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DETAILED SPECTROSCOPIC AND THERMODYNAMIC CHARACTERIZATION OF NICKEL(II) COMPLEXES WITH METHYL/PYRIDINE ATTAINED VIA FACTOR ANALYSIS

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Abstract

The molar absorptivity curves for $[NiL_n(MeOH)_{6-n}]^{2+}$ L = pyridine, 3-methylpyridine, 4-methylpyridine, n = 1- 4, have been simultaneously deduced by modeling composite absorbance data of a series of equilibrium solutions in dry methanol using equilibrium-restricted factor analysis, a technique for obtaining spectral and thermodynamic information for component species involved in solution equilibria. Furthermore, the stepwise formation constants at 296 K have been determined with a high degree of accuracy. For pyridine, $logK_{1-4}$ = 1.272(6), 0.669(9), 0.14(2), -0.32(2), respectively. For 3-methylpyridine, $logK_{1-4}$ = 1.802(9), 1.16 (1), 0.32(1), -0.46(1), respectively. For 4-methylpyridine, $logK_{1-4}$ = 2.808(9), 1.114(4), 0.411(4), -0.421(9), respectively. Unrestricted factor analysis was used to confirm the precise number of unique complexes in each case. The only additional complex for which some evidence was found was the *pentakis* version of the pyridine complex.

Keywords: Spectrophotometric Titration, Factor Analysis, Pyridine, Methylpyridine, Picoline, Nickel, Sivvu

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, with pyridine and its derivatives making up a substantial portion. As of August 2012, the Cambridge Structural Database contained 11171 structures that incorporated 6-coordinate nickel, and 4058 (36%) of them included at least one pyridine-based molecule in the coordination sphere (3). More specifically, there are 38 structures consisting of nickel with four coordinating pyridine molecules, 43 with four 4-methylpyridine (picoline) molecules and 35 with four 3-methylpyridines. The conformations of all 116 are *trans*. Despite this abundance, there are still far more potential complexes that have not been documented. In the database, there were no mixed complexes with two of the three pyridine and picoline molecules.

Obviously there is not application-driven interest in every possible complex of nickel(II), but there is also another reason why many of these complexes go unstudied. Mixed ligand complexes are decidedly more difficult to chemically isolate for characterization, and this has been the standard strategy for studying compounds in inorganic chemistry. In solution, mixed-ligand complexes generally equilibrate to a substantial degree with analogs containing different numbers of the various ligands. While precipitation can aid in purification, it is often tricky and may be impossible to target an arbitrary mixed-ligand complex.

Fortunately, there is a strategy for obtaining information about individual chemical species without the need to chemically isolate them. If sufficient and appropriate composite data can be measured, then it is possible to deconvolute the information via modeling. The roots of such an approach date back half a century (4), and more-than-sufficient computing power has been readily available for decades (5). Now, such analysis are becoming more feasible in all areas of chemistry and science (6). There is still however much care that must be taken to discern the appropriateness of the model.

There are three key questions for a solution phase mixture at equilibrium:

1) How many unique chemical species are there?
2) What is the spectroscopic signature of each?
3) What are the equilibrium constants for the chemical reactions that relate the species to each other and to the original components of the solution?

Whereas it is impossible to answer these questions for a single equilibrated solution, if the spectroscopic measurements for a series of solutions with appropriate compositional variation are obtained (7), and the composite signals are additive combinations of the signals for each individual species, then factor analysis can be used to characterize the entire system. Here we detail the use of factor analysis, both in an unrestricted form and in an equilibrium-restricted form to definitively answer these three questions for nickel(II) with pyridine, 3-picoline, or 4-picoline, based on the UV-vis absorbance measured throughout a titration experiment.

Experimental

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 pyridine, C_5H_5N, and picolines, C_6H_7N, from Aldrich (≥99%) were used without further purification.

