "the affinity of Cu(II) for oxygen donor sites of anionic ligands" is only valid, if in this conclusion the different chelate-ring sizes present in the complexes are taken into account because the size of chelate rings does influence the stability of ternary

Table II. Influence of the π-Acceptor Capability of the Amine in Cu(amine)(pyrocatecholate) and Cu(amine)(AMP) Complexes, As Expressed by the Values of $\Delta \log K_{Cu}$ (eq 1–3; 25 °C; $I = 0.1$, $NaClO_4$)

amine (A)	$\Delta \log K_{Cu/A/pyr}$[a]	$\Delta \log K_{Cu/A/AMP}$[b]
2,2′-bipyridyl	+0.43	+0.53
4-(2′-pyridyl)imidazole	+0.11	+0.20
2-picolylamine	−0.11	+0.04
4-(aminomethyl)imidazole	−0.35	−0.35
ethylenediamine	−0.76	−0.45

[a] From ref 24a. [b] Measured in water containing 10% dioxane; from ref 24b.

Table III. Characterization of the Stability of Several Ternary M(his)(L) and M(ha)(L) Complexes by Their Corresponding Values of $\Delta \log K_M$ (25 °C)

imidazole derivative	ligand (L)[2]	Ni^{2+}	Cu^{2+}	Zn^{2+}
his	ox		−0.56[b]	
	gly	−0.74[a]	−0.68[a]	−0.26[a]
	en	−1.04[a]	−1.15[a]/−1.38[b]	−0.44[a]
	bpy		−1.70[a]/−1.92[b]	
ha	gly	−0.73[a]	−0.65[a]/−0.64[c]	−0.43[a]
	en	−1.32[a]	−1.49[a]	−0.74[a]

[a] $I = 0.2$, KCl; ref 25a. [b] $I = 0.1$, KNO_3; ref 25b. [c] $I = 0.2$, KCl; ref 25c.

Table IV. Comparison of the Stability Constants of Several Ternary M(nitrilotriacetate)(imidazole)⁻ Complexes with the Corresponding Data of the Binary $M(imidazole)^{2+}$ Complexes (25 °C)

M^{2+}	$\log K^{M(nta)}_{M(nta)(im)}$[a]	$\log K^M_{M(im)}$[b]	$\Delta \log K_M$
Co^{2+}	2.35 ± 0.03	2.39 ± 0.09 (5)	−0.04
Ni^{2+}	3.01 ± 0.05	3.00 ± 0.06 (6)	+0.01
Cu^{2+}	4.35 ± 0.03	4.22 ± 0.07 (7)[c]	+0.13
Zn^{2+}	2.73 ± 0.03	2.57 ± 0.03 (6)	+0.16

[a] $I = 0.1$, $NaClO_4$; ref 12d. [b] $I = 0.1$–0.2; the values are the average of the constants listed in ref 26a–c. The range of error given is the standard deviation resulting from averaging the values of the literature; the number in parentheses gives the number of available constants. [c] Abbott et al.[18] determined $\log K^{Cu}_{Cu(im)} = 4.28 \pm 0.02$ (25 °C; $I = 0.2$, KNO_3).

