tained by reducing the calibration factor for the extinction coefficient. The corresponding results for the localized complexes, where the intensity is determined by ϵ, present a consistent set of data. On the other hand, the calculated intensities for the more delocalized systems (compounds **1**–**5**) are then too high. At first sight one might expect λ to be constant throughout the series containing the $Ru(NH_3)_5$ moiety. However, the varying degree of π interaction of the bridging ligand with the metal ion, expressed by ϵ, will be reflected in the geometrical surroundings of the two metal ions. Obviously, the two parameters ϵ and λ are not independent; a stronger electronic coupling reduces the differences of the two coordination geometries, synonymous to a decrease in λ. This is most clearly observed for the closely related complexes **6**–**9**, where the decoupling of the pyridine rings causes opposite trends in ϵ and λ. We observe the general tendency of increasing λ with decreasing ϵ through the whole series **6**–**18**. Smaller ϵ values also result when NH_3 is replaced by bpy (compare **1** and **17**, for example). The strong π interaction of the latter ligand with Ru(II) reduces the π interaction of the two metal ions through the bridging ligand. For all of the localized species considered in this survey the agreement between calculated and experimental half-widths and intensities is remarkably good.

Turning now to compounds **1**–**5** representing complexes with appreciable valence delocalization, we first notice a considerable discrepancy between calculated and observed intensities. The calculated extinction coefficients are on the same scale as for **6**–**18**. Arbitrarily reducing the scale for the more delocalized complexes would produce a better agreement. Such a procedure, however, cannot be justified within the scope of the model. Variation of λ to reduce the intensity leads to band shapes at variance with experiment (cf. compound **3**). The salient features of the delocalized complexes, narrow and intense IT bands, are unambiguously reproduced by the vibronic coupling model but are difficult to rationalize within the customary approach.[4]

From the relationship of λ and Δr,[1b] differences in bond lengths between 0.04 and 0.13 Å are calculated for a λ range from 1 to 3.7. Structural studies[5] of the mononuclear complexes $[(NH_3)_5Ru(pyr)]^{2+}$ (pyr is pyrazine) and $[(NH_3)_5Ru(pyr)]^{3+}$ show $|\Delta r|$ to be 0.03 Å for Ru–NH_3 and 0.09 Å for Ru–pyr, in encouraging agreement with the model calculations. In conclusion it can be said that the vibronic coupling model provides a simple and consistent approach. Particularly within a series of related compounds the parameters extracted from fitting the IT band rationalize the properties connected with mixed valence behavior.

The complexes with bipyridylacetylene[6] and quinoxaline were prepared according to standard procedures.[7] Spectra of their solutions in D_2O were run on a Cary 17.

Intervalence band profiles were calculated with use of a basis set of 50 vibrational quanta. Each vibronic transition was assumed to be a Gaussian $(1/\Delta\pi^{1/2})\exp[-(E - E_0)^2/\Delta^2]$. Δ was chosen empirically to produce a smooth band contour. With Δ equal to $1.4\nu^1$ the half-width of a single transition is 1166 cm^{-1}. Various aspects neglected by the model, like anharmonicity and solvation effects, may contribute to this large half-width. Trial calculations using a significantly smaller value hardly affected the numerical value of ϵ and λ but produced a structured absorption band at variance with experimental observations. All of the data summarized in Table I were calculated for T = 298 K and ν = 500 cm^{-1}. The program, written in Fortran IV, was executed on an IBM 3033.

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Allosterism, an Explanation for Cooperativity in Zinc(II) Cyanide and Nickel(II) Cyanide Complex Ion Formation

Sir:

