iron(III) is additional evidence that eq 11 and 12 do represent the empirical rate law. The dependence of k''_{Cu} upon $[\mathrm{Cu}^{2+}]$ at low $[\mathrm{Fe}^{2+}]$, contrary to the prediction of eq 14, may occur because eq 22 and 23 have become important at the high iron(III) and low iron(II) and copper(II) concentrations.

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Registry No. $\mathrm{Fe(H_2O)_6}^{3+}$, 15377-81-8; $\mathrm{HSO_3}^-$, 15181-46-1; Cu^{2+}, 15158-11-9.

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Lewis Acid Studies of Bis(2,2,6,6-tetramethyl-3,5-heptanediono)nickel(II)

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Equilibrium constants and enthalpies for the adduct formation reaction between the square-planar diamagnetic Lewis acid bis(2,2,6,6-tetramethyl-3,5-heptanediono)nickel(II) and the Lewis bases dimethyl sulfoxide, pyridine *N*-oxide, diethylamine, and triethylamine were determined under solvent conditions in which the reported enthalpies of the mono adduct formation reactions are found to correlate well with the Drago–Wayland equation $-\Delta H = E_\mathrm{A}E_\mathrm{B} + C_\mathrm{A}C_\mathrm{B}$, with $E_\mathrm{A} = 2.03$ and $C_\mathrm{A} = 0.640$ for the Ni complex. The solution magnetic moment of the diethylamino mono adduct was found to be $\mu = 3.25$ BM. This represents the first time E_A and C_A parameters have been determined for a Lewis acid which undergoes a change in spin state upon coordination.

Recent work by Partenheimer and Drago[1] showed that donor–acceptor reaction enthalpies could be correlated using the Drago–Wayland[2] double-scale equation

$$-\Delta H = E_\mathrm{A}E_\mathrm{B} + C_\mathrm{A}C_\mathrm{B} \qquad (1)$$

for bis(hexafluoroacetylacetonato)copper(II) as the Lewis acid in cyclohexane, thus extending the general usefulness of eq 1 to metal ion centers in coordination compounds. The significance of the *E* and *C* parameters has been discussed previously.[3,4]

In attempting to demonstrate further the general applicability to properly chosen coordination compounds,[1] we undertook a calorimetric investigation of the square-planar diamagnetic[5,6] bis(2,2,6,6-tetramethylheptane-3,5-diono)nickel(II) complex ($\mathrm{Ni(DPM)_2}$) which is known[7] to form paramagnetic six-coordinate complexes. The readiness with which the complexation reactions occurred implied that the intermediate adducts might very well be paramagnetic as well. A Lewis acid which underwent a change in spin state upon coordination would be unique and would be a good test of the general existence of E_A and C_A parameters for Lewis acids under the proper solvent conditions.

Another interesting aspect of this study was the steric requirements of the adducts. The tertiary butyl groups of the DPM moiety are quite bulky and seem to shield the coordination sites to a certain extent. Framework molecular scale models indicated that the dimethyl sulfoxide (DMSO), diethylamine ($\mathrm{NHEt_2}$), and pyridine *N*-oxide (pyO) mono adducts were best accommodated by assuming a trigonal-bipyramidal (TBP) geometry, with the Lewis base occupying an axial position—an effect which was readily accomplished in the models by a twisting away from the planar position of an oxygen on one of the DPM ligands. However, for the pyridine adduct and for the adducts of the various substituted pyridines the adduct molecular model could easily be accommodated in either a square-pyramidal (SP) or TBP arrangement. Hence there exists a possibility of obtaining two different sets of E_A, C_A parameters for $\mathrm{Ni(DPM)_2}$ in the different electronic conditions the TBP and SP geometries would necessitate, an interesting situation which could limit the broadest application of the Drago–Wayland concept.

This paper reports the evaluation of E_A and C_A parameters for $\mathrm{Ni(DPM)_2}$ with the nonpyridine donors. A subsequent paper will report E_A and C_A parameters from the various pyridine derivatives and report more completely the thermodynamic results of the $\mathrm{Ni(DPM)_2}$-pyridine systems.

