I (6%), IIa (13.5%), IIb (4.5%), and VI (10.5%). (Percentages are based on chromatographic peak areas assuming equal thermal conductivities for all components.) The component with the longest retention time, VI, showed ir bands at 1282 (m), 1144 (w), 1019 (m), 994 (m), 974 (s), 950 (s), and 9.08 (s) cm$^{-1}$. The nmr and ultraviolet data for this compound are presented in Table I.

**Reaction of IIa with Lithium Amide.**—Into a 10-ml glass reactor equipped with a gas inlet tube and a Teflon stopcock and containing 1 mmol of $LiNH_2$ were condensed 2.5 ml of $CF_2$-$ClCFCl_2$ and 1 mmol of IIa. The mixture was warmed to ambient temperature and stirred for 3 days. All volatile material was removed from the reactor by continuous pumping and condensed at −196°. The condensate was warmed to room temperature and distilled without pumping into another trap at −196°. The volatile products were identified by ir as *cis*-$N_2F_2$, $N_2F_4$, and unreacted IIa. The remaining material was a greenish yellow liquid which strongly oxidized KI solution and had an apparent atmospheric boiling point of 124° with slight decomposition. The ir spectrum in $CCl_4$ showed bands located at 3546 (s), 3425 (s), 1667 (s), 1512 (w), 1353 (m), 1267 (s), 1143 (m), 1086 (m), 1015 (m), 943 (s), 922 (s), and 897 (s) cm$^{-1}$. The nmr and ultraviolet data for compound VII are presented in Table I. Mol wt of $C_2H_2F_6N_6$: calcd, 224; found, 226 (cryoscopic in benzene).

A sample of VII was fluorinated in the presence of NaF in $CCl_2F_2$ at −96° using a $F_2$:$N_2$ ratio of 5 cm$^3$/min:80 cm$^3$/min for 5 hr. The major product was IIb together with traces of I and IIa.

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# Kinetics of Formation of Mixed Ligand Complexes. III. The Cobalt(II)–2,2′-Bipyridyl–Glycine System[1]

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Potentiometric titration studies involving ternary complexes of Cu(II)–bipy, Co(II)–bipy and Ni(II)–bipy have demonstrated the enhanced thermodynamic stabilities of many of these species.[2,3] We are reporting on the kinetics of formation of a ternary complex of Co(II)–bipy which is thermodynamically quite stable relative to the appropriate binary system (*cf.* Table I). The stability data for the binary systems are typical in that $\log K^{CoL}{}_{CoL_2} - \log K^{Co}{}_{CoL} \leq -0.7$.[4] However, for the ternary system, $\log K^{Co(bipy)}{}_{Co(bipy)(gly)} - \log K^{Co}{}_{Co(gly)} = -0.17$.[3]

TABLE I

STABILITY CONSTANTS AT $\mu = 0.1$ AND 25°

| L | $pK^{H}{}_{H_2L}$ | $pK^{H}{}_{HL}$ | Log $K^{Co}{}_{CoL}$ | Log $K^{CoL}{}_{CoL_2}$ | Log $K^{Co(bipy)}{}_{Co(bipy)L}$ |
|---|---|---|---|---|---|
| 2,2′-Bipyridyl[a] | . . . | 4.49 | 6.06 | 5.36 | . . . |
| Glycine[2,3,b] | 2.33 | 9.68 | 4.63 | 3.87 | 4.46 |
| Bromothymol blue[c] | . . . | 7.10 | . . . | . . . | . . . |

[a] G. Anderegg, *Helv. Chim. Acta*, **46**, 2397 (1963). [b] G. Anderegg, *ibid.*, **44**, 1673 (1961). [c] I. M. Kolthoff, *J. Phys. Chem.*, **34**, 1466 (1930).

## Experimental Section

The solutions[5] for the kinetic runs were always freshly prepared using aliquots of a cobalt stock and a carefully weighed amount of 2,2′-bipyridyl such that, in all experiments, $[Co^{2+}]_{total} = [2,2'\text{-bipy}]_{total}$. Previous thermodynamic work[2,3] has shown that under the conditions of these experiments at equilibrium there is negligible concentration of free cobalt ion and free bipyridyl. A weighed sample of glycine was added to the reaction mixture, the ionic strength was adjusted to 0.1 *M* with $KNO_3$, and the solution was made $2.5 \times 10^{-5}$ *M* in bromothymol blue. The solutions were degassed and maintained under a nitrogen atmosphere. The pH was adjusted with small amounts of $HNO_3$ and/or NaOH to ±0.01 pH unit (*cf.* Table II).