Preparation of Solutions

The following procedure was used for the preparation of all solutions. $Ni(BF_4)_2 \cdot 6H_2O$ was dehydrated in excess dimethoxypropane (DMP) (8). The resulting acetone and methanol co-solvents, as well as any DMP layer were removed under vacuum and replaced with dry methanol. Residual DMP helps to keep solution dry. Final nickel(II) concentration was about 0.1 M. Pyridine, 3-methylpyridine, and 4-methylpyridine were used without dilution. Methylpyridine is also known as picoline.

Spectrophotometric Titrations

Neat ligand was added drop-wise into metal cation solution at 296 K until about 100 equivalents were added. This proved to be a good range for the titration as the location of the curve

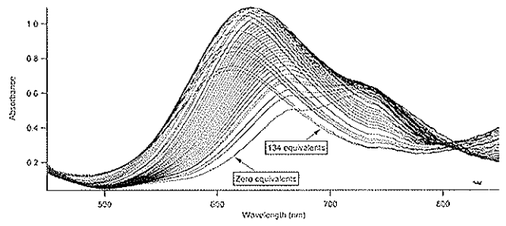

Figure 1. Raw absorbance data for the spectrophotometric titration of $Ni(BF_4)_2$ with pyridine in dry methanol at 296. $[Ni]^{2+}$ ~ 0.1 M. Pathlength is 2 cm.

maximum was changing minimally at this point. The absorbance was measured *in situ* using an Ocean Optics dip probe (TI300-VIS-NIR) and spectrometer (USB4000-VIS NIR) with deuterium/halogen light source (D2-mini-2). Care was taken with stirring and waiting to ensure that equilibrium was achieved at each step. 1 minute of time proved sufficient for absorbance data to stabilize. See Table 1 for detailed quantifications for each experiment. Figure 1 shows a typical dataset.

Analysis

There is much to be learned by deconstructing and modeling the absorbance datasets from each of the titrations. The problem is conveniently expressed using matrix algebra, which was first detailed by Wallace (9). Twenty five years later, Reeves *et al.* describe its application to a system with nickel(II) complexes and tridentate dyes (10). Others have used it to characterize more complicated systems like calixeranes (11) and enzyme cofactor interaction (12). The theory of such calculations is well established (13). In its most general form, it is called factor analysis, in which no boundaries are placed on the mathematical answer (14). It is often helpful to introduce restrictions to confine the model, such as non-negativity, unimodality, or chemical equilibria. In the latter case it can 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.

For all steps of the subsequent factor analysis, both unrestricted and restricted, we use the computer program Sivvu™, which is a set of Matlab protocols with graphical user interface that we have developed (15).

Results

According to the Beer-Lambert Law for absorbance, the data for a series of absorbance curves is comprised of an arbitrary number of additive components. In the case of a spectrophotometric titration, each chemical species with a unique molar absorptivity that exists at equilibrium during the titration contributes to the data set. Since nickel(II) can accommodate up to six monodentate ligands, it is an open question as to how many distinct nickel complexes form over the course of a titration with slightly bulky pyridine or picoline. Fortunately, unrestricted factor analysis can be used to abstractly analyze a dataset to determine the number of additive factors that exist in the data. Essentially, the analysis determines what fraction of the data can be reconstructed using a single factor. Then this factor is subtracted out from the data and the analysis is repeated on the remainder to find the next most significant factor. If there is random error in the data, as there certainly is in cases of scientific measurement, then the number of factors will technically be equal to the number of curves because no curve can be exactly constructed as a linear combination of the others (16). However, after a certain number of factors, the fraction of data that is newly accounted for will be small and relatively constant because it is only accounting for random noise in the data. This type of analysis can be done extremely easily on any block of numbers. In mathematical terms it is based on a manipulation called a singular value decomposition, which can be readily carried out by any mathematical computing program such as Matlab (17).

Table 1 lists the 1st ten factor weights for each spectrophotometric titration. As can be seen, each data set clearly consists of 5 significant factors. This therefore is strong evidence for the existence of *mono, bis, tris, and tetrakis* complexes besides the *methalonato* one. Beyond this the factor weights falls off gradually by about 10% each step. If there are more factors in any of the datasets, they are either very similar to the baseline itself or coincidently similar to some linear combination of the other 5 factors. Any signal from pyridine itself would likely fall into the first category. There is the possibility of factors in the second category due to the nature of these titration experiments. It is an unavoidable difficulty that if a *pentakis* species exists near the end of any of them, its concentration profile over the last solutions may mimic that of the *tetrakis*, making it difficult to resolve the two. If however the concentration profile of the *tetrakis* peaks and starts to decrease before the end of the titration, then the two signals can readily be differentiated mathematically.