Experimental Section

Materials and Preparation of $\mathrm{Ni(DPM)_2}$. Matheson Coleman and Bell Spectroquality benzene and cyclohexane were stored over Linde 4A molecular sieves and used without further purification. Pyridine (Baker), 4-methylpyridine, 3,5-dimethylpyridine, and 4-acetylpyridine were refluxed over KOH under a nitrogen atmosphere for 24 hr, then distilled under reduced pressure to a receiver containing Linde 4A molecular sieves, and stored under nitrogen. 4-(*N*,*N*-Dimethylamino)pyridine (Aldrich) and pyridine *N*-oxide (Aldrich) were dried thoroughly in a drying pistol over $\mathrm{P_2O_5}$ and vacuum sublimed. Reagent grade dimethyl sulfoxide (Baker) was stored over molecular sieves and used without further purification. Diethylamine ($\mathrm{NHEt_2}$) and triethylamine ($\mathrm{NEt_3}$) (Eastman) were used without purification. The 4-(methoxycarbonyl)pyridine (Eastman) was refluxed over molecular sieves under a nitrogen atmosphere, distilled, and stored under nitrogen.

The literature method[5] for the preparation of bis(2,2,6,6-tetramethylheptane-3,5-diono)nickel(II), $\mathrm{Ni(DPM)_2}$, gave only poor results, so the following procedure was employed. Forty millimoles of 2,2,6,6-tetramethylheptane-3,5-dione (HDPM) (Peninsular Chem-Research Inc.) was dissolved in 20 ml of 95% ethanol. To this was added a solution of 20 mmol of $\mathrm{Ni(NO_3)_2\cdot 6H_2O}$ (Mallinckrodt, AR grade) in 50 ml of a 50% ethanol-water mixture. Then a solution of 40 mmol of NaOH in 50 ml of a 50% ethanol–water mixture was added slowly to this with constant stirring. The green dihydrate of $\mathrm{Ni(DPM)_2}$ precipitated immediately. Stirring was continued for 10 min.

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The precipitate was filtered and air-dried overnight and then dried thoroughly at 110°, changing from green to purple. The crude Ni(DPM)$_2$ was sublimed at 0.1 mm at 120° or recrystallized from dry 1,2-dichloroethane, mp 226–228° (uncor) (lit. mp 217–221°), with an overall yield of 50–65%. The Ni(DPM)$_2$ was analyzed for Ni using the dimethylglyoxime method.[8] *Anal.* Calcd: N, 13.81. Found: Ni, 13.82.

Instruments. Solution spectra in the near-infrared and visible regions were recorded on a Cary 14 recording spectrophotometer using matched 1-cm quartz cells. The reference cell contained a solution of the ligand in the appropriate solvent at the same concentration as in the sample cell.

Nmr spectra used in the determination of solution magnetic moments were obtained on a Varian A-60D by the method of Evans.[9]

The calorimeter, a Guild Corp. solution calorimeter Model 400, was similar in design to that described by Arnett, *et al.*[10]

A test reaction between 0.1 M HCl and 0.5 M NaOH was run obtaining an average ΔH of -13.49 ± 0.09 kcal/mol. This is less than 1% from the best literature value.[11]

Procedure. The calorimetric procedure was as follows. Ni(DPM)$_2$ is very readily air oxidized in solution so the measurements were made under a constant flow of nitrogen, adjusted to minimize the drift in the base line. Aliquots of *ca.* 0.1–1.0 ml were added to the solution by means of a breakable addition tube which was equilibrated thermally for several minutes in the reaction dewar. The reaction heat was determined as previously described.[12-15]

A program developed by Puhl,[16] incorporating the copyrighted subroutine STEPIT,[17] was employed to determine iteratively, by a direct-search method, the "best" fit of the stepwise K's and ΔH's to the experimental data. One of two models was employed depending upon conditions: Model I: $A + B = AB, K_1, \Delta H_1$ (mono adduct only). Model II: $A + B = AB, K_1, \Delta H_1; AB + B = AB_2, K_2, \Delta H_2$ (mono and bis adducts simultaneously).

