of all protons with increasing temperature. Furthermore, it does not account for the failure to observe one of the expected five peaks for cyclohexane ring protons.

A second explanation may be more satisfactory, but it is not without flaws. Perhaps the close proximity of these protons to the metal ion provides a mechanism for spin relaxation and resultant line broadening which prevents their observation under the conditions employed. This could account for the observation of only four of the five expected peaks for cyclohexane ring protons, since H_1 (Figure 2) would occupy a similar position. It could also account for the excessive broadening of the reatively nearer H_a^e peak of $Ni(CyDTA)^{2-}$. The picture is further complicated by the fact that the axial en protons of $Ni(EDTA)^{2-}$ do give rise to a clear peak (at −10 ppm). It could be argued that the en ring is less rigid in $Ni(EDTA)^{2-}$ than in $Ni(CyDTA)^{2-}$, so that the axial en proton is not as near the nickel ion on the average in the former as in the latter. A greater contribution of pentadentate species for $Ni(EDTA)^{2-}$ could be invoked to permit this additional flexibility.

Conclusion and Prognosis.—We set out to employ nmr techniques to answer some questions concerning the structures and kinetic properties of nickel(II) chelates of EDTA, PDTA, and CyDTA. The nmr techniques have proven to be tremendously effective in providing some of the answers. No doubt the experiments described will provide a sound basis for obtaining other useful kinetic and structural information about these and related complexes. However, neither an unequivocal answer to the question of the coordination number of the ligand in solution nor a satisfactory rationale for the absence of certain resonances has been provided.

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CONTRIBUTION FROM THE WILLIAM A. NOYES LABORATORY,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS 61801

Spectrochemical Studies on Some Tetragonal NiL_2X_2 Complexes

BY ROBERT L. CHIANG[1] AND RUSSELL S. DRAGO*

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The electronic spectra of tetragonal nickel(II) complexes of the general formula NiL_2X_2 (L refers to NH_3, H_2O, C_5H_5N, or $C_6H_5NH_2$ and X is chloride or bromide) have been studied where L is the axial ligand. The spectra contain enough bands to permit us to calculate crystal field parameters (including all of the diagonal elements in their evaluation) and to have data left over to check our fit. Errors exist in previous reports of the parameters and in the assignments of transitions in some of these nickel(II) complexes. The crystal field parameters for the same ligand in different complexes (*e.g.*, NiL_4X_2 and NiL_2X_2) are compared and the spectrochemical parameters are compared with single-crystal X-ray results. The values for the McClure parameters $\delta\pi$ and $\delta\sigma$ are discussed.

Introduction

Continuing interest in the assignment of the electronic spectra and the evaluation of ligand field parameters, such as *Dq*, *Ds*, and *Dt*, has prompted a detailed crystal field calculation of some low-symmetry complexes.[2] In order to obtain a reliable set of parameters, the number of spectral bands should be greater than the number of parameters. The electronic spectra of tetragonally distorted nickel(II) complexes often satisfy this requirement. Consequently, it is possible to evaluate the parameters of such complexes with the inclusion of all off-diagonal matrix elements from the strong-field point of view.[3] The system reported here consists of complexes of the form NiL_2X_2, where L_2 represents two ammonia, aniline, water, or pyridine ligands and X_2 represents two chlorines or two bromides. In each of the complexes reported here, the metal ion is surrounded by four bridging halide ions forming a polymeric chain and by two other ligands giving six-coordination[4] about the nickel(II). The site symmetry is assumed to be D_{4h} and the electronic spectra fit this model. The spectra of some of these complexes were previously[2a,4c,5] observed, but a complete analysis was not attempted.

In this study, the *Dq* values for the various ligands were calculated along with the McClure $\delta\pi$ and $\delta\sigma$[6] parameters. The spectral bands have been assigned on the basis of the signs and relative magnitudes of $\delta\sigma$ and

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[1] Abstracted in part from the Ph.D. thesis of R. L. Chiang, University of Illinois, Urbana, Ill., 1971.

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[5] D. M. L. Goodgame, E. Goodgame, and W. J. Weeks, *J. Chem. Soc.*, 5194 (1964).

[6] D. S. McClure, "Advances in the Chemistry of Coordination Compounds," S. Kirschner, Ed., Macmillan, New York, N. Y., 1961, p 498.

$\delta\pi$.[7] Band assignments different from those reported[2,4c,5] have been made for the spectrum of Ni(C_5H_5N)$_2X_2$. The *Dq* values calculated from the assignments of these authors for pyridine and halide are not reasonable when compared with similar complexes. A new assignment is attempted and all the ligand field parameters are calculated. The results are much more reasonable and illustrate the utility of this complete analysis in making band assignments.