In the equilibrium constants for stepwise substitution of an anionic ligand X^{x-} for water in the first coordination shell of a metal ion $M(OH_2)_N{}^{m+}$, one expects, and generally finds, anticooperativity. That is, intermediate complexes, $M(OH_2)_{N-n}X_n{}^{m-nx}$ with $0 < n < N$ have a larger maximum relative concentration than expected statistically,[1] and the factor by which the concentration of ligand must change to cause a particular change of $\bar{n}/N$ is larger than corresponds to that for the statistical case, e.g., the 9-fold change in ligand concentration required to change $\bar{n}/N$ from 0.25 to 0.75. Electrostatic repulsion of anionic ligands for one another is a reasonable explanation for this generally observed anticooperativity. Thus, the cyanonickel(II) system is particularly remarkable. The maximum relative concentration of $NiCN^+$ is no larger than ~0.10, and an ~1.7-fold increase of concentration of cyanide ion is sufficient to change $\bar{n}/4$ from 0.25 to 0.75.[2] This extreme cooperativity exceeds even that for the binding of oxygen by sheep hemoglobin (at pH 9.1 and 19 °C) for which the maximum relative concentration of Hb_4O_2 is ~0.3, and an ~2.0-fold change of concentration of oxygen is sufficient to change $\bar{n}/4$ from 0.25 to 0.75.[3] Less extreme is the mild cooperativity exhibited by the cyanozinc(II) system in which an ~4.1-fold change of the concentration of cyanide ion causes $\bar{n}/4$ to change from 0.25 to 0.75.[4] The purpose of this communication is discussion of the cooperativity exhibited by these metal complex ion systems using the model for allosteric transitions proposed by Monod, Wyman, and Changeux.[5]

In this model, the protein (e.g., hemoglobin) exits in two different forms which can bind the ligand (oxygen); cooperativity is manifested if the *form* of the protein which is *less stable* in the absence of ligand *binds the ligand more strongly than does the more stable form.* The changes of structure of the aquometal ions and the dominant tetracyanometal complex

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(1) For $N = 4$, the maximum relative concentration expected statistically for species with $n = 1$ and 3 is 0.422 $((^3/_4)^3)$ and for species with $n = 2$ is 0.375 $(^3/_8)$. For $N = 6$, the maximum relative concentration expected statistically for species with $n = 1$ and 5 is 0.402 $((^5/_6)^5)$, for species with $n = 2$ and 4 is 0.329 $(5 \times 2^4/3^5)$ and for species with $n = 3$ is 0.313 $(^5/_{16})$. The values of these quotients, calculated by combining statistically related values of equilibrium constants with appropriate ligand concentrations, can be derived also by using simple probability. The maximum statistically expected relative concentration of a species $M(OH_2)_{N-n}X_n{}^{m-nx}$ is $(n/N)^n((N - n)/N)^{N-n}(N!/((N - n)!n!))$.
(2) H. Persson, *Acta Chem. Scand., Ser. A*, **28**, 885 (1974).
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Table I. Results of Calculations on the Nickel(II) Cyanide Cyanide Complexes

	Assumed Values			
β_1/L mol^{-1}	3×10^6	3×10^6	7×10^5	2×10^5
β_3/L^3 mol^{-3}	1×10^{22}	1×10^{22}	1×10^{22}	2×10^{16}
a_s	0.1	0.2	0.1	0.1
	Derived Values			
k	7×10^{-10}	1×10^{-8}	6×10^{-10}	2×10^{-29}
r	2.3×10^5	6×10^4	1×10^6	1×10^{11}
β_2/L^2 mol^{-2}	4×10^{13}	4×10^{13}	3×10^{13}	5×10^9

ion in each of these systems encourages application of this model. Each of these aquometal ions is a regular octahedral species $M(OH_2)_6^{2+}$. The limiting cyanozinc(II) ion is tetrahedral $Zn(CN)_4^{2-}$. The dominant tetracyanonickel(II) ion is a square-planar complex, which in aqueous solution is appropriately considered to be a tetragonally distorted *trans*-$Ni(OH_2)_2(CN)_4^{2-}$ species. In addition this species is diamagnetic, in contrast with the paramagnetic aquonickel(II) ion. At high concentrations of cyanide ion, nickel(II) ion forms diamagnetic complexes with five- and six-coordinated cyanide ions.[6]