In the case of model II (NHEt$_2$ and pyO donors), since there are four variables and only a limited number of data points, at least one of these, preferably two, must be known with some certainty to put any confidence in the results.[18] This condition was met by first measuring ($\Delta H_1 + \Delta H_2$) by adding the Ni(DPM)$_2$ to a solution of excess base in the calorimeter, thus fixing the total heat of reaction. Hence by specifying one K and one ΔH, the remaining two parameters are fixed. In the situations encountered here, with the NHEt$_2$ and pyO donors, a good estimate of ΔH_1 was also available, a situation corresponding to condition 2(a) in the notation of Maier and Drago.[18] Under these conditions there is some uncertainty in K_1 and K_2 since these tend to change much more quickly than ΔH_1 or ΔH_2. But since we were interested primarily in the enthalpies, this was of only small concern.

Results

Spectra. Ni(DPM)$_2$ absorbs relatively strongly in the visible region (ϵ 60 at 535 nm).[5] The formation of the complexes results in a diminishing in intensity of the purple color with added base until the solutions take on the green to blue color characteristic of six-coordinate nickel(II). Hence, it will be very difficult to make any spectral analysis of the mono adducts: they are masked on one side by Ni(DPM)$_2$ and on the other side by the bis adduct. Results with the DMSO and NEt$_3$ systems indicate that the mono adducts are virtually colorless and absorb in the visible–near-ir region only very weakly.

The spectra of the bis adducts are typical of six-coordinate Ni(II).[7]

Spectrophotometric titration of Ni(DPM)$_2$ with diethylamine at 535 nm (Figure 1) indicated (a) that the first step in the adduct formation is a simple 1:1 complex as evidenced by the extrapolated ratio of [NHEt$_2$]/[Ni(DPM)$_2$] and (b) that reaction between the two is essentially quantitative (K_1 unmeasurably large), a fact confirmed by the calorimetry experiment in which the first five data points yielded ΔH_1 quantitatively (Table III). It was assumed that the other bases formed simple 1:1 adducts as well, since the fit of the calorimetric data to this model is good.

A choice between the use of model I and the use of model II was made on the basis of the presence or absence of a sharp isosbestic point when the [base]/[Ni(DPM)$_2$] ratio was varied over the entire concentration range used in the calorimetry experiment. A sharp isosbestic point which indicated only one equilibrium—that of the mono adduct formation—was observed for the DMSO and the NEt$_3$ adducts. This isosbestic point was lost only upon addition of a large excess of ligand indicating the formation of the 2:1 complex. Hence model I was used to fit these thermochemical data. Model II was used for diethylamine and the pyridine N-oxide systems, since the isosbestic point was lost well before the [base]/[Ni(DPM)$_2$] = 1.

Attempts to determine the stepwise thermodynamic parameters for the pyridine and substituted pyridine complexes met with no success. While values for $K_1, K_2, \Delta H_1$, and ΔH_2 were obtained, the large uncertainty in the numbers makes them practically meaningless. It appears as though the computer is merely "smoothing out" the results, obtaining an average of ΔH_1 and ΔH_2 of about -10 kcal each.

Consistent with this is our inability to obtain an isosbestic point in the spectrophotometric titration of Ni(DPM)$_2$ with pyridine—although the extrapolated [py]/[Ni(DPM)$_2$] is still 1:1—in either cyclohexane or benzene (Figure 2).

The calorimetric data are listed in Table I for the determination of the overall enthalpies of reaction, $\Delta H_T = \Delta H_1 + \Delta H_2$, and Table II summarizes these results.

The values of ΔH_T for the various pyridine derivatives are included for completeness. Table III lists the data for the simultaneous determination of the enthalpies and equilibrium constants for Ni(DPM)$_2$ with DMSO, pyO, NHEt$_2$, and NEt$_3$.

The equilibrium constants, enthalpies of formation, and related thermodynamic parameters are summarized in Table IV, and Table V correlates the enthalpies of formation using eq 1. The enthalpies determined for DMSO, NHEt$_2$, and pyO were used to fit E_A and C_A graphically by rearrangement of eq 1, *i.e.*

$$C_A = \frac{-\Delta H}{C_B} - E_A \frac{E_B}{C_B} \qquad (2)$$

Values of $E_A = 2.03$ and $C_A = 0.64$ fit the data as shown in Table V. The calculated enthalpy for NEt$_3$ is somewhat higher than the observed value.