Experimental Section

The following compounds were prepared as described in the literature: $Ni(C_5H_5N)_2Cl_2$,[2] $Ni(C_5H_5N)_2Br_2$,[2] $Ni(C_6H_5NH_2)_2Cl_2$,[8] and $Ni(C_6H_5NH_2)_2Br_2$.[8] In all instances elemental analyses confirm that we had prepared the compound sought.

$Ni(NH_3)_2X_2$ complexes, where $X^- = Cl^-$ or Br^-, were prepared in the following manner. About 2 g of $Ni(NH_3)_6X_2$ was heated at 110° under vacuum. The color change of the salts is from purple to yellow and, after the change is complete, the yellow powder is collected. *Anal.* Calcd for $Ni(NH_3)_2Cl_2$: Ni, 35.87; N, 17.11; H, 3.69. Found: Ni, 35.76; N, 17.06; H, 3.69. Calcd for $Ni(NH_3)_2Br_2$: Ni, 23.24; N, 11.09; H, 2.39. Found: Ni, 23.14; N, 11.02; H, 2.41.

$Ni(H_2O)_2Cl_2$ is prepared by refluxing $Ni(H_2O)_6Cl_2$ powder in isopropyl alcohol. The color change is from green to yellow, and, after the reaction is complete, the yellow powder is collected and dried *in vacuo*. *Anal.* Calcd for $Ni(H_2O)_2Cl_2$: Ni, 35.44; Cl, 42.80; H, 2.43. Found: Ni, 35.52; Cl, 42.74; H, 2.37.

Spectrophotometric Measurements.—Mull spectra were recorded on a Cary Model 14RI spectrophotometer. The sample preparation was described previously.[2a]

Calculations.—The calculations employed to fit the spectra have been described.[2a]

Results and Assignments

The spectral data obtained at liquid nitrogen temperature are shown in Table I. The relationship between the free-ion octahedral and tetragonal field splitting of the d orbitals is illustrated in Figure 1. The results of the ligand field calculations are shown in Tables II and III. The band assignments become very difficult when the bands overlap with each other or with ir overtones forming shoulders. In the cases of low-symmetry complexes with medium ligand field strengths, spin-forbidden transitions sometimes are intense,[9] further increasing the difficulty of the assignment.

TABLE I

ELECTRONIC SPECTRAL DATA AT 77°K (CM^{-1})

Compd	$^3B_{1g} \rightarrow$ $^3B_{2g}$	$\rightarrow {}^3E_g$	$\rightarrow {}^3E_g$	$\rightarrow {}^3A_{2g}$	$\rightarrow {}^3E_g$	$\rightarrow {}^3A_{2g}$
$Ni(NH_3)_2Cl_2$	7800	8030	13,300^a	14,600	23,530	25,680
$Ni(C_5H_5N)_2Cl_2$	...	8580	13,400^a	14,360	23,850	24,650
$Ni(C_6H_5NH_2)_2Cl_2$	8170	8550	...	14,000	...	23,700
$Ni(H_2O)_2Cl_2$	7300^b	7700^b	12,600	13,200	...	23,200
$Ni(NH_3)_2Br_2$	7680	...	13,000^a	14,140	22,920	24,600
$Ni(C_5H_5N)_2Br_2$	...	8200	12,900^a	14,150	22,900	23,900
$Ni(C_6H_5NH_2)_2Br_2$	7660	8180	...	13,250	22,300	...

^{a} Shoulder. ^{b} Approximate value.

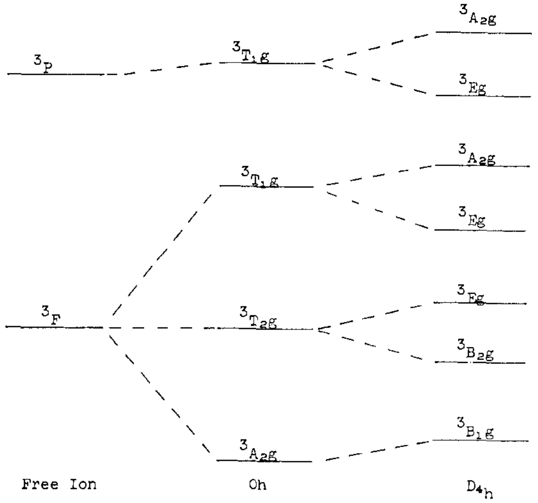

Figure 1.—Correlation diagram for the triplet states of a d^8 configuration with a strong axial ligand.

