Detailed Spectroscopic, Thermodynamic, and Kinetic Characterization of Nickel(II) Complexes with 2,2′-Bipyridine and 1,10-Phenanthroline Attained via Equilibrium-Restricted Factor Analysis

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The molar absorptivity curves of the mono and bis nickel(II) complexes of 2,2′-bipyridine and 1,10-phenanthroline have been deduced from the composite absorbance data of a series of equilibrium solutions in methanol using equilibrium-restricted factor analysis, a technique for extracting spectral and thermodynamic information for component species involved in solution equilibria. The solutions achieve equilibrium slowly ($t_{1/2} \approx 100$ min) as the amounts of the tris and methanolato complexes are initially in excess. The relative formation constants at 293 K have been determined with a high degree of accuracy, especially for the bipyridine complexes: $\log(K_1/K_2) = 0.340(4)$ and $\log(K_2/K_3) = 1.091(6)$. Solubility limitations compromised the accuracy of the thermodynamic results for the phenanthroline complexes.

Introduction

A prolific amount of literature exists concerning nickel-(II) and its chemical applications from organic catalysis[1] to biomimetic[2] systems. Such work is built upon a large body of foundational research into the nature of the metal cation and its coordination chemistry. One of the most fundamental systems is nickel(II) with 2,2′-bipyridine (bpy), along with that of the closely related ligand 1,10′-phenanthroline (phen). In 1953, Basolo, Hayes, and Neumann reported the absorption spectra of the bis and tris phen complexes of nickel(II) in water.[3] Interestingly, they also looked to measure the spectra of the analogous bpy complexes, but believed that a rapid equilibrium between various complexes occurred. Despite this obfuscating development, they observed that the spectra of the corresponding phenanthroline and bipyridine complexes were "strikingly similar". Given that the solution-phase bis-(phen)−nickel(II) and tris-(phen)−nickel(II) complexes were pure, it was straightforward to calculate the spectrum of the mono-(phen)−nickel(II) complex as they did

(the spectrum of solvated nickel(II) is obviously also known). However, if any of the complexes equilibrate to a substantial degree, it becomes a very convoluted, though not intractable problem, to isolate the unknown spectra of the pure species. Vosburgh and Cooper, for example, discuss how Job's method may be extended in limited cases to identify complex ions in solution even when multiple species equilibrate.[4]

This same type of problem can arise in supramolecular or biochemical systems in which key species of interest exist only in equilibrium, and isolating them chemically is haphazard to impossible. Additionally, many technologically relevant systems are chemical mixtures that have synergistic functionality. A plethora of examples exist in the literature in which easily obtainable composite data is deconvoluted to isolate information about chemical species without the need to chemically isolate them.[5]

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We now demonstrate the efficacy of equilibrium-restricted factor analysis (ERFA) to extract spectral information of different components in an equilibrium mixture. This method also provides thermodynamic data in a straightforward manner. The results for solution equilibria involving nickel-(II) polypyridyls are closely compared to independently determined results from the literature.

Experimental Procedures

Reagents. $Ni(BF_4)_2 \cdot 6H_2O$ (AlphaAesar) was heated gently under vacuum to remove any excess water. Methanol was dried in a Seca solvent system by GlassContour. The 2,2′-bipyridine (bpy) and (anhydrous) 1,10-phenanthroline (phen) ligands from Aldrich (≥99%) were used without further purification.

Preparation of Solutions. 2.0949 g (6.1542 mmol) of $Ni(BF_4)_2 \cdot 6H_2O$ was dehydrated in excess dimethoxypropane (DMP). The resulting acetone and methanol cosolvents, as well as any DMP layer were removed under vacuum and replaced with 78.7854 g of dry methanol, resulting in a 0.06154 M Ni^{2+} solution ($d = 0.80215$ g/mL). Stock solutions of bpy′ (0.06472 M, $d = 0.7911$ g/mL) and phen (0.1025 M) in methanol were also made. To 30 1 mL aliquots of the nickel(II) stock solution was added from 0 to 3 mL of ligand stock solution followed by sufficient methanol to achieve a total volume of around 4 mL. The exact amounts of solution added were measured by weight to four decimal places. The solutions were then allowed to reach equilibrium over the course of 72 h. No precipitates formed for the bipyridine solutions, as the solubility of $[Ni(bpy)_3](BF_4)_2$ in methanol (25 mM) was not exceeded. Even with less concentrated solutions, $[Ni(phen)_3](BF_4)_2$ precipitated from solutions with more than 2.2 equiv of phenanthroline because the solubility of the complex in methanol is only 2.3 mM. Further dilutions afforded unworkably low signal-to-noise ratios.