It has been pointed out[13] that saturated hydrocarbons are preferred as solvents. Comparison of ΔH_T for the Ni(DPM)$_2$-pyridine system in cyclohexane and in benzene indicates that, while there is a difference, this difference is barely beyond the limits of experimental error and the use of benzene instead of cyclohexane—necessitated by the limited solubility of a number of the bis adducts—seems to pose no problems.

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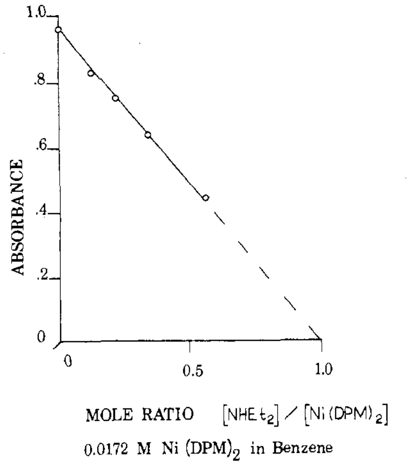

Figure 1. Spectrophotometric titration of $Ni(DPM)_2$ with diethylamine in benzene.

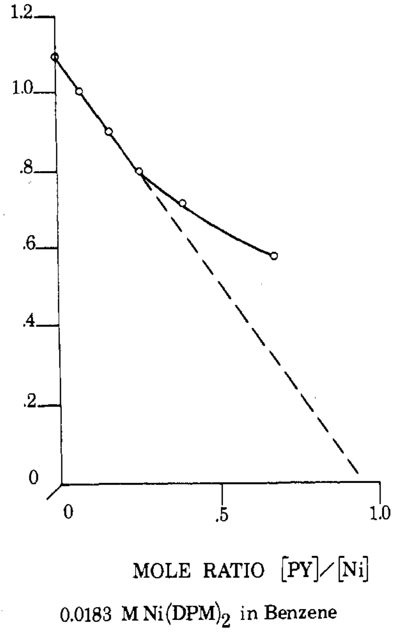

Figure 2. Spectrophotometric titration of $Ni(DPM)_2$ with pyridine in benzene.

Discussion

Stoichiometry and Stereochemistry. The spectrophotometric titrations of $Ni(DPM)_2$ with $NHEt_2$ and py confirmed the nature of the intermediate adducts as 1:1 as opposed to that of the related pyridine adduct of bis(acetylacetonato)nickel(II) which consists of one pyridine per two nickels[19] and which is thought to be dimeric.[20]

Attempts to arrive at some conclusion regarding the possible structure of the mono adducts led us to consider the relative stabilities of the two limiting cases for five-coordination, trigonal bypyramid (TBP) and square pyramid (SP). Ciampolini[21] has indicated that many factors are responsible for differences in stability between SP and TBP configurations, such as metal-ligand attractions, ligand-ligand repulsions, and crystal field stabilization energy (CFSE).

With respect to CFSE, the SP arrangement is preferred by anywhere from 2 to 15 kcal mol^{-1} over the TBP,[21] assuming strictly an electrostatic approach. However, Fackler[15] has argued that there is considerable covalent character to the metal-chelate bonds and possibly some metal-chelate π bonding.

Table I. Calorimetric Data for a $Ni(DPM)_2$ Solution Added to a Solution of Excess Base