(4) Sigel, H. In "Metal Ions in Biological Systems"; Sigel, H., Ed.; Marcel Dekker: New York and Basel, 1973; Vol. 2, p 63.
(5) Sigel, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 394.
(6) L'Heureux, G. A.; Martell, A. E. *J. Inorg. Nucl. Chem.* **1966**, *28*, 481.
(7) (a) Bonomo, R. P.; Musumeci, S.; Rizzarelli, E.; Sammartano, S. *Inorg. Chim. Acta* **1975**, *14*, 251; *Talanta* **1976**, *23*, 253. Maggiore, R.; Musumeci, S.; Rizzarelli, E.; Sammartano, S. *Inorg. Chim. Acta* **1976**, *18*, 155. Arena, G.; Calì, R.; Rizzarelli, E.; Sammartano, S.; Barbucci, R.; Campbell, M. J. M. *J. Chem. Soc., Dalton Trans.* **1977**, 581; **1978**, 1090. (b) Munakata, M.; Harada, M.; Niina, S. *Inorg. Chem.* **1976**, *15*, 1727. (c) Agrawal, B. K.; Chandra, M.; Agarwala, B. V.; Dey, A. K. *Indian J. Chem., Sect. A* **1978**, *16A*, 340; *Transition Met. Chem.* **1978**, *3*, 243. (d) Mohan, M. S.; Bancroft, D.; Abbott, E. H. *Inorg. Chem.* **1979**, *18*, 344.
(8) Sigel, H.; Huber, P. R.; Griesser, R.; Prijs, B. *Inorg. Chem.* **1973**, *12*, 1198. Sigel, H.; Prijs, B. *Chimia* **1975**, *29*, 134. Fischer, B. E.; Sigel, H. *Inorg. Chem.* **1979**, *18*, 425.
(9) Bourg, A. C. M.; Joss, S.; Schindler, P. W. *Chimia* **1979**, *33*, 19.
(10) Griesser, R.; Sigel, H. *Inorg. Chem.* **1970**, *9*, 1238; **1971**, *10*, 2229.
(11) (a) Perrin, D. D.; Sayce, I. G.; Sharma, V. S. *J. Chem. Soc. A* **1967**, 1755. Perrin, D. D.; Sharma, V. S. *Ibid.* **1968**, 446; **1969**, 2060. (b) Huber, P. R.; Griesser, R.; Prijs, B.; Sigel, H. *Eur. J. Biochem.* **1969**, *10*, 238.
(12) (a) Koltun, W. L.; Fried, M.; Gurd, F. R. N. *J. Am. Chem. Soc.* **1960**, *82*, 233. (b) Tang, P.; Li, N. C. *J. Inorg. Nucl. Chem.* **1964**, *26*, 1606. (c) Driver, R.; Walker, W. R. *Aust. J. Chem.* **1968**, *21*, 671. (d) Israeli, J.; Saulnier, H. *Inorg. Chim. Acta* **1968**, *2*, 482.
(13) Sigel, H.; Fischer, B. E.; Prijs, B. *J. Am. Chem. Soc.* **1977**, *99*, 4489.
(14) Sigel, H.; McCormick, D. B. *Acc. Chem. Res.* **1970**, *3*, 201.
(15) Freeman, H. C. In "Inorganic Biochemistry"; Eichhorn, G. L., Ed.; Elsevier: Amsterdam, London, and New York, 1973; Chapter 4.
(16) (a) Colman, P. M.; Freeman, H. C.; Guss, J. M.; Murata, M.; Norris, V. A.; Ramshaw, J. A. M.; Venkatappa, M. P. *Nature (London)* **1978**, *272*, 319. (b) Sundberg, R. J.; Martin, R. B. *Chem. Rev.* **1974**, *74*, 471. (c) A list of biological complexes involving the imidazole group is given in Table VI of ref 13.
(17) Martin, R. B.; Prados, R. *J. Inorg. Nucl. Chem.* **1974**, *36*, 1665.
(18) Mohan, M. S.; Bancroft, D.; Abbott, E. H. *Inorg. Chem.* **1979**, *18*, 1527.

complexes.[19] With this in mind it is immediately obvious from Table I that imidazole does indeed *enhance* the affinity of Cu(II) for O donors compared to N donors, thus leading to discriminating properties of $Cu(im)^{2+}$ and $Cu(im)_2^{2+}$: the $\Delta \log K_M$ values for the 6-membered chelates of malonate or 5-sulfosalicylate are larger than those of histamine; similarily, the 5-membered chelate of glycinate is preferably formed compared to 2,2′-bipyridyl.[20,22,23]

To summarize: the results of Table I do then indeed *support*, and *not* contradict, the conclusion shortly indicated at the end of the introductory paragraph. They are in line with the π accepting properties of the imidazole group, which are less pronounced than those of the pyridyl moiety, as is confirmed by the stability data given in Table II for several amine/Cu^{2+}/pyrocatecholate and AMP systems.[24] Moreover, the stability increasing effect *and* the discriminating qualities of the imidazole moiety in ternary complexes do not hold only for Cu^{2+} but also for the other metal ions of the second half of the 3d series.[4,13] This is confirmed by the results (Table III) obtained recently for ternary complexes containing histidinate or histamine[25] and is in agreement with the stability of $M(nitrilotriacetate)(imidazole)^-$ complexes (Table IV).[12d,26a–c] The coordination tendency of imidazole to $M(nta)^-$ is comparable with that to $M(aq)^{2+}$, i.e., the $\Delta \log K_M$ values are around zero, and the increased stability becomes clearly unequivocal if the data are compared with the statistical (st) value,[27] $\Delta \log K_{st} = -0.5$. This contrasts with the coordination tendency of ammonia toward $Cu(nta)^-$ which is much lower than the one toward $Cu(aq)^{2+}$; i.e., $\Delta \log K_{Cu}$ is now strongly negative:[28] $\Delta \log K_{Cu} = \log K^{Cu(nta)}_{Cu(nta)(NH_3)} - \log K^{Cu}_{Cu(NH_3)} = 2.55$ (cf. ref 29) $- 4.19$ (cf. ref 30) $= -1.64$. The observation[31] that adenosine forms through the coordination of N(7) a complex with Ni(hydrogen triphosphate)$^{2-}$ which is 11 times more stable than the one with $Ni(aq)^{2+}$ must also be noted in this connection, especially as the 3d ions may coordinate to N(7) of the imidazole part of the purine moiety of nucleotides.[31a] Hence, we may still conclude,[4] but now with even a more profound legitimation: "One starts to understand why mixed-ligand complexes are so widely used in nature, and one is tempted to predict that in many (more)[16c] naturally occurring mixed-ligand complexes an imidazole group together with a ligand having O donors is involved".[32]