Additional solutions for kinetic measurements were made the same way. Within 90 s of mixing, a UV−vis absorbance spectrum was taken, and more spectra were collected periodically over the next 5−12 h.

Preparation of Tris-2,2′-bipyridine−nickel(II) Tetrafluoroborate. Portions of 0.8858 g (2.602 mmol) of $Ni(BF_4)_2 \cdot 6H_2O$ and 1.9800 g of bpy (12.68 mmol) were added to 20 mL of methanol. Red crystals began forming immediately as the mixture was agitated. The suspension was stirred for 10 min at room temperature after which the precipitate was vacuum-filtered, washed with diethyl ether, and air-dried. A mass of 0.8693 g of precipitate was isolated (48% yield). Elemental analysis was performed by M-W-H Laboratories, Phoenix, AZ. Anal. Calcd for $NiC_{30}H_{24}N_6B_2F_8$: C, 51.41; H, 3.45; N, 11.99. Found: C, 51.60; H, 3.61; N, 11.95. A mass of 9.49 mg of the solid was redissolved into a 5 mL solution of methanol in order to measure the absorbance directly.

Preparation of Tris-1,10-phenanthroline−nickel(II) Tetrafluoroborate. Portions of 0.1033 g (0.3035 mmol) $Ni(BF_4)_2 \cdot 6H_2O$ and 0.3536 g (1.7838 mmol) of phen·H_2O were added to 10.0 mL of methanol and stirred for 20 min.

Pink crystals formed and were collected by vacuum filtration and washed with diethyl ether. A mass of 0.1135 g of precipitate was collected (43%).

Spectrophotometry. All absorbance spectra were measured every nanometer from 450 to 900 nm at 293 K with a Cary 100 UV−vis spectrophotometer at 293 K using a baseline of the solvent methanol, a beam width of 2.0 nm, a path length of 1.0 cm, and a scan rate of 600 nm/min. Besides the spectra of the solutions, each data set included the spectra of nickel(II) and the ligand in the solvent alone.

Mathematical Treatment of Spectrophometric Data. The absorbance curves for a family of solutions made up of various amounts of components in equilibrium are essentially determined by the molar absorptivity curves of those components and the equilibrium constants for the chemical reactions between them. Therefore, the measured absorbance values can be modeled to yield simultaneous estimates of the equilibrium constants and any unknown or inaccessible molar absorptivity curves, assuming that the number of distinct solutions is sufficiently large to uniquely determine the unknown quantities.

Several computer programs exist for such modeling of absorbance data of multiple solutions for equilibrium systems,[6] and the theory of such calculations is well established.[7] It is often called factor analysis,[8] but might be more accurately be referred to as equilibrium-restricted factor analysis (ERFA) because the concentrations (or activities) of the components in solution are forced to satisfy the mathematical parameters of equilibria for a set of chemical reactions provided by the user. There are also model-free methods that do not require a chemical model.[9]

We have written our own code in the form of *Matlab* protocols with a graphical user interface named *Sivvu* so that we can easily enter arbitrary compositions. The details of our program can be found in the Supporting Information or on our website.[10] The program searches for the free-energy values that result in the smallest deviation of the measured and calculated absorbance values. In the process, the molar absorptivity values are determined by least-squares analysis of the overexpressed system of linear equations, which are each an implementation of the Beer−Lambert law, one for each absorbance datum. The problem is conveniently expressed using matrix algebra, which was first detailed by Wallace.[11] Twenty-five years later, Reeves et al. described its application to a system with nickel(II) complexes and tridentate dyes.[12]

In such calculations, it is necessary to determine the true number of chemical species in the system. Including additional hypothetical species can obviously help to mathematically model the absorbance data more closely, but would not represent a chemically meaningful answer. Fortunately, this number can be determined from the absorbance data directly because the structure of any matrix can be readily analyzed for orthogonal factors.[13] For example, if a series of absorbance curves all intersect at an isosbestic point, this indicates visually that there are just two distinct chemical species contributing to the absorbance, each with a unique molar absorptivity curve. With three or more species absorbing simultaneously, no isosbestic points will occur (except for the rare possibility of all the species having the same molar