Mol of Ni-$(DPM)_2$ × 10^4	$-E$, cal	$-\Delta H$, kcal/mol	Mol of Ni-$(DPM)_2$ × 10^4	$-E$, cal	$-\Delta H$, kcal/mol
0.9718 *M* Diethylamine in Benzene					
0.7815	1.479	18.92	2.721	5.258	19.32
1.589	3.071	19.33			
0.7169 *M* Triethylamine in Benzene					
0.7570	0.7543	9.964	2.349	2.314	9.853
1.562	1.569	10.04	3.116	3.116	10.00
0.5144 *M* Pyridine *N*-Oxide in Benzene					
0.9526	1.430	14.90	4.116	6.104	14.83
2.212	3.321	15.01	5.497	8.311	15.12
3.325	5.001	15.04			
1.410 *M* Dimethyl Sulfoxide in Benzene					
0.9970	0.5203	5.219	3.870	1.960	5.065
2.358	1.187	5.034			
0.07864 *M* 4-(*N*,*N*-Dimethylamino)pyridine in Benzene					
0.8920	1.830	20.52	2.889	6.156	21.31
1.826	3.906	21.39	4.256	7.221	21.27
0.2014 *M* 4-Methylpyridine in Benzene					
1.046	2.126	20.32	3.114	6.343	20.37
1.799	3.752	20.86			
0.2206 *M* 3,5-Dimethylpyridine in Benzene					
0.9520	1.833	19.25	3.046	5.891	19.34
1.878	3.648	19.42	3.942	7.593	19.26
0.4965 *M* Pyridine in Benzene					
0.7926	1.509	19.04	3.606	6.899	19.13
2.145	4.087	19.05	4.267	8.152	19.10
0.4884 *M* 4-Acetylpyridine in Benzene					
0.8000	1.505	18.81	2.943	5.542	18.83
1.941	3.636	18.73			
0.4866 *M* Pyridine in Cyclohexane					
0.9806	1.942	19.81	2.636	5.266	19.98
1.884	3.763	19.97	3.536	7.047	19.93
0.1241 *M* 4-(Methoxycarbonyl)pyridine in Cyclohexane					
1.119	2.206	19.71	3.922	7.784	19.85
2.437	4.798	19.69			

Table II. Summary of Calorimetric Results

Base[a]	$-\Delta H_T$,[b] kcal/mol
Diethylamine	19.19
Triethylamine	9.96
Pyridine *N*-oxide	14.98
Dimethyl sulfoxide	5.10
4-(*N*,*N*-Dimethylamino)pyridine	21.12
4-Methylpyridine	20.52
3,5-Dimethylpyridine	19.32
Pyridine	19.08
Pyridine (cyclohexane)	19,92
4-(Methoxycarbonyl)pyridine (cyclohexane)	19.75
4-Acetylpyridine	18.79

[a] In benzene except where noted. [b] All values are ±0.2 kcal/mol.

Also, most of the high-spin five-coordinate nickel(II) complexes isolated to date are TBP, although this may be due to the choice of ligands, rather than to electronic considerations.[22]

Inspection of molecular models of the mono adducts very strongly suggests that for the oxygen and aliphatic nitrogen

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Table III

Triethylamine–Model I

10^2[Ni(DPM)$_2$], *M*	[$C_6H_{15}N$], *M*	$-E$, cal		Vol., l.
		Obsd	Calcd	
0.7778	0.07634	0.4833	0.4566	0.2084
0.7771	0.1844	1.0131	1.067	0.2086
0.7763	0.3004	1.698	1.677	0.2088
0.7756	0.3977	2.145	2.155	0.2090
0.7748	0.5055	2.624	2.650	0.2092
0.7712	1.048	4.767	4.665	0.2102
0.7679	1.503	5.934	5.880	0.2111
0.7650	1.954	6.7717	6.786	0.2119
0.7617	2.438	7.453	7.528	0.2128

Pyridine *N*-Oxide–Model II

10^2[Ni(DPM)$_2$], *M*	10^5[C_5H_5NO], *M*	$-E$, cal		Vol., l.
		Obsd	Calcd	
0.8114	0.1684	1.459	1.334	0.2084
0.8106	0.3646	2.794	2.726	0.2086
0.8098	0.5622	3.974	3.938	0.2088
0.8090	0.7891	4.950	5.095	0.2090
0.8083	1.0813	5.820	6.263	0.2092
0.8071	1.4340	7.118	7.309	0.2095
0.8056	1.8560	8.147	8.224	0.2099
0.8037	2.3540	9.087	9.028	0.2104
0.8031	3.242	10.621	10.078	0.2109

