N, 11.49. Found: C, 21.47; H, 4.01; N, 11.18.

Electrochemistry. Cyclic voltammetry was performed with a PAR Model 170 Electrochemistry System in a conventional three compartment electrochemical cell. Formal potentials were determined at a Pt flag working electrode relative to the saturated calomel electrode (SCE) at 22 ± 2 °C. Measurements were carried out on millimolar concentrations of the complexes in acetonitrile solution containing 0.1 M $[(C_2H_5)_4N]ClO_4$ (TEAP) supporting electrolyte as well as in 0.12 M DCl–D_2O solution.

$E_{1/2}$ values for the Ru(III)/Ru(II) couples were taken as the average of the anodic and cathodic peak potentials. Electrochemical reversibility was based on the peak-to-peak separation (ΔE_p) for the complementary anodic and cathodic cyclic voltammetric waves relative to the theoretically predicted value of 59 mV for a one-electron redox process.

Near-Infrared Spectra. Near-infrared spectra were run on 1.1×10^{-3} M solutions on a Cary Model 14 spectrophotometer over the wavelength range 1600–800 nm. Solutions of the half-oxidized mixed-valence ions were generated by controlled potential electrolyses in the same three compartment electrochemical cell using a semicyclindrical Pt gauze electrode. A solution of known concentration of the fully reduced (2,2) ion was prepared in the argon-deaerated electrochemical solvent of choice and loaded into an argon-flushed electrochemical cell by syringe technique, taking care to avoid dilution from solvent in the auxillary electrode compartment. After exhaustive electrolysis the solution was transferred by syringe technique to an argon-flushed 1-cm quartz cell fitted with a special Teflon inert valve.

Acknowledgment. P.M.H. and N.A.L. thank the Natural Science and Engineering Research Council of Canada for a coop grant in support of this research. We both also wish to thank H.T. for his hospitality while we were at Stanford University. P.M.H. was on sabbatical leave during the winter and spring of 1978, and N.A.L. was a NRC postdoctoral fellow 1977–1979. This work was initiated during that period.

Registry No. **1**, 77482-12-3; **2**, 77482-14-5; **3**, 77482-15-6; **4**, 77482-16-7; $[(NH_3)_5RuNCPh]^{2+}$, 31418-68-5; $[(NH_3)_5RuNCCH{=}CH_2]^{2+}$, 44916-13-4; $[(NH_3)_5Ru(H_2O)](PF_6)_2$, 34843-18-0; FcCN, 1273-84-3; FcCH=CHCN, 32626-63-4.

Correspondence

Application of the Vibronic Coupling Model to a Series of Binuclear Mixed-Valence Ruthenium Complexes

Sir:

Mixed-valence properties of binuclear complexes $X_5M^{II}LM^{III}X_5$ have been recently discussed by Schatz and co-workers[1] in terms of a vibronic coupling model. The essential step of this approach consists in the computation of the absorption band profile of the low-energy intervalence transition (IT), emphasizing its vibronic nature. The crucial vibrational coordinate q is represented by the antisymmetric combination of the normal coordinates for the breathing mode of the two constituent subunits $M^{II}X_6$ and $M^{III}X_6$, assumed to be adequately described by octahedral symmetry. Two parameters of this one-dimensional problem essentially define the mixed-valence behavior, the vibronic coupling λ and the electronic coupling ϵ. The vibronic coupling is shown to be proportional to Δr, the difference of the metal–ligand distances in the M(II) and M(III) subunits.[1b] The potential energy surfaces related to the intervalence transfer are given by eq 1, where W, as well as ϵ and λ, is expressed in units of ν, the wavenumber of the totally symmetric stretching vibration of the mononuclear subunits. In order to facilitate calculations the approximation $\nu(M^{II}X_6) = \nu(M^{III}X_6)$ is made.