For a system containing a dominant octahedral aquometal ion which also can form tetrahedral species, the equations relating the empirical overall equilibrium constants β_n with this model are given in eq 1. The numerical coefficients in

$$\begin{gathered}\beta_1 = q_o(6 + 4kr) \qquad \beta_2 = q_o^2(3 + 12a_o + 6kr^2a_t) \\ \beta_3 = q_o^3(12a_o^2 + 8a_o^3 + 4kr^3a_t^3) \\ \beta_4 = q_o^4(3a_o^4 + 12a_o^5 + kr^4a_t^6) \qquad \beta_5 = 6q_o^5a_o^8 \\ \beta_6 = q_o^6a_o^{12}\end{gathered} \tag{1}$$

these equations are statistical factors, and the parameters used in this formulation of the problem applied to the cyanozinc(II) system are as follows: q_o, the statistically corrected equilibrium constant for formation of octahedral $Zn(OH_2)_5(CN)^+$ from $Zn(OH_2)_6^{2+}$; k, the relative concentration of the tetrahedral aquometal ion ($k = [Zn(OH_2)_4^{2+}]/[Zn(OH_2)_6^{2+}]$); r, the ratio of the statistically corrected equilibrium constants for formation of $Zn(OH_2)_3CN^+$ and $Zn(OH_2)_5CN^+$ (i.e., $r = q_t/q_o$ if q_t is the statistically corrected equilibrium constant for formation of $Zn(OH_2)_3CN^+$ from $Zn(OH_2)_4^{2+}$); a_t and a_o, the factors in an equilibrium constant arising because the reaction involves the placement of ligands at adjacent sites of the coordination polyhedron (a_t for tetrahedral coordination and a_o for octahedral coordination).[7] These equations reveal the basis for cooperativity in this model. With $k << 1$ and $r >> 1$, the contribution of the form which is unimportant for the hydrated ion and the monoligand complex can become important, even highly dominant, for the higher complexes. With the ligand negatively charged, a_o and a_t are expected to be less than 1. With five adjustable parameters and only four items of information, the experimental values[4] $\beta_1 = (2.2 \pm 0.5) \times 10^5$ L mol^{-1}, $\beta_2 = (1.06 \pm 0.06) \times 10^{11}$ L^2 mol^{-2}, $\beta_3 = (4.8 \pm 0.5) \times 10^{16}$ L^3 mol^{-3}, and $\beta_4 = (3.7 \pm 0.8) \times 10^{21}$ L^4 mol^{-4}, it clearly is not possible to find a unique match of the parameters. But preliminary calculations show that the value of a_o over a large range 0.1–1.0 does not have an appreciable effect on the values of the other parameters, which are $q_o = 3.1 \times 10^4$ L mol^{-1}, $k = 2.9 \times 10^{-3}$, $r = 1.2 \times 10^2$, and $a_t = 0.44$. Ligand–ligand separation probably is smaller in the octahedral species, and it is reasonable that $a_o < a_t$. If $a_o = 0.1$, the relative concentrations of tetrahedral and octahedral species of each composition are given in eq 2–6. In these calculations

$$\frac{[Zn(OH_2)_4^{2+}]}{[Zn(OH_2)_6^{2+}]} = k = 0.0029 \tag{2}$$

$$\frac{[Zn(OH_2)_3(CN)^+]}{[Zn(OH_2)_5(CN)^+]} = \frac{4kr}{6} = 0.23 \tag{3}$$

$$\frac{[Zn(OH_2)_2(CN)_2]}{[Zn(OH_2)_4(CN)_2]} = \frac{6kr^2a_t}{3 + 12a_o} = 26.2 \tag{4}$$

$$\frac{[Zn(OH_2)(CN)_3^-]}{[Zn(OH_2)_3(CN)_3^-]} = \frac{4kr^3a_t^3}{12a_o^2 + 8a_o^3} = 1.3 \times 10^4 \tag{5}$$

$$\frac{[Zn(CN)_4^{2-}]}{[Zn(OH_2)_2(CN)_4^{2-}]} = \frac{kr^4a_t^6}{3a_o^4 + 12a_o^5} = 1.0 \times 10^7 \tag{6}$$

we see the tetrahedral species becoming dominant as the number of bound cyanide ions increases. It is an additional feature of this model that octahedral species could again become important at very high concentrations of cyanide. The ratio of the concentrations of pentacyanozinc(II) ion and tetracyanozinc(II) ion would become 0.05/0.95 at a concentration of cyanide ion in eq 7, clearly an inaccessible con-

$$[CN^-] = \frac{0.05}{0.95}\frac{\beta_4}{\beta_5} = \frac{0.05}{0.95}\frac{kr^4a_t^6q_o^4}{6q_o^5a_o^8} = 1.2 \times 10^5 \text{ mol L}^{-1} \tag{7}$$

centration. (If a_o were assumed to be 0.2, this quotient would decrease to 3.8×10^4 mol L^{-1}, still an inaccessible concentration.)