Diethylamine–Model II

10^2[Ni(DPM)$_2$], *M*	10^5[$C_4H_{11}N$], *M*	$-E$, cal		Vol., l.
		Obsd	Calcd	
0.7312	0.6260	0.9794	0.9750	0.2083
0.7304	1.271	1.9885	1.980	0.2085
0.7298	2.138	3.377	3.331	0.2087
0.7287	2.967	4.688	4.622	0.2090
0.7277	3.781	5.930	5.887	0.2093
0.7259	5.141	7.968	7.973	0.2098
0.7242	6.532	9.868	9.963	0.2103
0.7218	8.465	11.745	11.804	0.2110
0.7198	10.155	12.707	12.776	0.2116
0.7180	11.583	13.441	13.470	0.2121

Dimethyl Sulfoxide–Model I

10^2[Ni(DPM)$_2$], *M*	10^2[C_2H_6SO], *M*	$-E$, cal		Vol., l.
		Obsd	Calcd	
1.398	0.5908	2.429	2.223	0.2087
1.395	1.248	4.221	4.162	0.2092
1.392	1.959	5.633	5.744	0.2097
1.388	2.675	6.769	6.932	0.2102
1.385	3.419	7.249	7.859	0.2107
1.382	4.058	8.423	8.479	0.2111
1.379	4.702	9.060	8.978	0.2115
1.376	5.268	9.536	9.343	0.2119
1.372	6.169	10.305	9.815	0.2121

Table IV. Stepwise Results of Ni(DPM)$_2$ with Various Bases in Benzene

Base	K_1, l./mol	K_2, l./mol	$-\Delta H_1$, kcal	$-\Delta H_2$, kcal
$NH(C_2H_5)_2$	Large	37.1	7.53	11.66
$N(C_2H_5)_3$	82.9		7.49	2.47
C_5H_5NO	286	5.0	5.68	9.3
$(CH_3)_2SO$	57.6		4.50	0.61
C_5H_5N	898	20,000	6.1	13.0

Table V. Calculated and Experimental Enthalpies for Ni(DPM)$_2$ in Selected Bases

Base	E_B	C_B	ΔH_1(obsd), kcal/mol	ΔH_1(calcd),[a] kcal/mol
$N(C_2H_5)_2H$	0.924	8.78	7.53 ± 0.15	7.49
DMSO	1.36	2.86	4.50 ± 0.17	4.59
C_5H_5NO	1.35	4.52	5.68 ± 0.2	5.63
$N(C_2H_5)_3$[b]	1.03	10.9	7.49 ± 0.36	9.07

[a] ΔH_1(calcd) is obtained using $E_A = 2.03$, $C_A = 0.640$. [b] Not used in calculating E_A, C_A parameters.

donors, the trigonal-bipyramidal configuration has *significantly* less steric strain than the square-pyramidal configuration. For the $NHEt_2$, DMSO, and pyO adducts, in the TBP arrangement there is no strain indicated by models except in certain rotational configurations.

For the pyridine mono adducts, there is no strain indicated in any rotational configurations in either SP or TBP.

For the bis adducts, models strongly suggest that there exist rotational configurations in either a cis or a trans donor configuration for which there is no steric strain in the py and substituted py, $NHEt_2$, and pyO moieties. Severe crowding is indicated in the DMSO and NEt_3 moieties.

These ideas obtained from molecular models are consistent in all points with our results (and our present lack of results for the 1:1 py systems) as outlined below.

(1) The internal consistency of the thermochemical data implies that for pyO, $NHEt_2$, and DMSO in the 1:1 adduct there exist configurations for which there is no bond strain, at least as reflected in ΔH_1.

(2) The existence of a consistent set of E_A and C_A parameters for the aliphatic N and O donors implies similar electronic and structural environments for all the adducts. Thus a TBP or pseudo-TBP arrangement which can minimize and/or eliminate, within experimental error, any steric crowding seems more probable.

(3) The lack of a spectrally or thermochemically well-defined 1:1 step in the py complexes, as well as the characterization of such a step for the others, is most consistently interpreted as due to the formation of a SP 1:1 adduct in the py system requiring little reorganization of the Lewis acid site (Ni(II)) followed by the ready formation of a trans bis adduct again requiring little structural rearrangement.