Furthermore, this same process of factor analysis can be carried out on subsets of a dataset to determine when during the titration the different factors existed. Figure 2 shows such an evolving factor analysis for the pyridine titration. This corroborates the assignment of each of the 5 mathematical factors to a member of the series $[NiPy_n(CH_3OH)_{6-n}]^{2+}$ (n = 0-4) as each one increases in sequence as expected for a titration experiment in which the ligand is being added. The same analysis in the reverse direction further verifies this assignment. Together, these forward and reverse factor analyses show where each factor begins and ends over the course of the titration (18). In the case of the pyridine titration, the first two factors exist at the onset and disappear after about 2 equivalents and 5 equivalents, respectively. The third exists from about 0.2 to 13 equivalents. The fourth and fifth factors appear at around 2 and 8 equivalents, respectively and persist

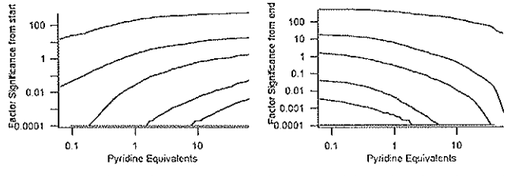

Figure 2. Evolving factor analysis for the pyridine titration dataset. The evolution from the start (left) graphs the factor significance for the sub-dataset from the beginning to a particular point defined by the *x*-axis. The evolution from the end (right) graphs the factor significance for the sub-dataset from a particular point to the end.

until the end.

Such analysis of the structure of the data is crucial when dealing with an open-ended chemical system such as nickel(II) with pyridine or picoline in which the exact number of distinct coordination complexes cannot be ascertained *a priori*.

With the confidence as to the potential identity of the complexes that comprise the absorbance dataset, the data can be readily modeled according to thermodynamic parameters of chemical equilibrium:

$[Ni(CH_3OH)_6]^{2+} + L \rightleftharpoons [NiL(CH_3OH)_5]^{2+} + CH_3OH \quad K_1$

$[NiL(CH_3OH)_5]^{2+} + L \rightleftharpoons [NiL_2(CH_3OH)_4]^{2+} + CH_3OH \quad K_2$

$[NiL_2(CH_3OH)_4]^{2+} + L \rightleftharpoons [NiL_3(CH_3OH)_3]^{2+} + CH_3OH \quad K_3$

$[NiL_3(CH_3OH)_3]^{2+} + L \rightleftharpoons [NiL_4(CH_3OH)_2]^{2+} + CH_3OH \quad K_4$

(possibly $[NiL_4(CH_3OH)_2]^{2+} + L \rightleftharpoons [NiL_5(CH_3OH)]^{2+} + CH_3OH \quad K_5$)

In each case, the step-wise binding constants for these reactions were refined by minimizing the residuals between the observed and calculated data. These values are shown in Table 1 along with several figures of merit. The 95% confidence intervals on the binding constants were determined by re-optimizing the binding constants 40 times on random subsets of 50% of the data to determine a standard deviation, which can then straightforwardly be converted into confidence intervals of choice by assuming a T-distribution.

Furthermore, since every different set of binding constants leads to a unique set of molar absorptivity curves for the absorbing species, these latter values were simultaneously optimized. Figure 3 shows the optimized molar absorptivity curves for all complexes.

Discussion

The use of both unrestricted and equilibrium-restricted factor analysis has afforded the molar absorptivity spectra and binding constants from equilibrated solutions of nickel(II) with various pyridine-based ligands. The spectra of many of these species have never been ascertained previously because they are difficult or even impossible to chemical isolate.