TABLE II

CALCULATED AND OBSERVED SPECTRA (CM^{-1}) FOR SELECTED COMPLEXES AT 77°K

—$Ni(NH_3)_2Br_2$—		—$Ni(An)_2Br_2$—		—$Ni(H_2O)_2Cl_2$—		
ν_{obsd}	ν_{calcd}	ν_{obsd}	ν_{calcd}	ν_{obsd}	ν_{calcd}	
7,680	7,728	7,660	7,692	7,300^b	7,367	$^3B_{1g} \rightarrow {}^3B_{2g}$
...	7,869	8,180	8,210	7,700^b	7,773	$\rightarrow {}^3E_g$
13,000^a	13,108	...	13,042	12,600	12,589	$\rightarrow {}^3E_g$
14,140	14,123	13,520	13,559	13,200	13,154	$\rightarrow {}^3A_{2g}$
22,920	22,894	22,300	22,346	...	22,513	$\rightarrow {}^3E_g$
24,600	24,570	...	22,723	23,200	23,202	$\rightarrow {}^3A_{2g}$

—$Ni(py)_2Cl_2$—		—$Ni(py)_2Br_2$—	
ν_{obsd}	ν_{calcd}	ν_{obsd}	ν_{calcd}
...	7,907	...	7,699
2,580	8,554	8,200	8,247
13,400^a	13,654	12,900^a	13,196
14,360	14,409	14,150	14,124
23,850	23,929	22,900	22,955
24,650	24,691	23,900	23,923

^{a} Shoulder. ^{b} Approximate value.

TABLE III

RESULTS OF CALCULATED PARAMETERS (CM^{-1})

Complex	*B*	Dq^{xy}	*Ds*	*Dt*	Dq^z	$\delta\pi$	$\delta\sigma$
$Ni(NH_3)_2Cl_2$	791	805	−1258	−84	952	1677	2044
$Ni(C_5H_5N)_2Cl_2$	848	790	−438	−89	946	435	823
$Ni(C_6H_5NH_2)_2Cl_2$	804	813	−85	−57	913	−15	234
$Ni(H_2O)_2Cl_2$	824	767	−377	−56	865	426	670
$Ni(NH_3)_2Br_2$	787	773	−993	−85	922	1277	1649
$Ni(C_5H_5N)_2Br_2$	796	770	−600	−90	928	675	1069
$Ni(C_6H_5NH_2)_2Br_2$	764	769	−232	−64	881	188	468

$Ni(NH_3)_2Br_2$ can be considered as a representative example. The spectra shown in Figure 2 indicate that three transitions can be assigned confidently, *i.e.*, $^3A_{2g}(^3T_1, P)$, $^3E_g(^3T_1, P)$, and $^3A_{2g}(^3T_1, F)$. Clearly, the high-energy band arises from the P state and the assignment of $^3A_{2g}(P)$ and $^3E_g(P)$ is predictable in view of the greater field strength of NH_3 compared to that of bromide. Our final wave functions are consistent with this. The next high-energy band must arise from the F state. Assignment of this band to $^3E_g(P)$ would require an unreasonably large distortion. There is a low-energy band at 12,900 Å with shoulders. Since only four parameters—*Dq*, *Ds*, *Dt*, and *B*—are required to describe all of the triplet states, we can assign this maximum at around 12,900 Å as the transition to $^3B_{2g}(^3T_2, F)$ and calculate the positions of the other two transitions. When this is done, the calculated values all agree with the experimental observations within the

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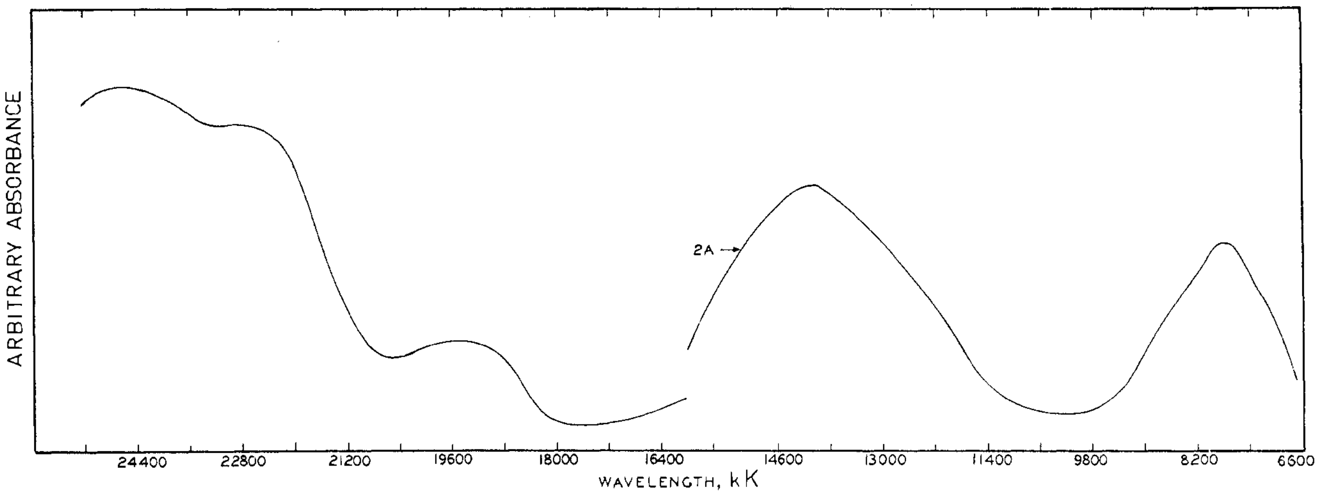