The above is to be contrasted to the $NHEt_2$ and pyO cases. If they are considered to form TBP mono adducts, then the bis adducts, formed only reluctantly compared to the py adducts, can be attained only after considerable further structural rearrangement of the 1:1 adduct. This is true whether the final bis adduct is cis or trans in arrangement. If these mono adducts are viewed as SP, then one must consider that the tendency to form bis adducts is diminished either because only the cis adducts are stable in these systems or because there is limited rotational freedom in all of the bis adducts.

At present, we can only suggest that most probably the TBP configuration more closely approximates the stereochemistry of the mono adducts for all but the py donors.

It can be argued that the differences between TBP and SP are slight, of the order of only a few kilocalories, and that they are readily interconvertible.[23] However, the difference is not so slight as to render the problem trivial, since they do demand somewhat different crystal field approaches spectrally and conceivably they could lead to different sets of E_A and C_A parameters for Ni(DPM)$_2$.

Frontal Strain. It is interesting to compare the frontal strain of the triethylamine adducts of Ni(DPM)$_2$ and Cu(hfac)$_2$. The difference between the observed and calculated enthalpies for the formation of Ni(DPM)$_2$·NEt_3 adduct is 1.6 kcal, this most probably being due to "frontal strain" or "steric strain"[2] between the two bulky moieties involved in

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(23) See ref 22, pp 25 and 26, and J. A. Huheey, "Inorganic Chemistry: Principles of Structure and Reactivity," Harper and Row, New York, N. Y., 1972, pp 376-385, and references therein for an extensive discussion of five-coordination and the ease of interconversion in sterically unrestricted molecules.

the adduct. This is to be compared with 3 kcal found for the $Cu(hfac)_2 \cdot NEt_3$ adduct,[1] despite the fact that the $Ni(DPM)_2$ is more bulky. It was noted[1] that the $Cu(hfac)_2$ adducts are probably SP, whereas we have indicated that a TBP arrangement probably more closely approximates the equilibrium conformation of $Ni(DPM)_2$ mono adducts. Hence, while $Ni(DPM)_2$ in a square-planar configuration may be more bulky than $Cu(hfac)_2$, $Ni(DPM)_2$ in the complex apparently becomes less bulky than $Cu(hfac)_2$ by twisting into a TBP geometry, effectively removing one of the four $-C(CH_3)_3$ groups and opening up the first coordination site. The tendency for bis(chelate)copper complexes to remain SP even in the presence of bulky ligands[24] has been attributed to a loss of crystal field stabilization energy which would be greater than the gain in configurational stability obtained by assuming a TBP geometry.

Magnetic Moments. The magnetic moment of the diethylamine mono adduct is $\mu = 3.25$ BM. This represents the first Lewis acid system correlated with eq 1 to date which is known to undergo a change in spin state upon coordination. This value for μ is consistent with what has been previously reported[25] for high-spin five-coordinate Ni(II), in which Ni(II) was found to be in a TBP coordination. It is interesting to compare qualitatively the enthalpies of adduct formation with the structurally similar bis(hexafluoroacetylacetonato)copper(II), $Cu(hfac)_2$, in view of the magnetic differences in the two acids. The rather large differences in observed enthalpies (on the order of 10 kcal/mol) are probably due in part to the electron-releasing effects of four *tert*-butyl groups in $Ni(DPM)_2$ compared to the strongly electron-withdrawing effects of four trifluoromethyl substituents analogously situated in $Cu(hfac)_2$.

It seems likely that the change in spin state and any accompanying changes in Ni-O bond lengths[26] and/or rehybridization of Ni orbitals that together comprise the reorganization process for this acid also contribute to this difference. This should be particularly true if the geometry change of the $Ni(DPM)_2$ moiety is from square planar to part of a TBP arrangement.