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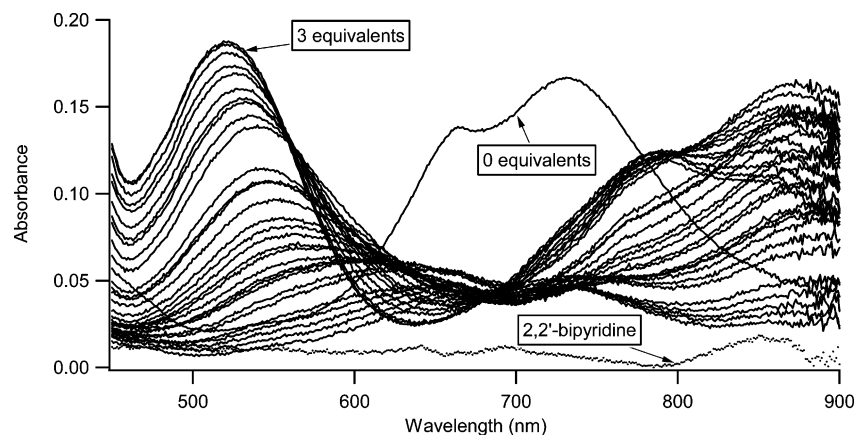(13) Hugus, Z. Z., Jr.; El-Awady, A. A. *J. Phys. Chem.* **1971**, *75*, 2954−2957.

Figure 1. Total absorbance data for bpy/Ni(II) system used in ERFA. Thirty-one solutions of ~0.02 M Ni(BF$_4$)$_2$ in methanol with 0−3 equiv of bpy and a curve of bpy by itself.

absorptivity at a single wavelength), but data can still be analyzed to determine the number of fundamental curves required to additively reconstruct the data. More specifically, this part of the analysis indicates what fraction of the data can be reconstructed as a linear combination of an arbitrary number of fundamental curves. An additional curve will always increase the fraction of data accounted for with the model; however, after a certain number of curves, the rate of improvement levels out because it is only accounting for random noise in the data. Such pure factor analysis is used in a wide variety of fields.[14]

All equilibrium concentrations are calculated on the basis of activity, the different computational models of which may affect the exact values of the free energy of the reactions, and the units of absorptivity. For this paper, several theoretical models for activity coefficients were tested including those of the extended Debye−Hückel law,[15] Scatchard,[16] and Davies.[17] All used a value of $A = 1.69$ (for methanol at 293 K). For the extended Debye−Hückel law, the effective solution diameters of the ionic species were approximated at 6 Å, and the B parameter used was 0.20. For our data, there is almost no detectable difference between the results of the different models. Consequently, the activity coefficients were all set to unity and the molar absorptivity values are calculated in units of absorbance·cm^{-1}·M^{-1}.

The standard deviations of the free-energy values are calculated by reoptimizing on subsets of the data with a random 10% of the wavelengths ignored and subsequently quantifying the variation in the optimized free-energy values.

In the case of the kinetic data, the scans were started every 2 min and took about 102 s to move from 900 to 450 nm. The raw absorbance data was therefore interpolated linearly to account for the lag time between the start and end of each scan. For example, the last true absorbance value of the fifth scan will be 102/120ths of the way between the corresponding measured values of the fourth and fifth scans.

Results

Figure 1 shows the measured absorbance data for the 32 equilibrium solutions with bpy that were modeled with

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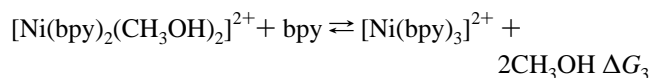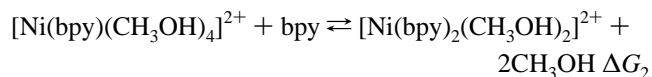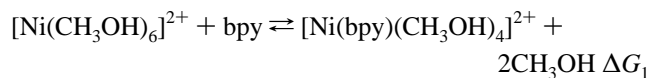(15) Debye, P.; Hückel, E. *Physik. Z.* **1923**, *24*, 185−206.
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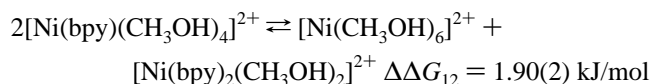(17) Davies, C. W. *Ion Association*; Butterworths: Washington, DC, 1962; p 17.