In each case, the data could be satisfactorily modeled assuming six absorbing species: five nickel(II) complexes with 0 - 4 ligands, and the ligand by itself (Table 1). Despite the lack of any spectroscopic transitions for the ligand in methanol for the wavelength range studied, it proved critical

Table 1. Experimental Parameters and Fitting Results for Spectrophotometric Titrations of $Ni(BF_4)_2$ in dry methanol.

Ligand	Pyridine	3-Picoline	4-Picoline
Temperature (K)	296	296	296
Number of Solutions	42	38	42
Ni(II) Initial Molarity	0.1114	0.0920	0.1108
Ni(II) Final Molarity	0.0508	0.04502	0.0546
Ligand Equivalents	0 → 134	0 → 117	0 → 90
1st Ten Factor Weights	33.183 6.155 1.936 0.324 0.089 0.016 0.015 0.015 0.014 0.013	30.227 5.319 1.623 0.334 0.078 0.026 0.023 0.023 0.021 0.019	33.230 5.873 1.912 0.497 0.111 0.022 0.019 0.019 0.016 0.015
Factors in Model	6 / 7	6	6
Unrestricted Reconstruction	99.2915% / 99.3024%	98.9671%	99.1556%
Equilibrium Restricted Reconstruction	99.2770% / 99.3282%	98.9380%	99.1331%
RMS Residual	0.0006228 / 0.0006166	0.00077096	0.00083949
Final R^2	99.9998% / 99.9998%	99.9996%	99.9996%
$logK_1$	1.196(3) / 1.272(6)	1.802(9)	2.808(9)
$logK_2$	0.588(1) / 0.669(9)	1.16 (1)	1.114(4)
$logK_3$	-0.208(2) / 0.14(2)	0.32(1)	0.411(4)
$logK_4$	-1.38(9) / -0.32(2)	-0.46(1)	-0.421(9)
$logK_5$	NA / -1.2 (unrefined)	NA	NA
Activity Model	None	None	None
Wavelength Range	450 – 850 nm	450 – 850 nm	450 – 850 nm
Molar Absorptivity	nm(absorptivity) / nm(absorptivity)	nm(absorptivity)	nm(absorptivity)
$[Ni(CH_3OH)_6]^{2+}$:	667s(2.3)/737(2.7) / 667s(2.3)/737(2.7)	666s(2.3)/733(2.7)	667s(2.2)/733(2.6)
$[NiL(CH_3OH)_5]^{2+}$:	660(4.1)/722s(3.4) / 660(4.0)/722s(3.3)	664(3.5)/718s(3.2)	664(3.3)/722s(3.3)
$[NiL_2(CH_3OH)_4]^{2+}$:	642(5.3)/726s(2.8) / 644(5.1)/726s(2.9)	654(4.6)/724s(3.2)	650(5.5)/734s(2.6)
$[NiL_3(CH_3OH)_3]^{2+}$:	619(6.7)/743s(2.2) / 633(5.5)/743s(2.4)	635(6.1)/744s(2.5)	627(6.7)/736s(2.6)
$[NiL_4(CH_3OH)_2]^{2+}$:	592(8.6) / 620(6.7)	613(7.3)	612(8.0)
$[NiL_5(CH_3OH)]^{2+}$:	NA / ~590(8)	NA	NA
Data Contributions			
Ligand:	3.92% / 3.74%	7.07%	4.26%
$[Ni(CH_3OH)_6]^{2+}$:	13.69% / 12.73%	6.29%	4.92%
$[NiL(CH_3OH)_5]^{2+}$:	24.87% / 22.18%	11.87%	14.61%
$[NiL_2(CH_3OH)_4]^{2+}$:	30.68% / 22.90%	22.08%	24.43%
$[NiL_3(CH_3OH)_3]^{2+}$:	24.09% / 18.81%	30.75%	32.84%
$[NiL_4(CH_3OH)_2]^{2+}$:	2.74% / 16.40%	21.95%	18.94%
$[NiL_5(CH_3OH)]^{2+}$:	0.0% / 3.22%	0.0%	0.0%