TABLE II

RESULTS OF THE RELAXATION EXPERIMENTS

| $[Co^{2+}]_{tot}$ = $[bipy]_{tot}$, *M* | $[Gly]_{tot}$, *M* | pH | $\tau_{obsd}$, msec |
|---|---|---|---|
| $2.49 \times 10^{-3}$ | $2.49 \times 10^{-3}$ | 6.60 | 0.71 |
| $2.49 \times 10^{-3}$ | $3.74 \times 10^{-3}$ | 6.68 | 0.67 |
| $2.49 \times 10^{-3}$ | $3.74 \times 10^{-3}$ | 6.35 | 0.82 |
| $2.49 \times 10^{-3}$ | $1.25 \times 10^{-3}$ | 6.54 | 1.50 |
| $2.49 \times 10^{-3}$ | $1.25 \times 10^{-3}$ | 7.00 | 1.09 |
| $1.25 \times 10^{-3}$ | $2.49 \times 10^{-3}$ | 6.75 | 1.50 |
| $1.25 \times 10^{-3}$ | $6.24 \times 10^{-4}$ | 6.82 | 2.88 |
| $1.25 \times 10^{-3}$ | $6.24 \times 10^{-4}$ | 7.15 | 2.39 |
| $1.25 \times 10^{-3}$ | $1.25 \times 10^{-3}$ | 6.84 | 1.78 |
| $1.25 \times 10^{-3}$ | $1.25 \times 10^{-3}$ | 7.08 | 1.67 |
| $4.99 \times 10^{-4}$ | $4.99 \times 10^{-4}$ | 7.10 | 5.87 |
| $4.99 \times 10^{-4}$ | $4.99 \times 10^{-4}$ | 6.85 | 6.31 |
| $4.99 \times 10^{-4}$ | $7.48 \times 10^{-4}$ | 6.89 | 4.93 |

The study of the ternary complex formation was carried out by application of the temperature-jump technique;[6] the final temperature after the "jump" was 25°. In all cases, solutions containing cobalt(II), bipyridyl, glycine, potassium nitrate, and bromothymol blue showed a single relaxation effect. Blank tests in the absence of either cobalt(II) or glycine showed no relaxation effect in the time range of the instrument. Each relaxation time represents an average of at least three photographic determinations, with the relative error of these measurements at ±10%.[7]

## Results and Discussion

The equilibria which must be considered under the experimental conditions described in Table II are

$$Co(bipy)^{2+} + gly^- \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} Co(bipy)(gly)^+ \quad (1)$$

$$Co(bipy)^{2+} + Hgly \underset{k_{21}'}{\overset{k_{12}'}{\rightleftharpoons}} Co(bipy)(gly)^+ + H^+ \quad (2)$$

$$H_2gly^+ \rightleftharpoons H^+ + Hgly \quad (3)$$

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(1) (a) Part I: R. F. Pasternack and H. Sigel, *J. Amer. Chem. Soc.*, **92**, 6146 (1970); (b) part II: R. F. Pasternack, P. R. Huber, U. M. Huber, and H. Sigel, *Inorg. Chem.*, **11**, 276 (1972).

(2) R. Griesser and H. Sigel, *ibid.*, **9**, 1238 (1970).

(3) R. Griesser and H. Sigel, *ibid.*, **10**, 2229 (1971).

(4) L. G. Sillén and A. E. Martell, *Chem. Soc., Spec. Publ.*, **No. 17** (1964).

(5) The reagents employed were Baker reagent grade nitrate salts of potassium and cobalt(II) used without further purification. Glycine and 2,2,-bipyridyl were purchased from Eastman Organic Chemicals. The course of the reaction was followed by use of Eastman Organic Chemicals bromothymol blue as an indicator.

(6) R. F. Pasternack, K. Kustin, L. A. Hughes, and E. Gibbs, *J. Amer. Chem. Soc.*, **91**, 4401 (1969).

(7) Calculations were carried out on the Ithaca College RCA 70/35 computer. The equilibrium concentrations of the species in solution were calculated using a Newton–Raphson routine.

$$\mathrm{Hgly} \rightleftharpoons \mathrm{H^+} + \mathrm{gly^-} \tag{4}$$

$$\mathrm{HIn} \rightleftharpoons \mathrm{H^+} + \mathrm{In^-} \tag{5}$$

Reactions 1 and 2 are coupled to the more rapid processes shown in eq 3–5.