Table 1. The 10 Largest Mathematic Factors for the Sets of Absorbance Data Compared to Those of a Set of Random Numbers
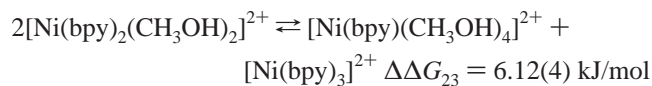
	Ni(II)/bpy	Ni(II)/phen	random
1	21.9847	17.0226	1.2608
2	4.7678	3.0259	1.2315
3	3.3491	1.0267	1.2008
4	0.6387	0.2391	1.1636
5	0.1647	0.1336	1.1568
6	0.0738	0.1197	1.1436
7	0.0648	0.1139	1.1355
8	0.0603	0.1120	1.1180
9	0.0549	0.1066	1.0971
10	0.0534	0.0989	1.0865

ERFA. (It is not necessary to have the same overall nickel concentration for each solution.) The eigenvalues of this data shown in Table 1 indicate that there are five additive factors that comprise the information within the data sets for Ni(II)/bpy solutions (besides random noise) because the fifth value (0.1647, Table 1) is the last one that is substantially greater (at least twice) than the following value (0.0738, entry 6, Table 1). These expectedly correspond to the four nickel complexes along with free ligand, which are modeled according to the following chemical reactions:

$$[Ni(CH_3OH)_6]^{2+} + bpy \rightleftharpoons [Ni(bpy)(CH_3OH)_4]^{2+} + 2CH_3OH \; \Delta G_1$$

$$[Ni(bpy)(CH_3OH)_4]^{2+} + bpy \rightleftharpoons [Ni(bpy)_2(CH_3OH)_2]^{2+} + 2CH_3OH \; \Delta G_2$$

$$[Ni(bpy)_2(CH_3OH)_2]^{2+} + bpy \rightleftharpoons [Ni(bpy)_3]^{2+} + 2CH_3OH \; \Delta G_3$$

The free energy values for these three reactions are difficult to ascertain accurately through this process because the substitution reactions are so exergonic, making the concentrations relatively insensitive to the ΔG values. However, the ligand redistribution equilibria that correspond to $\Delta\Delta G$ values can be determined quite precisely:

$$2[Ni(bpy)(CH_3OH)_4]^{2+} \rightleftharpoons [Ni(CH_3OH)_6]^{2+} + [Ni(bpy)_2(CH_3OH)_2]^{2+} \; \Delta\Delta G_{12} = 1.90(2) \text{ kJ/mol}$$

$$2[Ni(bpy)_2(CH_3OH)_2]^{2+} \rightleftharpoons [Ni(bpy)(CH_3OH)_4]^{2+} +$$
$$[Ni(bpy)_3]^{2+} \quad \Delta\Delta G_{23} = 6.12(4) \text{ kJ/mol}$$

That is, the addition of a second bpy ligand releases 1.90(2) kJ of free energy per mole less than the addition of the first (log $K_{12} = 0.340(4)$), and the addition of the third bpy ligand releases 6.12(4) kJ of free energy per mole less than the addition of the second one (log $K_{23} = 1.091(6)$). The corresponding values for the analogous chemical reactions with phen are 6.44(2) kJ (log $K_{12} = 1.139(4)$) and 12.19(4) kJ (log $K_{23} = 2.158(7)$).

Figures 2 and 3 show the molar absorptivity values and the concentration profiles, respectively, that result from the optimization. (The latter curves are not smooth because the exact amount of nickel cation in each solution is not necessarily the same.) Essentially, when matrices containing the very numbers used to generate these two graphs are cross multiplied, the result is a matrix that contains the calculated absorbance data. The root-mean-square residual of all the data points is 0.00106, and residuals by solution are shown as bars in Figure 3. The $[Ni(CH_3OH)_6]^{2+}$ complex accounts for 10.8%, of the total absorbance over all 32 solutions, $[Ni(bpy)(CH_3OH)_4]^{2+}$ for 15.8%, $[Ni(bpy)_2(CH_3OH)_2]^{2+}$ for 37.9%, and $[Ni(bpy)_3]^{2+}$ for 35.1%. Free bpy accounts for the remaining 0.4%.

Figure 4 shows the kinetic data for a single solution of nickel(II) and bpy. Each curve can be modeled accurately as a linear combination of the four molar absorptivity curves from the equilibrium studies (Figure 2). The evolution of the resultant nickel complex concentrations over time is shown in Figure 5. The change in concentration of the complexes for various experiments is described in Table 2.