$$W_{1,2} = \frac{q^2}{2} \pm (\epsilon^2 + \lambda^2 q^2)^{1/2} \qquad (1)$$

ϵ, λ, and ν define the complete vibronic manifold, and hence the shape of the IT band can be calculated as the superposition of transitions between vibronic levels. Two limiting situations are obtained from eq 1: (i) for $\epsilon \approx 0$ (localized limit), $W_2 - W_1 \approx 2\lambda q$; (ii) for $\lambda \approx 0$ (delocalized limit), $W_2 - W_1 \approx 2\epsilon$. The condition $dW_1/dq = 0$ for eq 1 defines potential minima at $q_{\min} = \pm((\lambda^4 - \epsilon^2)/\lambda^2)^{1/2}$. Thus, crossover from the valence-trapped (two minima, class II according to Robin and Day[2]) to the valence-delocalized case (one minimum at $q = 0$, class III) occurs when $|\epsilon|$ approaches λ^2. With the observed energy $W_2 - W_1$ of the IT band and the appropriate limit, reasonable starting values for ϵ and λ are estimated for computing band shapes. The best fit of the calculated band to the experimental one is obtained by a systematic variation of λ and ϵ.

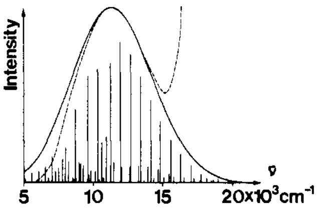
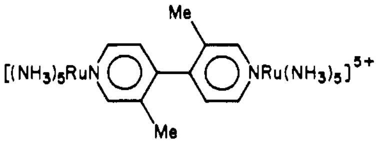


Figure 1. Observed (broken line)[8] and calculated (solid line) intervalence band for



The vertical sticks represent individual vibronic transitions, their intensities scaled by the Boltzmann population factor. The best fit corresponds to $\epsilon = -2.46$ and $\lambda = 3.58$.

The application of the vibronic coupling model to the pyrazine-bridged ruthenium dimer, the Creutz–Taube complex, led to the conclusion that this mixed-valence species is strongly delocalized.[1b] In order to test the range of validity of the model, we calculated IT band shapes for a series of mixed-valence ruthenium complexes, the mononuclear species being either $Ru(NH_3)_5$ or $Ru(bpy)_2Cl$. Whenever possible we used the line drawings of published solution spectra; otherwise the comparison between observed and calculated spectra was based on the energy, the intensity, and the half-width of IT bands reported in the literature. The resulting model parameters ϵ and λ as well as the spectroscopic data (**1**–**16** measured in D_2O, **17** and **18** in acetonitrile) are summarized in Table I. A representative example is illustrated in Figure 1. The solvent dependence of IT band positions for localized complexes implies a solvent dependence of λ. Medium effects on band intensity and half-width, however, are not reported. This phenomenon therefore could not be considered in our analysis. The close proximity of the solvent parameters for D_2O and

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[1] (a) Piepho, S. B.; Krausz, E. R.; Schatz, P. N. *J. Am. Chem. Soc.* **1978**, *100*, 2996. (b) Schatz, P. N.; Wong, K. Y. *Prog. Inorg. Chem.*, in press.

[2] Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247.

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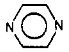
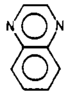
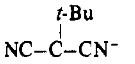
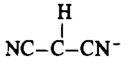
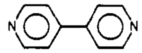
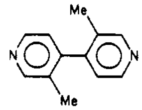
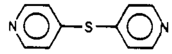
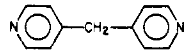
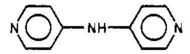
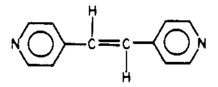
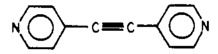
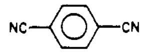
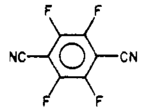
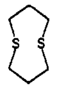
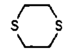
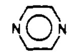
Table I. Observed and Calculated Data for Mixed-Valence Complexes $X_5Ru^{II}LRu^{III}X_5$