The use of standard techniques for deriving expressions for relaxation times leads to an equation of the form

$$1/\tau = Ak_{12} + Bk_{12}'$$

where $\tau$ is the relaxation time, $A$ and $B$ are functions of equilibrium constants and concentrations, and $k_{12}$ and $k_{12}'$ are the rate constants for attack of $\mathrm{Co(bipy)^{2+}}$ by $\mathrm{gly^-}$ and Hgly, respectively.[1] A plot of $(\tau B)^{-1}$ *vs.* $A/B$ is shown in Figure 1. Consistent with earlier reports, attack by the zwitterion (Hgly) is zero within experimental error;[1] the value of $k_{12} = 1.6 \times 10^6\ M^{-1}\ \mathrm{sec}^{-1}$. This result may be compared with kinetic results for the binary systems[8]

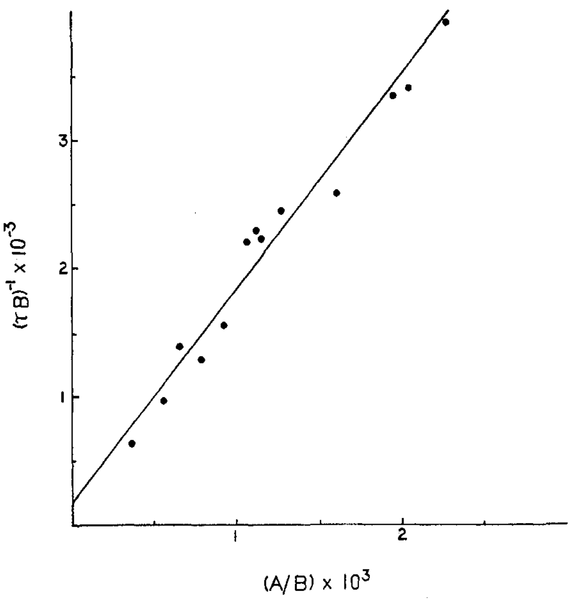

Figure 1.—A plot of $(\tau B)^{-1}$ *vs.* $A/B$ for the $\mathrm{Co(bipy)^{2+}}$–glycine system. The slope yields a value of $k_{12} = (1.6 \pm 0.3) \times 10^6\ M^{-1}\ \mathrm{sec}^{-1}$ and the intercept is $k_{12}' = 230 \pm 500\ M^{-1}\ \mathrm{sec}^{-1}$. We therefore conclude that $k_{12}' \approx 0$ for this system.

$$\mathrm{Co(H_2O)_6^{2+}} + \mathrm{gly^-} \underset{34}{\overset{1.5 \times 10^6}{\rightleftharpoons}} \mathrm{Co(gly)(H_2O)_4^+} \tag{6}$$

$$\mathrm{Co(gly)(H_2O)_4^+} + \mathrm{gly^-} \underset{330}{\overset{2.0 \times 10^6}{\rightleftharpoons}} \mathrm{Co(gly)_2(H_2O)_2} \tag{7}$$

$$\mathrm{Co(bipy)(H_2O)_4^{2+}} + \mathrm{gly^-} \underset{55}{\overset{1.6 \times 10^6}{\rightleftharpoons}} \mathrm{Co(bipy)(gly)(H_2O)_2^+} \tag{1}$$

Results for the complexation reactions of highly labile metal ions, and in particular cobalt(II) and nickel(II), are usually consistent with a mechanism in which the rate-determining step is the loss of a water molecule from the inner coordination sphere of a thermodynamically stable species.[9,10] For the formation of a monosubstituted complex, the observed rate constant for the reaction is then $k_1 = K_{a1}k_{o1}$ where $K_{a1}$ is the equilibrium constant for ion pair formation and depends primarily on the charge type of the interacting ions[11] and $k_{o1}$ is the rate constant for the breaking of a metal–water bond. For the formation of a higher order complex, as, for example, the bisubstituted complex species, the observed rate constant, $k_2$, is given by $k_2 = SK_{a2}k_{o2}$. Here $S$ is a statistical factor and is approximately $^5/_{12}$ for a bidentate attack of an octahedral complex already substituted in two cis positions.[1] As before, $K_{a2}$ is an equilibrium constant for ion-pair formation and $k_{o2}$ is the rate constant for loss of a water molecule from the already substituted metal-containing species. The presence of a nonaquo ligand in the inner coordination sphere affects the lability of the remaining water molecules, and, therefore, $k_{o2}$ is ligand dependent.[9,10]