The absorbance data from the Ni(II)/phen system exhibits only four factors because there are no longer any solutions with excess ligand. The error analysis for the Ni/phen system is similar with an rms residual of 0.00109. However, the contribution to the total absorbance is skewed away from the tris complex. The $[Ni(CH_3OH)_6]^{2+}$ complex accounts for 12.5% of the total absorbance over all 23 solutions, $[Ni(phen)(CH_3OH)_4]^{2+}$ for 33.8%, $[Ni(phen)_2(CH_3OH)_2]^{2+}$ for 48.6%, and $[Ni(phen)_3]^{2+}$ for 5.1%. Not surprisingly, there is no free phen detected in any of the solutions. The molar absorptivity values that resulted from ERFA on the solutions of phen and nickel(II) were also then used to ascertain the kinetic behavior of these solutions as equilibrium was approached. In this case, the half-lives of the species in solution were on the order of several hours.

Discussion

The use of ERFA has afforded molar absorptivity spectra and relative thermodynamic values from substantially equilibrated solutions, in accord with those previously observed for isolated Ni(II) polypyridyls. The approach can prove valuable in the study of systems where the synergy of a number of components is crucial to the behavior, as is often true in supramolecular or nanotechnological systems.

Solutions containing nickel(II) and bpy equilibrate substantially. For example, with 1.6 equiv of ligand in a 0.1 M solution of Ni(II) (solution No. 17), four different complexes are present in significant amounts at equilibrium. Sixty years ago it was straightforward to calculate the spectrum of a complex if the spectra of all other complexes could be ascertained independently, but modern computing protocols make it possible to deconvolute totally composite data into information about pure chemical species without ever having to chemically isolate any of them. We have designed our own program, *Sivvu*, which makes it especially easy to input absorbance data for up to 255 solutions with arbitrary compositions while still accounting for any systematic changes in solution density and relatively straightforward to interactively tailor a model for the data in a matter of minutes.

The absorbance data in the Ni(II)/bpy system involves the molar absorptivity curves for each of the three different complexes as well as that of the nickel solvato complex and that of free bpy. This matches the overall mathematical structure of the absorbance data, for which precisely five spectra are required to account for all of the data except random noise. More quantitatively, five purely mathematical factors can account for 96.58% of the information contained in the data set. The molar absorptivity curves for the four nickel(II) complexes in our final model along with that for the free bpy account for 96.54% of the data, even as the concentrations of the complexes must conform to equilibrium restrictions as governed by the equilibrium constants of the chemical reactions.

There is still a slim chance that a sixth distinct chemical species exists in this series of solutions if its molar absorptivity is a linear combination of the first five. We have seriously pursued two possibilities: (1) There are two bis complexes, cis and trans, or (2) a bridged complex forms that incorporates two metal cations coordinated to a single bpy ligand. The former is almost certainly true; however, we cannot achieve any noticeable improvement in the overall fit of our model by differentiating between a cis and trans complex. This agrees with the result of Basolo et al. in which they found that no optical activity could be detected in either aqueous or alcoholic solutions of $[Ni(bpy)_2Cl_2]$ derived from enantiomerically pure $[Ni(bpy)_3]Cl_2$.[3] The latter possibility improves the fit marginally (from 0.00106 to 0.00103 in total rms residual) and even leads to a curve for the bridge complex that is reasonable, though noisy. The free energy of chelation, which is typically negative, would need to be around a positive 8 kJ/mol. Therefore, we do not include it in our final model.