		exptl				calcd for vibronic coupling model				
no.		ν(IT)^a	$\epsilon_{max}{}^b$	Δ^c	ref	ϵ^d	λ^d	ν(IT)^a	$\epsilon_{max}{}^b$	Δ^c
			$(NH_3)_5Ru^{II}LRu^{III}(NH_3)_5$							
1		6.37	5000	1.4	*e*	−5.9	2.7	6.36	9000	1.5
2		6.02	>2000	1.3	*f*	−5.58	2.65	6.03	9000	1.5
3	NC−CN	6.99	410	1.6	*g*	−6.5 −3.1	2.90 2.97	6.98 6.95	8000 700	1.6 6.1
4	 $NC-C(t\text{-}Bu)-CN^-$	8.55	16 000	2.2	*h*	−8.55	0.50	8.56	21 300	1.2
5	 $NC-C(H)-CN^-$	7.81	>10 000		*h*	−7.7	2.0	7.87	19 000	1.2
6		9.71	920	5.2	*i*	−4.9	3.39	9.70	870	6.5
7		11.24	165	6.2	*i*	−2.46	3.58	11.26	160	6.8
8		11.7	70		*k*	−1.7	3.64	11.73	70	6.8
9		12.35	30	7.1	*i*	−1.2	3.72	12.33	30	7.0
10		10.87	1010	6.4	*i*	−5.9	3.56	10.88	1000	6.7
11		10.42	760	5.3	*i*	−4.8	3.49	10.41	700	6.6
12		10.87	640	5.4	*f, i*	−4.7	3.54	10.85	630	6.8
13		11.7	580	5.2	*h*	−4.9	3.66	11.72	570	6.8
14		~10	600		*h*	−4.2	3.43	10.06	600	6.5
15		8.47	75	>5	*l*	−1.2	3.17	8.45	70	6.1
16		10.29	6	>5	*l*	−0.4	3.44	10.27	5	6.5
			$(bpy)_2ClRu^{II}LRu^{III}(bpy)_2Cl$							
17		7.69	450	5	*m*	−2.6	3.06	7.71	430	5.8
18		7.35	40	5.5	*j*	−0.8	2.99	7.32	40	5.8

[a] Absorption maximum of IT band, in 1000 cm^{-1}. [b] Extinction coefficient, M^{-1} cm^{-1}. [c] Full width at half-height of IT band, in 1000 cm^{-1}. [d] Parameters of vibronic coupling model as multiples of the vibrational frequency $\nu = 500$ cm^{-1} (see text); error bounds are approximately ±0.2 for ϵ and λ. [e] References 1 and 7. [f] This work. [g] Tom, G. M.; Taube, H. *J. Am. Chem. Soc.* 1975, *97*, 5310. [h] Krentzien, H. Ph.D. Thesis, Stanford University, Stanford, CA, 1976. [i] Reference 8. [j] Powers, M. J.; Meyer, T. J. *Inorg. Chem.* 1978, *17*, 2955. [k] Fischer, H.; Tom, G. M.; Taube, H. *J. Am. Chem. Soc.* 1976, *98*, 5512. [l] Stein, C. A.; Taube, H. *J. Am. Chem. Soc.* 1978, *100*, 1635. [m] Callahan, R. W.; Keene, F. R.; Meyer, T. J.; Salmon, D. J. *J. Am. Chem. Soc.* 1977, *99*, 1064.

acetonitrile[3] justifies the inclusion of compounds **17** and **18** in our comparative survey.

A survey of the data for compounds **6–18** shows the λ values to lie within a rather narrow range from 2.99 to 3.72. It is this parameter which primarily determines the energy of the IT band in agreement with the assignment of these complexes to the valence-trapped case. On the other hand, the electronic coupling ϵ, regulating the band intensity, varies between −0.4 and −5.9. The extinction coefficients were calculated with use of the Creutz–Taube complex as point of reference. For compounds **6–18**, however, the intensities came out too small, and highly asymmetric band shapes were produced. Good agreement between calculated and observed bands was ob-

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(3) Powers, M. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 1785.

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 $\nu = 500$ cm^{-1}. The program, written in Fortran IV, was executed on an IBM 3033.

Acknowledgment. We thank the Swiss National Science Foundation for financial support (Grant No. 2.427-0.79).

Registry No. **1**, 35599-57-6; **2**, 77137-31-6; **3**, 57143-29-0; **4**, 60953-21-1; **5**, 77305-45-4; **6**, 54065-65-5; **7**, 77305-52-3; **8**, 77305-48-7; **9**, 64763-49-1; **10**, 77305-49-8; **11**, 77305-51-2; **12**, 77305-50-1; **13**, 77305-47-6; **14**, 77305-46-5; **15**, 66402-84-4; **16**, 66403-18-7; **17**, 59978-63-1; **18**, 66808-68-2.

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[5] Creutz, C. *Inorg. Chem.* **1978**, *17*, 3723.

[6] Tanner, M.; Ludi, A. *Chimia* **1980**, *34*, 23.

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[8] Sutton, J. E. Ph.D. Thesis, Stanford University, Stanford, CA, 1979.

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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