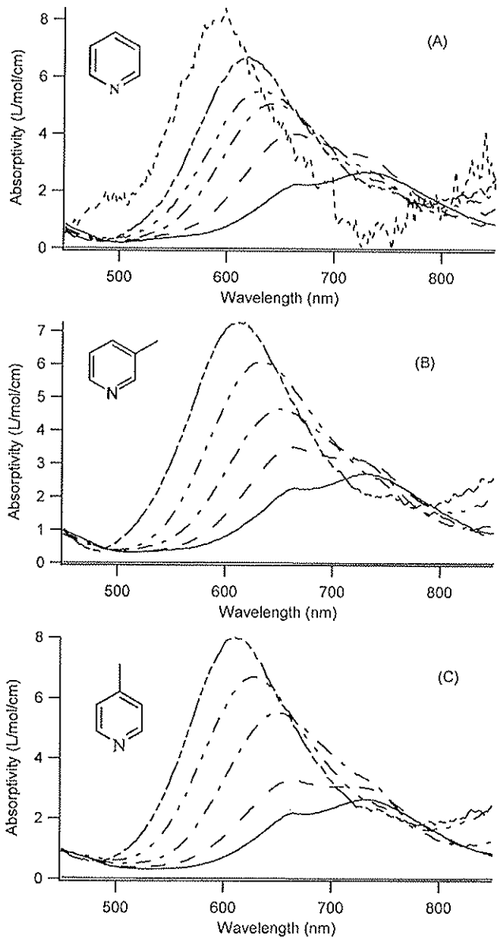

Figure 3. Optimized molar absorptivity values for $[NiL_n(CH_3OH)_{6-n}]^{2+}$ for L = (a) pyridine, (b) 3-methylpyridine, (c) 4-methylpyridine. n = 0 (solid); n = 1 (dashed); n = 2 (dot dash); n = 3 (dot dot dash); n = 4 (dot dot dot dash); n = 5 (dotted).

to include the ligand as an absorbing factor because of its high concentration by the end of the titration. As can be seen in Figure 3, the absorptivity curve for pyridine is essentially, but not exactly, coincident with the baseline as expected.

Introducing the possibility of a *pentakis* complex had mixed results. For both picoline titration results, it proved superfluous. This is evident because the molar absorptivity of the extra species is driven outrageously high even as its concentration is driven towards zero in order to accommodate random noise in the data without affecting the rest of the model. This is not surprising because the concentration profiles for the *tetrakis* species were already descending by the end of both picoline titrations, whereas any profile for a *pentakis* species would still be ascending so as not to be embedded in the same mathematical factor. However, in the case of the pyridine titration, the profile of the *tetrakis* and

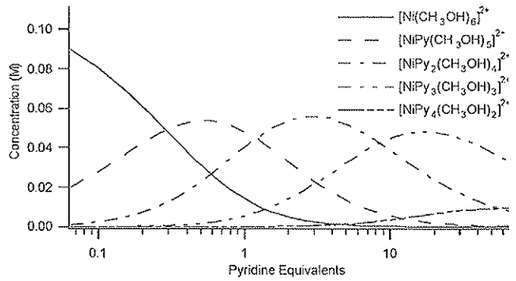

Figure 4. Concentration profiles for the 6-factor model of pyridine titration. Notice how profile for *tetrakis* has not peaked by the end of the experiment.

that of a potential *pentakis* species could be irresolvedly embedded in the same mathematical factor because the concentration profile of the former never descends (Figure 4) Indeed the introduction of a *pentakis* species significantly improves the model in reasonable ways, however the binding constant, K_5, must be pinned. If it is allowed to freely optimize, the factor is still partially used to account for random error in the data. A value of -1.2 for $\log K_5$ was determined to give the most reasonable molar absorptivity profile for the *pentakis* complex. The complete results for this model are shown alongside the other one in Table 1.

Overall the fit to the data is outstanding. The root-mean square of the residual errors (the point-by-point difference between the observed and modeled values) for all three titration experiments are all less than 0.00085 and the R^2 values are all greater than 99.9996% (Table 1).