Values for the rate constants for the rate-determining steps for reactions 6, 7, and 1 can be calculated; we use $K_a = 2$ for a $+2, -1$ interaction and $K_a = 1$ for a $+1, -1$ interaction.[11] We, therefore, obtain that $k_{o1} \approx 8 \times 10^5\ \mathrm{sec}^{-1}$, $k_{o2} \approx 5 \times 10^6\ \mathrm{sec}^{-1}$, and $k_{o12} \approx 2 \times 10^6\ \mathrm{sec}^{-1}$, respectively. The presence of bipyridyl in the inner coordination sphere of the cobalt ion apparently labilizes the metal–water bonds by a factor of 2.5 while the presence of glycinate leads to a factor of 6. The enhancement of rate is usually considered to be a measure of the net electron donation of the ligand; increase of electron density on the metal ion correlates with the relative lability of metal to water bonds.[12] Therefore, the value of $k_{o12}$ leads us to conclude that the presence of bipyridyl in the inner coordination sphere results in a smaller electron density on the metal ion than does the presence of glycinate. As has been shown, charge type does not correlate well with the extent of electron density donated by the ligand.[13] Rather, this effect is likely due to the relatively low-lying $\pi^*$ ligand orbitals in bipyridyl which leads to considerable back-donation from the metal ion, the net effect of which is the lowering of the electron density on the cobalt ion. This back-donation manifests itself kinetically as a recent review of kinetics of water-exchange reactions clearly indicates.[14]

Therefore, the enhanced stability of the Co(II)–bipy–gly ternary complex relative to $\mathrm{Co(gly)_2}$ is not a manifestation of a large forward rate constant for the former species. A comparison of the reverse rate constants indicates the source of this extra stability. As discussed above, the presence of bipyridyl in the inner coordination sphere makes a smaller change in the electron density on the cobalt ion than does the glycinate anion. Furthermore, in $\mathrm{Co(gly)_2}$ the negatively charged glycinate is removed from a *neutral* species which contains *two* glycinates. All of these factors, electron-donating ability of the bound ligand, coulombic interactions, and a statistical effect combine to give a reverse rate constant for the ternary complex, $k_{21}$, which is comparable to $k_{-1}$ and is much smaller than $k_{-2}$. Therefore, the stability of the ternary complex,

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[8] G. Davies, K. Kustin, and R. F. Pasternack, *Inorg. Chem.*, **8**, 1535 (1969).

[9] M. Eigen and R. G. Wilkins, *Advan. Chem. Ser.*, **No. 49**, 55 (1965).

[10] K. Kustin and J. Swinehart, *Progr. Inorg. Chem.*, **13**, 107 (1970).

[11] (a) R. M. Fuoss, *J. Amer. Chem. Soc.*, **80**, 5059 (1958); (b) M. Eigen, *Z. Phys. Chem. (Frankfurt am Main)*, **1**, 176 (1954); (c) A. Kowalak, K. Kustin, R. F. Pasternack, and S. Petrucci, *J. Amer. Chem. Soc.*, **89**, 3126 (1967).

[12] K. Kustin and R. F. Pasternack, *J. Phys. Chem.*, **73**, 1 (1969).

[13] D. W. Margerum and H. M. Rosen, *J. Amer. Chem. Soc.*, **89**, 1088 (1967).

[14] J. P. Hunt, *Coord. Chem. Rev.*, in press.

since the forward rate constants are the same for all the substitution reactions, eq 6, 7, and 1, is comparable to that of the monosubstituted complex rather than the bisubstituted complex.

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## Geometries of Ethylene and Acetylene in Platinum–Ethylene and –Acetylene Complexes

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The literature is replete with examples of the prediction of geometry within the framework of MO theory for both *ab initio* and semiempirical calculations. Varying degrees of success have been achieved in computing a predicted geometry by means of extended Hückel semiempirical calculations. Predicting geometry implies a quantitative bias and consequently noniterative modes of computation have generally been used for the development of computational methods (or qualitative results).[1]

Blizzard and Santry, by using CNDO calculations, have investigated changes in the bond angles of acetylene as a function of the population of various orbitals in order to compute the geometry of transition metal–acetylene complexes.[2]

The observed[3] cis-bent configurations of the acetylenes in these complexes was hypothesized to be the result of extensive population of an acetylene $\pi$-antibonding orbital, analogous to an excited state of acetylene.[2] Unfortunately, however, the calculations suffered from the rather severe approximation that they were unable to include the metal.