In considering the nickel(II) cyanide system, use will be made of values of some of the parameters for the zinc(II) cyanide system, just derived. It is reasonable that the value of q_o for the nickel(II) system would be larger than its value for the zinc(II) system. (There is crystal field stabilization for octahedral cyanonickel(II) ion.) It is reasonable also that the magnitude of a_o for the nickel(II) system would be similar to that for the zinc(II) system. These assumptions are useful because the experimentally derived parameters for the nickel(II) system are limited. The equilibrium constants obtained from pH measurements at 25.0 °C ($I = 3.0$ mol L^{-1}) by Persson are[2] $\beta_1 = (1.08 \pm 0.4) \times 10^7$ L mol^{-1}, $\beta_2 < 9 \times 10^{13}$ L^2 mol^{-2}, $\beta_3 < 1 \times 10^{22}$ L^3 mol^{-3}, and $\beta_4 = (1.16 \pm 0.08) \times 10^{31}$ L^4 mol^{-4}. (Other types of measurements by Persson do not support the value of β_1 obtained from the pH measurements, and he concludes that this value can be considered an upper limit.) Kolski and Margerum[8] on the basis of a fourth-order dependence upon total cyanide concentration of the rate of formation of tetracyanonickel(II) ion place upper limits upon the values of β_1, β_2, and β_3: for solutions with $I = 0.1$ mol L^{-1} at 25 °C, $\beta_1 < 10^5$ L mol^{-1}, $\beta_2 < 3 \times 10^{11}$ L^2 mol^{-2}, $\beta_3 < 2 \times 10^{16}$ L^3 mol^{-3}; their value of β_4 ($\beta_4 = 3.2 \times 10^{30}$ L^4 mol^{-4}) is close to that derived by Persson.[2] The studies of infrared spectra by Penneman et al.[6] establish the stabilities of the pentacyano- and hexacyanonickel(II) ions: $K_5 = 0.279$ L mol^{-1} and $K_6 = 0.095$ L mol^{-1} (25 °C, $I = 4.0$ mol L^{-1}).

A wide range of values of parameters support the conclusions: (a) the dominant monocyanonickel(II) ion is the paramagnetic species and (b) the predominant tetracyano-

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(6) R. A. Penneman, R. Bain, G. Gilbert, L. H. Jones, R. S. Nyholm, and G. K. N. Reddy, *J. Chem. Soc.*, 2266 (1963).

(7) The factor a_o is the same as the factor β in the treatment of equilibrium constants for replacement of water molecules in the coordination shell of chromium(III) by methanol or ethanol molecules (C. C. Mills, III, and E. L. King, *J. Am. Chem. Soc.*, **92**, 3017 (1970)). The factor a_t is the same as the ratio of successive statistically corrected equilibrium constants for formation of beryllium(II) fluoride complexes (R. E. Mesmer and C. F. Baes, Jr., *Inorg. Chem.*, **8**, 618 (1969)). It also is the same as the factor α in Pauling's treatment of cooperativity in oxygen binding by hemoglobin (L. Pauling, *Proc. Natl. Acad. Sci. U.S.A.* **21**, 186 (1935)).

(8) G. B. Kolski and D. W. Margerum, *Inorg. Chem.*, **7**, 2239 (1968).