(19) (a) Sigel, H.; Huber, P. R.; Pasternack, R. F. *Inorg. Chem.* **1971**, *10*, 2226. (b) Sigel, H.; Caraco, R.; Prijs, B. *Inorg. Chem.* **1974**, *13*, 462.
(20) The data of the ternary aspartate complexes must be neglected in this comparison because aspartate may function as a tridentate ligand.[21]
(21) (a) Evans, C. A.; Guevremont, R.; Rabenstein, D. L. In "Metal Ions in Biological Systems"; Sigel, H., Ed.; Marcel Dekker: New York and Basel, 1979; Vol. 9, p 41. (b) Martin, R. B. *Ibid.*, p 1.
(22) In additon Abbott et al.[18] state: "The contrasting behavior of bpy and imidazole is demonstrated by the species distribution plots for the bpy/Cu(II)/mal and the im/Cu(II)/mal systems. In the former system the concentration of the ternary complex reaches a maximum of ca. 92% while in the latter system the ternary complexes are at a concentration of less than 50% over the pH range 2–8". This conclusion is misleading, to say the least, because bpy is a bidentate ligand and imidazole a monodentate one; the given different concentrations for the two ternary systems demonstrate mainly the well-known chelate effect. Even if for the Cu^{2+}/im/mal system $\Delta \log K_{Cu}$ would be +1.0 log unit (for Cu^{2+}/bpy/mal, $\Delta \log K_{Cu} = +0.3$),[10,18] the concentration of the ternary imidazole complexes would still be much lower than that of Cu(bpy)(mal) because $\log K^{Cu(mal)}_{Cu(mal)(bpy)} = 8.4$ (ref 18), a value which is still by a factor of 1000 larger than $\log K^{Cu(mal)}_{Cu(mal)(im)} = 4.28$ (ref 18) + 1.0 = 5.3—and there can be no doubt a $\Delta \log K_{Cu}$ value of +1.0 log unit for the Cu^{2+}/im/mal system would have been celebrated as a tremendous stability increase. It may be added that the overall stability constants[18] $\beta^{Cu}_{Cu(mal)(bpy)} = 10^{13.2}$ and $\beta^{Cu}_{Cu(mal)(im)_2} = 10^{11.15}$ cannot be compared because their dimensions are different.
(23) Part of the observed discrimination may possibly arise from steric effects, but the results listed in Tables III and IV (cf. also the last paragraph of the text) should in this context also be viewed (positive values for $\Delta \log K_M$ can never originate from steric hindrance).[28]
(24) (a) Huber, P. R.; Griesser, R.; Sigel, H. *Inorg. Chem.* **1971**, *10*, 945. (b) Huber, P. R.; Sigel, H. *Z. Naturforsch. B* **1972**, *27*, 1319.
(25) (a) Sóvágó, I.; Kiss, T.; Gergely, A. *J. Chem. Soc. Dalton Trans.* **1978**, 964. (b) Brookes, G.; Pettit, L. D. *J. Chem. Soc. Dalton Trans.* **1977**, 1918. (c) Gergely, A.; Sóvágó, I. *J. Inorg. Nucl. Chem.* **1973**, *35*, 4355.
(26) (a) Sillén, L. G.; Martell, A. E. "Stability Constants of Metal-Ion Complexes"; *Chem. Soc. Spec. Publ.* **1964**, *No. 17*; **1971**, *No. 25*. (b) Perrin, D. D. "Stability Constants of Metal-Ion Complexes"; Pergamon Press: Oxford, 1979; Part B. (c) Smith, R. M.; Martell, A. E. "Critical Stability Constants"; Plenum Press: New York and London, 1975; Vol. 2. (d) Smith, R. M.; Martell, A. E. "Critical Stability Constants"; Plenum Press: New York and London, 1976; Vol. 4.
(27) At a regular octahedral (oh) coordination sphere six edges are available for the entering imidazole, while only two possibilities remain if four positions are occupied by nta^{3-}; as the probability of dissociation is the same for the binary and ternary complexes, i.e., 1, the statistical value is $^2/_6 = 0.333$, i.e., $\Delta \log K_{st/oh} = -0.5$. For the square-planar (or distorted octahedral)[5] coordination sphere of Cu^{2+} the value is $^1/_4$ (or $^1/_6$) = 0.25 (0.167), i.e., $\Delta \log K_{st/sp(do)} = -0.6$ (–0.8).
(28) The steric restrictions within the coordination sphere of Cu^{2+} are rather somewhat smaller for NH_3, than for imidazole, as is evident from a comparison of the differences between the successive stability constants of the corresponding binary complexes (for NH_3 see ref 26d; for imidazole see ref 18). Hence, the observed differences *cannot* be explained by steric effects.
(29) 25 °C; $I = 0.1$, $NaNO_3$. Still, E. *Anal. Chim. Acta* **1979**, *107*, 105.
(30) 25 °C; $I = 0$–2. The value is the average of the constants listed in ref 26a,d.
(31) (a) Martin, R. B.; Mariam, Y. H. In "Metal Ions in Biological Systems"; Sigel, H., Ed.; Marcel Dekker: New York and Basel, 1979; Vol. 8, p 57. (b) Mariam, Y. H.; Martin, R. B. *Inorg. Chim. Acta* **1979**, *35*, 23.
(32) The support of our research by the Swiss National Science Foundation is gratefully acknowledged.