Consider the following hypothetical two-step process for the formation of the 1:1 adducts

$$Ni(DPM)_2\ (S = 1) \rightarrow Ni(DPM)_2{}^*\ (S = 3);\quad \Delta H_R$$

$$Ni(DPM)_2{}^*\ (S = 3) + B \rightarrow Ni(DPM)_2B\ (S = 3);\quad \Delta H_{AD}$$

Where S is the spin multiplicity and ΔH_{AD} is the hypothetical enthalpy of the donor-acceptor interaction that "would have been" observed in the absence of the reorganization process for the acid. One would expect ΔH_{DA} to be large and exothermic and the reorganization energy, ΔH_R, to be endothermic and perhaps quite appreciable. Their sum is of course the measured reaction heat, ΔH_1. Apparently the ΔH_R term, including a change in spin state, is incorporated into the E_A and C_A parameters of $Ni(DPM)_2$, just as the reorganization enthalpy of boron trifluoride appears in the E_A and C_A parameters for that acid.[3]

Table VI. Relative Softness of Various Lewis Acids

Acid	C_A	E_A	C_A/E_A
I_2	1.0	1.0	1.0
IBr	1.9	2.2	0.86
$Cu(hfac)_2$	1.5	3.1	0.49
$Ni(DPM)_2$	0.64	2.0	0.32
$B(CH_3)_3$	1.8	5.8	0.31
$HCCl_3$	0.1	5.1	0.02

The parameters E and C refer to electrostatic (dipole-dipole) and covalent bond forming abilities of the acid or base in an adduct. By symmetry $Ni(DPM)_2$ has no dipole moment, yet the E_A value of 2.03 implies a significant dipole contribution to the bonding in any adduct. This in turn implies that the "acid" form of $Ni(DPM)_2$ is an excited state which possesses a significant dipole moment and which, as this study has shown, is paramagnetic. The observation of a significant electrostatic or dipolar contribution to the observed enthalpies is consistent with the formation of TBP 1:1 adducts.

It has been suggested[1] that, in comparing hardness or softness for a series of Lewis acids, the quantity C_AC_B/E_AE_B indicates the relative covalent character of the acid-pyridine bonds and also the relative softness of the acids. This can be factored into $(C_A/E_A)(C_B/E_B)$, and since the second term is fixed for a given reference base, we really need only look at the first term for relative softness of a series of acids. Inspection of Table VI indicates that $Ni(DPM)_2$ is similar in softness to trimethylboron when acting as an acid and is significantly a harder or more electrostatic acid than is $Cu(hfac)_2$.

We are currently in the process of trying to evaluate reliable stepwise parameters for the series of substituted pyridines donors, for which ΔH_T's have already been reported. We will report on these results and their significance in the application of the Drago-Wayland equation generally.

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Registry No. $Ni(DPM)_2$, 14481-08-4; diethylamine, 109-89-7; triethylamine, 121-44-8; pyridine *N*-oxide, 694-59-7; dimethyl sulfoxide, 67-68-5; 4-(*N,N*-dimethylamino)pyridine, 1122-58-3; 4-methylpyridine, 108-89-4; 3,5-dimethylpyridine, 591-22-0; pyridine, 110-86-1; 4-acetylpyridine, 1122-54-9; 4-(methoxycarbonyl)pyridine, 2459-09-8; $Ni(DPM)_2(diethylamine)_2$, 21534-31-6; $Ni(DPM)_2$(triethylamine), 42087-44-5; $Ni(DPM)_2$(pyridine N-oxide$)_2$, 21534-28-1; $Ni(DPM)_2$(dimethyl sulfoxide), 42087-46-7; $Ni(DPM)_2(pyridine)_2$, 42087-47-8.

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(24) S. Ooi and Q. Fernando, *Chem. Commun.*, 532 (1967).

(25) I. Bertini, M. Ciampolini, P. Dapporto, and D. Gatteschi, *Inorg. Chem.*, 11, 2253 (1972).

(26) See ref 6 and R. C. Elder, *Inorg. Chem.*, 1, 2316 (1968). These X-ray structural studies indicate that the Ni-O bond length of six-coordinate paramagnetic $Ni(acac)_2(py)_2$ is 0.2 Å longer than that of four-coordinate diamagnetic $Ni(DPM)_2$.