nickel(II) ion is the diamagnetic species. Treatment of the nickel(II) cyanide system in terms of equations analogous to those used for the zinc(II) cyanide system and the justified assumption just given yields $q_o = {}^1/_6\,\beta_1$ and $kr^4q_o{}^4a_s{}^4 = \beta_4$, in which the symbols, q_o, k, and r have the significance already described and a_s is the factor for the square-planar coordination in the diamagnetic species analogous to a_o and a_t, already defined. Table I summarizes the results of calculations based upon the value of β_4, derived experimentally from pH data, and certain assumed values of β_1, β_3, and a_s. The two values assumed for β_1 in columns 1–3 are intermediate between the upper limit derived from the pH data and the lower limit taken to be the experimental value for cyanozinc(II) ion. The value assumed for β_3 in these columns is the upper limit established by the pH data, and values of $a_s = 0.1$ and 0.2 were assumed on the basis of the value of $a_t = 0.44$ obtained in the treatment of zinc(II) cyanide complexes. In the fourth column, values of β_1 and β_3 are assumed which are closer to the limits established by Kolski and Margerum,[8] and their value of β_4 also is used. We see in the results of these calculations that the derived value of k is extremely sensitive to the value of β_3 and more sensitive to the assumed value of a_s than it is to the assumed value of β_1; we see also the derived values of β_2 are less than the experimentally derived upper limit.

The derived values of k ranging from $\sim 10^{-8}$ to $\sim 10^{-29}$ correspond for the process

$$Ni(OH_2)_6{}^{2+} \text{ (paramagnetic)} = Ni(OH_2{}^e)_4(OH_2{}^a)_2{}^{2+} \text{ (diamagnetic)}$$

to values of $\Delta G°$ equal to +46 kJ mol^{-1} to +170 kJ mol^{-1}. With the change of entropy (under standard conditions) small, this range of energy change can be taken as the range within which the value of $\Delta H°$ lies. The maximum value is similar to the energy difference between the octahedral paramagnetic ground state ($^3A_{2g}$) and the octahedral diamagnetic excited state (^1E_g), $\sim$14 000 cm^{-1} ($\sim$170 kJ mol^{-1}).[9] Jahn–Teller distortion of the octahedral diamagnetic species stabilizes the singlet state, and the true stability of diamagnetic $Ni(OH_2{}^e)_4(OH_2{}^a)_2{}^{2+}$ is greater than the stability of the undistorted octahedral species.

Since the pentacyanonickel(II) and hexacyanonickel(II) complexes are diamagnetic, the values of β_5 and β_6 for the paramagnetic species of these compositions, which can be estimated from the parameters q_o and a_o, must be smaller than the observed values, which are $\beta_5 = 3.2 \times 10^{30}$ L^5 mol^{-5} and $\beta_6 = 3.1 \times 10^{29}$ L^6 mol^{-6}. (In these calculations, experimental values derived from measurements at two different values of ionic strength, 3.0 and 4.0 mol L^{-1}, are used without any attempt to estimate the small error in this procedure.) The calculated values of these quantities for the octahedral paramagnetic isomers based upon $a_o = 0.2$ and $q_o = 5 \times 10^5$ L mol^{-1} are $\beta_5 = 6q_o{}^5a_o{}^8 = 4.8 \times 10^{23}$ L^5 mol^{-5} and $\beta_6 = q_o{}^6a_o{}^{12} = 6.4 \times 10^{25}$ L^6 mol^{-6}. As required for consistency with the data, the values are small compared to the experimental values.

The Monod–Wyman–Changeux model provides a tidy explanation for the cooperativity, mild for cyanozinc(II) complexes and dramatic for cyanonickel(II) complexes. A similar explanation may be appropriate for other cyanometal systems (e.g., cyanide complexes of iron(II) and iron(III)) in which a high-spin aquometal ion is converted to a low-spin completely coordinated cyano complex, with species having intermediate numbers of coordinated cyanide ions being undetected.

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Registry No. $Zn(OH_2)_6{}^{2+}$, 15906-01-1; $Ni(OH_2)_6{}^{2+}$, 15365-79-4; $Zn(CN)_4{}^{2-}$, 19440-55-2; *trans*-$Ni(OH_2)_2(CN)_4{}^{2-}$, 77399-16-7.

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Additions and Corrections

1981, Volume 20

James B. Casey, William J. Evans, and Warren H. Powell*: A Descriptor System and Principles for Numbering Closed Boron Polyhedra with at Least One Rotational Symmetry Axis and One Symmetry Plane.

Pages 1336–1338. Footnote *a*, which is missing from Table I, should read as follows: In the notation for the reference axis and reference plane, two or three numbers separated by commas enclosed in parentheses indicate polyhedral edges and faces, respectively.—Warren H. Powell