Not only is the absorbance data modeled accurately but the resulting molar absorptivity curves closely agree with previous work wherever comparisons can be made. Table 3 lists the peak positions of the *Sivvu* model for the bpy system which is based exclusively on the absorbance data from the 32 solutions represented in Figure 1. Even the curves for free bpy and the methanolato complex, though they are measured directly, are freely altered during the optimization to achieve the best possible fit between measurement and model and yet match those direct measurements admirably. It is peculiar to note that the curve for the methanolato complex that we measured is reproduced well in the model
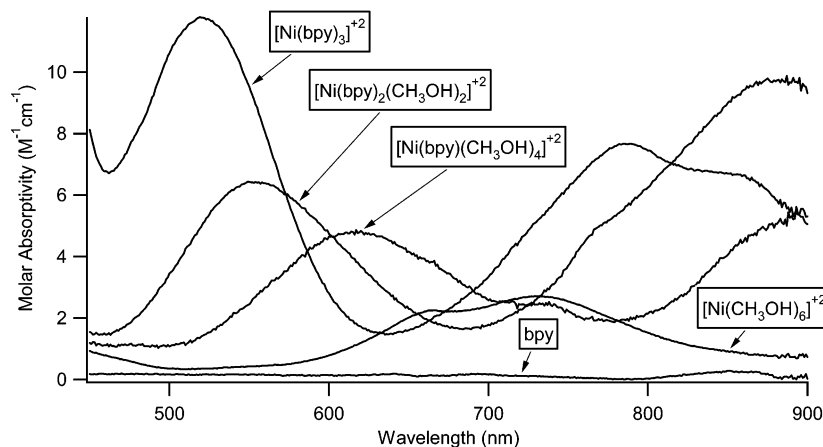
Figure 2. Molar absorptivity values for the five absorbing species present in a methanol solution of Ni(II) and bpy as determined by ERFA.
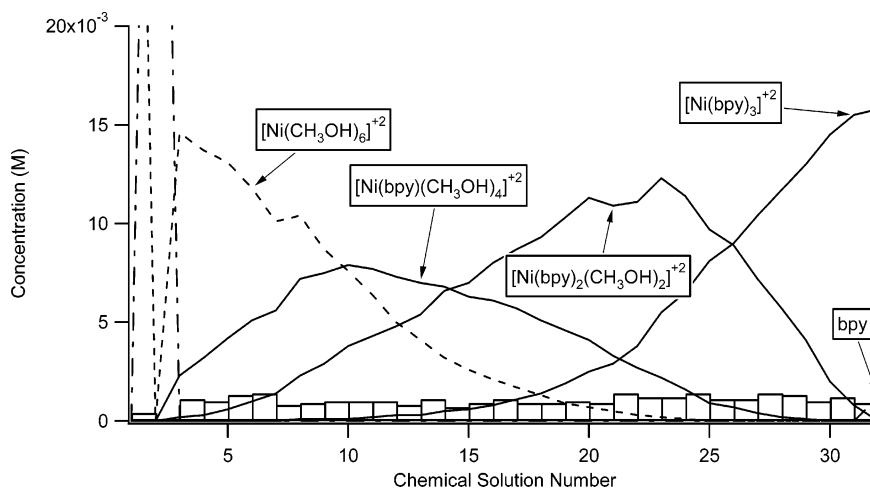

Figure 3. Concentration profiles for the 32 equilibrium solutions of $Ni(BF_4)_2$ and bpy. Bars represent the root-mean-square residual for each solution. The highest residual is 0.0014 absorbance units.
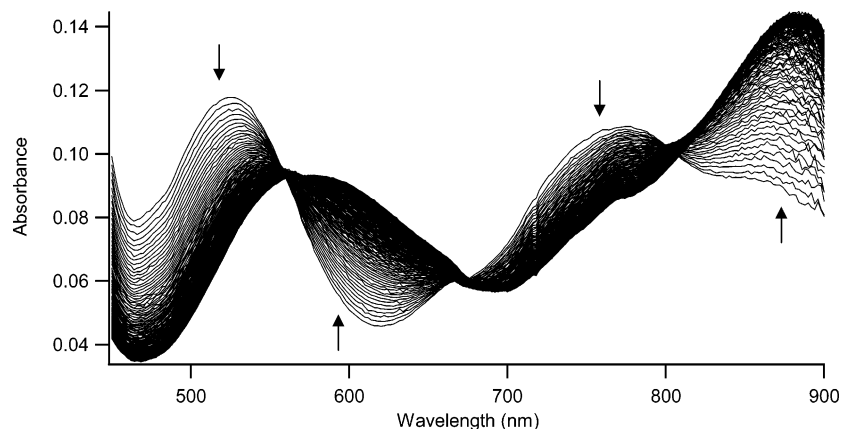

Figure 4. Absorbance data of a single solution of 0.105 mmol $Ni(BF_4)_2$ and 0.105 mmol bpy in 3 mL of methanol over a 6 h time period.

but does not match well one spectrum of the perchlorate salt reported in the literature, which describes more intense, longer wavelength transitions.[18] This is likely due to the other anions present in their case such as chloride and phosphite, which are more strongly coordinating than tetrafluoroborate. In addition, we note that the aqueous nickel(II) salt exhibits

transitions that are about 10 nm more energetic than those of our methanolato complex.