Institute of Inorganic Chemistry
University of Basel
CH-4056 Basel, Switzerland

Helmut Sigel

Received September 24, 1979

Congruence of Product Stereochemistry and the Site of Metal–Carbonyl Bond Breaking in Substitution Reactions of Octahedral Metal Carbonyl Complexes Proceeding via Fluxional Intermediates[1]

Sir:

It has long been known that, in octahedral metal carbonyl complexes containing stereochemically different carbonyls, randomization of a stereospecifically introduced label (usually ^{13}C) can occur on the time scale of ligand substitution.[2] The development of an understanding of this process for $Mn(CO)_5Br$, in particular, involved the work of several research groups over a decade.[3–10]

Since where scrambling occurs the site of initial metal–carbon bond breaking[11] need not reflect the stereochemistry of the reaction product where CO is replaced by another ligand (L), there has also been considerable interest in the elucidation of the bond-breaking site for a variety of octahedral species.[9,10,12–16] It is the purpose of this correspondence to point

(1) Part 50 of the series, "Octahedral Metal Carbonyls". For part 49, see ref 26. This work was sponsored by the Robert A. Welch Foundation under Grant No. B-434.
(2) D. J. Darensbourg, M. Y. Darensbourg, and R. J. Dennenberg, *J. Am. Chem. Soc.*, **93**, 2807 (1971).
(3) A. Wojcicki and F. Basolo, *J. Am. Chem. Soc.*, **83**, 525 (1961).
(4) W. Hieber and K. Wollmann, *Chem. Ber.*, **95**, 1552 (1962).
(5) H. D. Kaesz, R. Bau, D. Hendrickson, and J. M. Smith, *J. Am. Chem. Soc.*, **89**, 2844 (1967).
(6) B. F. G. Johnson, J. Lewis, J. R. Miller, B. H. Robinson, and A. Wojcicki, *J. Chem. Soc. A*, 692 (1968).
(7) T. L. Brown, *Inorg. Chem.*, **7**, 2673 (1968).
(8) P. W. Robinson, M. A. Cohen, and A. Wojcicki, *Inorg. Chem.*, **10**, 2081 (1971).
(9) A. D. Berry and T. L. Brown, *Inorg. Chem.*, **11**, 1165 (1972).
(10) J. D. Atwood and T. L. Brown, *J. Am. Chem. Soc.*, **97**, 3380 (1975).
(11) There is also evidence for nondissociative scrambling in such systems. See, e.g., D. J. Darensbourg and B. J. Baldwin, *J. Am. Chem. Soc.*, **101**, 6447 (1979), and references cited therein.