Of high importance are the binding constants, which have been determined quite accurately. Unlike the method of Drago, which focuses on a single wavelength to model a 1:1 binding event (19), Sivvu™ uses all the wavelengths simultaneously to model binding constants. The resulting values behave as generally expected. The picolines bind tighter than the pyridine because of the additional electron donation available from the methyl groups. Furthermore, 4-picoline definitely binds more tightly than 3-picoline due to the advantageous position of the methyl group in the *para* position. Overall, the values compare well to previous literature values (20), but there are marked differences. Much more distinction is found between the first binding constant for pyridine and those for the picolines. From potentiometric titrations (usually in the presence of nitrate), the logs of all three were found to be between 1.87 and 2.11 (21), but this analysis indicates that that for pyridine is considerably smaller and that for 4-picoline is considerably larger. Furthermore, others have found that even the fourth binding constant for each of the picolines was larger than 3 (22), but this analysis indicates them to be below 0.5. No published value for the fourth binding constant of pyridine could be found, which is not surprising given the value and potential ambiguity determined through this work.

The major advantage of using factor analysis in the modeling of data is the simultaneous determination of the full molar absorptivity curves for each of the chemical species. Not only is this information tremendously useful for determining the nature of the chemical species, particular if it is a coordination compound, but it provides a completely external verification of the model. Because the calculations

performed by Sivvu™, and other programs like it, incorporate nothing based on crystal field theory or the like, when it produces results that match the theory, it is an overwhelming indicator that the chosen model is basically correct. Clearly, the resulting curves for these three titration experiments confirm the reliability of the model. The peak positions blue-shift monotonically as ligand is substituted for solvent. The peak heights also increase as expected due to the introduction of ligands with available π-orbital systems. The peaks for the complexes with either of the two picolines are basically identical. The 6-factor model for the pyridine titration data suggests that pyridine shifts the *d-d* transitions more than the picolines. This seems unreasonable since in comparable crystal structures, the Ni-N bond length for 4-picoline complexes is significantly shorter (~1.9 Å) than its pyridine counterpart (~2.1 Å) (23). By contrast, the 7-factor model for the pyridine titration data yields molar absorptivity curves that are slightly red-shifted compared to that of the picolines, making it the model of choice.

So it seems likely that an additional factor, significantly the *pentakis* complex, exists and should be accounted for in the model. This corroborates Rosenthal and Drago who cite conclusive evidence for even the *hexakis* complex for $Ni(ClO_4)_2$ with pyridine in nitromethane (24).

Another advantage of using factor analysis in the modeling of data comes from the enhancement of signal as a substantial portion of the experimental noise is eliminated. Given that there are just six (or seven) absorbers that contribute to the data, the entire dataset can theoretically be modeled with just one factor for each absorber. Opportunely, each factor possesses an amount of error on par with a single absorbance curve in the dataset. Therefore whereas the measured data contains the sum total of the error of all the absorbance curves, the model data assumes only the sum total of the error from the six (or seven) factors. Thus much of the random noise is left behind. This can be quantified for the title experiments.

The equilibrium-restricted model for the 4-picoline titration accounts for 99.1331% (Table 1) of the complete date set, but with no restrictions, only 99.1556% can be accounted for because the remaining 0.8444% is associated with factors 7 – 42 (the total number of curves in the dataset), which has been determined to represent nothing but random noise. Incidentally, this amount of noise corresponds to data point errors with a standard deviation of 0.0007 absorbance units, which is typical of the dip probe spectrometer set up used.

Despite this signal enhancement, not all error can be eliminated because some remains embedded in the factors. This can readily be seen in the molar absorptivity curve for $[NiPy_5(CH_3OH)]^{2+}$ shown in Figure 3. Because this species was present only in small amounts even at the end of the titration, the signal to noise ratio for this factor is still quite high. The general shape can be readily discerned, but the precise values for the molar absorptivity at any particular wavelength could not be determined more accurately.

In conclusion, composite data, such as the spectral absorbance of chemical species 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. The approach should 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.

The program Sivvu™ in particular possesses the tools and transparency of operation to allow the user to discern and decide how best to analyze data sets, particularly ones with open end points.

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