The model also accurately determines the molar absorptivity of the tris bpy complex, which can also be easily measured separately and has been reported previously.[19] The experimental goal of this work though is to elucidate the

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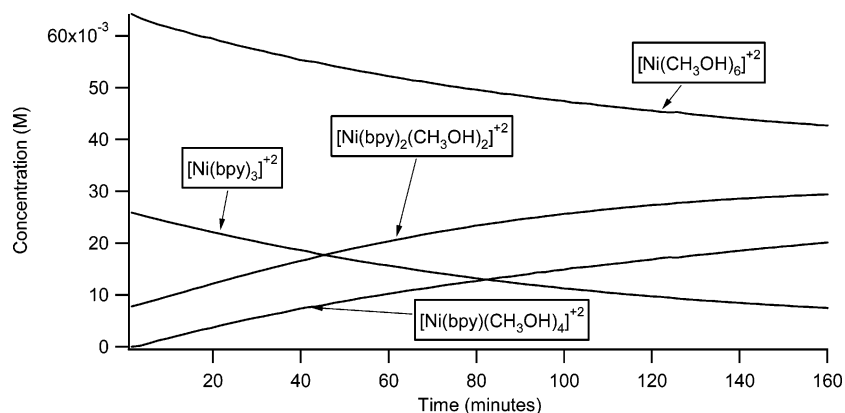
Figure 5. Concentration of Ni(II) complexes over time after 0.105 mmol Ni(BF$_4$)$_2$ and 0.105 mmol bpy were initially reacted in 3 mL of methanol.

Table 2. Percentage (%) of Nickel(II) Complex Initially in Solution Less the Percentage at Equilibrium Achieved Some Days Later

	equivalents of bpy				
complex	0.647	0.915	1.886	1.994	2.530
[Ni(CH$_3$OH)$_6$]$^{2+}$	24	28	21	18	10
[Ni(bpy)(CH$_3$OH)$_4$]$^{2+}$	−31	−40	−8	−2	0.5
[Ni(bpy)$_2$(CH$_3$OH)$_2$]$^{2+}$	−11	−5	−48	−50	−27
[Ni(bpy)$_3$]$^{2+}$	18	17	34	34	18

Table 3. Peak Positions (nm) and Molar Absorptivity Values in Parentheses for the Spectroscopic Transitions of Nickel Complexes with bpy and phen in Dry Methanol between 450 and 900 nm As Determined by ERFA of Multiple Solutions at 293 K

complex	$^3A_2 \rightarrow {}^3T_1$ (F)	$^3A_2 \rightarrow {}^3T_2$ (F)	$^3A_2 \rightarrow {}^1E$ (D)	ref
[Ni(CH$_3$OH)$_6$]$^{2+}$	662(2.2)		728(2.7)	a
[Ni(bpy)(CH$_3$OH)$_4$]$^{2+}$	615(4.8)	~900(>5.4)	730(2.4)	a
[Ni(bpy)$_2$(CH$_3$OH)$_2$]$^{2+}$	552(6.4)	880(9.7)	~768(4.9) sh	a
[Ni(bpy)$_3$]$^{2+}$	518(11.8)	786(7.7)	~850(6.7) sh	a
[Ni(bpy)$_3$]$^{2+}$	521(11.6)	791(7.1)	870(5.7)	19
[Ni(phen)(CH$_3$OH)$_4$]$^{2+}$	589(2.8)	759(2.3) sh	885(4.2)	a
[Ni(phen)(CH$_3$OH)$_4$]$^{2+}$	620(2)	NA	~1000(3)	3
[Ni(phen)$_2$(CH$_3$OH)$_2$]$^{2+}$	538(5.9)	775(4.3) sh	874(6.5)	a
[Ni(phen)$_2$(CH$_3$OH)$_2$]$^{2+}$	560(6)	NA	905(8)	3
[Ni(phen)$_3$]$^{2+}$	522(13.4)	784(7.9)	~870(~6)	a
[Ni(phen)$_3$]$^{2+}$	520(11)	785(6.5)	~890(~4) sh	3
[Ni(phen)$_3$]$^{2+}$	518(11.9)	787(6.8)	866(5.5)	19

a This work.

Table 4. Equilibrium Constants for the Substitution of bpy for Solvent on Nickel(II)

log K_{12}	log K_{23}	log K_1	solvent	method	ref
0.340(4)	1.091(6)	14(4)	MeOH	spectrometry + ERFA^a	b
0.1	0.9	6.9	41.5% MeOH	competition with Cu^{2+}	20
0.75	0.44	6.28	20% EtOH	polarography	21
0.70	0.35	6.25	20% EtOH	potentiometry	21
0.34	1.36	6.8	H$_2$O	potentiometry	22
0.36	1.24	6.8	H$_2$O	glass electrode	23
0.21	0.66	7.07	H$_2$O	distribution	23
0.25	0.35	7.13	H$_2$O	calorimetry	24

^{a}Equilibrium-restricted factor analysis. ^{b} This work.