Both zerovalent and divalent platinum–acetylene and –olefin complexes have recently been calculated by noniterative rather than self-consistent techniques.[4,5] Although no angles were scanned within the organic group, extensive population of the $\pi$-antibonding orbitals normally associated with the olefin or acetylene was found, implying partial support for Blizzard and Santry. In fact, population of the olefin or acetylene $\pi$ antibonding orbitals is part of a synergic stabilizing mechanism in complexes of this type implied by Blizzard and Santry and computationally verified in these laboratories.[6]

Justification for noniterative computations is becoming increasingly available. Moffat has demonstrated that among a homologous series of molecules represented by various basis sets, differences in energy converged to a constant value more rapidly for smaller basis sets than did the energies.[7] This result, coupled with others which indicate that certain molecular properties such as conformational barriers are as accurately calculated by either iterative or noniterative techniques,[8] leads us to believe that noniterative calculations are more valuable than has generally been recognized. As long as the convergence properties of the system of equations representing a molecular situation remain parallel, the trends and relative energies predicted *via* noniterative computations for a series of compounds should be as valid as self-consistent or iterative modes.

This is an elementary result of the variation theorem. A first-order error in the wave function leads to a second-order error in energy. Since the convergence of the iteration process will be approximately parallel for different similar molecules, the error in the noniterative calculations will be second order. Hence chemical trends may be discussed in a meaningful fashion and possibly utilized for prediction.

Use of a noniterative mode of semiempirical MO calculation for the purpose of predicting geometries seemed especially appealing. Fixing the basis set comparisons among various geometries is computationally economical and consistently[9] more reliable than in iterative schemes. The results of such geometrical studies for the platinum–olefin and –acetylene complexes $(PH_3)_2Pt(C_2H_2)$, $(PH_3)_2Pt(C_2H_4)$, and *trans*-$(NH_3)Pt(C_2H_4)Cl_2$ are reported here. The method of calculation and functions employed have been previously reported.[4,5]

The variation in the total overlap populations (summed over all pairs of atoms), overlap energies, and one-electron orbital energy sums was studied as a function of the CCH and HCH angles to determine the most stable configuration. The angle $\delta$ (Figure 1) was varied from 0 to 90° and $\omega$ from 100 to 120° (these angles are the dihedral angles of interest within the organic moiety). Comparison with X-ray data has facilitated evaluation of the method.[3] This is in contrast to the previous studies on the barrier to rotation of the organic

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(1) See for example the following series of papers: (a) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179 (1962); (b) R. Hoffmann and W. N. Lipscomb, *ibid.*, **36**, 3489 (1962); (c) R. Hoffmann, *ibid.*, **39**, 1397 (1963); (d) R. Hoffmann, *ibid.*, **40**, 2754 (1964); (e) R. Hoffmann, *ibid.*, **40**, 2474 (1964); (f) R. Hoffmann, *ibid.*, **40**, 2480 (1964).

(2) (a) A. C. Blizzard and D. P. Santry, *J. Amer. Chem. Soc.*, **90**, 5749 (1968); (b) H. W. Kroto and D. P. Santry, *J. Chem. Phys.*, **47**, 792 (1967); (c) H. W. Kroto and D. P. Santry, *ibid.*, **47**, 2736 (1967).

(3) (a) J. O. Glanville, J. M. Stewart, and S. O. Grim, *J. Organometal. Chem.*, **7**, 9 (1968); (b) C. Panattoni, G. Bombieri, U. Belluco, and W. H. Baddley, *J. Amer. Chem. Soc.*, **90**, 798 (1968); (c) P. R. H. Alderman, P. G. Owston, and J. M. Rowe, *Acta Crystallogr.*, **13**, 149 (1960).

(4) (a) J. H. Nelson, K. S. Wheelock, L. C. Cusachs, and H. B. Jonassen, *Chem. Commun.*, 1019 (1969); (b) J. H. Nelson, K. S. Wheelock, L. C. Cusachs, and H. B. Jonassen, *J. Amer. Chem. Soc.*, **91**, 7005 (1969).

(5) K. S. Wheelock, J. H. Nelson, L. C. Cusachs, and H. B. Jonassen *ibid.*, **92**, 5110 (1970).

(6) Although Blizzard and Santry discussed transition metal–acetylene complexes in terms of $\sigma$ and $\pi$ bonding, this was used to rationalize the cis-bent configuration rather than proposing a synergic mechanism.

(7) J. B. Moffat, *Can. J. Chem.*, **48**, 1820 (1970). Moffat employed the SCF method but the dependence on the iteration process is parallel to that used here.

(8) K. S. Wheelock, H. B. Jonassen, and L. C. Cusachs, *Int. J. Quantum Chem.*, in press.

(9) L. C. Cusachs and D. J. Miller, *Advan. Sulfur Chem.*, in press; J. H. Corrington, H. S. Aldrich, C. W. McCurdy, and L. C. Cusachs, *Int. J. Quantum Chem.*, in press; L. C. Cusachs, J. B. Flory, C. W. McCurdy, and H. S. Aldrich, *J. Amer. Chem. Soc.*, in press.