The final piece of the model that *Sivvu* optimizes is the free energy values or equivalently, the equilibrium constants, for the ligand exchange reactions. These values for bpy have been measured in many ways, as shown in Table 4. The relative free energies for ligand substitution can be determined very precisely using ERFA because the data encompass most of the possible reaction coordinates for these ligand hopping reactions. This is not true of the reactions that substitute strong bidentate ligands with solvent molecules, which are so exergonic as to be nearly quantitative. The model yields an unconstrained optimized value of log K_1 of 14(4), which is obviously high even for 100% methanol. However, if this value is constrained at 7, the relative values decrease by less than 1%, and the total rms increases by only 0.05%. The molar absorptivity values do not change appreciably either. Our relative values, log K_{12} and log K_{23}, compare well with previous results and confirm that the addition of the third bpy ligand is considerably less exergonic than that of the second at 293 K, as expected, simply based on sterics.

Once the molar absorptivity curves of all four bpy complexes are known, it is straightforward to analyze the kinetics of Ni(II)/bpy solutions that had not yet achieved equilibrium. They all slowly ($t_{1/2} \approx 100$ min) transition from bluish gray to reddish gray. Regardless of the ratio of ligand to metal, significant amounts of all four complexes were initially detected, even though the four complexes were not yet at equilibrium. Also, the initial amounts of the tris and methanolato complexes always decreased while the initial amounts of the mono and bis complexes tended to increase as equilibrium was approached. So even though the ligand

molar absorptivity curves for the mono and bis complexes in solution, shown in Figure 2 and described in Table 3. It is useful for the sake of comparison to label the transitions of all the complexes in terms of octahedral symmetry even though the mono and bis complexes contain two different ligands that lower the symmetry. The major transitions of these complexes exhibit only subtle splittings, which appear as shoulders on the low-energy side of the peak. The energy of the major peaks blue shift predictably as bpy ligands replace solvent methanols. The absorptivity of the transition from $^3T_1$ (F) increases monotonically as expected, yet that from the $^3T_2$ (F) does not. Overall the model leads to molar absorptivity curves for the complexes that are commensurate with crystal field theory.

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solution is added to nickel(II) solution, the tris complex forms in very rapid initial reactions that replace solvent molecules with bpy.[25] The subsequent equilibration reactions by which a bpy ligand moves from one nickel complex to another proceed much slower.

This suggests that the activation barriers between the complexes are substantial, yet still small compared with the free energy values for the ligand-solvent substitution reactions. It is remarkable to note that since all four species equilibrate at comparable rates, the set of time-dependent absorbance curves seem to exhibit isosbestic points at 554, 670, and 794 nm.

For the phen system, the results afforded by ERFA do not agree with the literature as well as those for the bpy system. Four equilibrium-restricted factors account for 92.51% of the data whereas four purely mathematical factors account for 92.78% of the data. Both percentages are lower than in the bpy case because the concentrations of the Ni(II)/phen solutions were considerably lower, leading to more noise in the absorbance data. Basolo et al. reported the molar absorptivity values for the three possible phen complexes ($[Ni(phen)_n(MeOH)_{6-2n}]^{2+}$, $n = 1-3$) because they did not believe that equilibration was significant enough to compromise their measurements,[3] and their results match ours and those of others for the tris complex.[19,26] For the mono and bis complexes, there are clearly some significant differences between our results and theirs. For example, the $^3A_2 \rightarrow {}^3T_2$ (F) transition is not identifiable in their figure, but is in our data. Our curves can still be used to analyze our equilibrating solutions, and despite a less satisfying fit, the half-lives of the Ni(II)/phen complexes are on the order

of a few hours. Finally, our results for the thermodynamic parameters of the phen system do not agree with the literature. Our values for both log K_{12} and log K_{23} are greater than 1 whereas Irving et al. establish much smaller values with a variety of methods.[23]

Ultimately, the limitations of such methods must be recognized. These minor yet significant discrepancies in the results of the phen system likely stem from the incompleteness of our data set: considerable spectroscopic information is lost as the tris complex precipitates out of our set of solutions. Also, the farther a free-energy value is from zero, the less accurately it can be determined through direct modeling, but competitive coordination studies can be used to address this.

In conclusion, composite data, such as the spectral absorbance of chemicals in equilibrium, can be deconvoluted to deduce accurate information about those individual chemicals without the need to chemically isolate them. This thermodynamic information can then be used to model other aspects of the system such as nonequilibrium situations. This allows for the fundamental investigation of complicated and synergistic chemical systems based on facile measurements, provided complete data sets, such as the bpy data set, can be acquired.

Supporting Information Available: *Sivvu* program information in PDF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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