Figure 2.—Mull spectrum of $Ni(NH_3)_2Br_2$ at liquid nitrogen temperature.

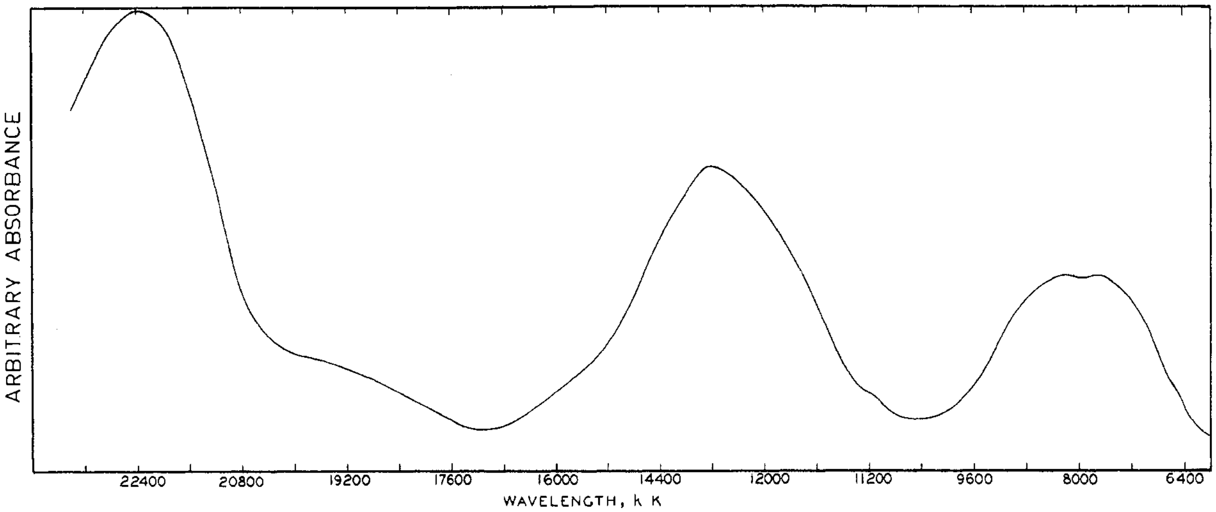

Figure 3.—Mull spectrum of $Ni(C_6H_5NH_2)_2Br_2$ at liquid nitrogen temperature.

experimental error as shown in Table II. The transition to $^3E_g(^3T_2, F)$ is located very close to the $^3B_{2g}(^3T_2, F)$ transition so only a broad asymmetric band is observed. The spin-allowed band $^3E_g(^3T_1, F)$ is predicted to occur at about 13.1 kK and there is a shoulder on the second energy band around 13 kK. If the maximum in the low-energy band is assigned to ^3E_g instead of $^3B_{2g}$, the predicted transition to $^3B_{2g}$ at 5000 cm^{-1} is not observed and ridiculous parameters are obtained. The agreement between experimental results and the calculated band positions for our initial assignments provides strong support for these assignments.

The assignment of the spectra of $Ni(C_6H_5NH_2)_2Br_2$ proceeds along similar lines. However, only four transitions can be observed. By analogy to the previous spectrum, these are assigned to $^3B_{2g}(^3T_2, F)$, $^3E_g(^3T_2, F)$, $^3A_{2g}(^3T_1, F)$, and $^3E_g(^3T_1, P)$. The agreement between our calculated and experimental values is presented in Table II. Referring to Figure 3, we note that the transitions to $^3E_g(^3T_1, F)$ and $^3A_{2g}(^3T_1, F)$ are unresolved as are those to $^3A_{2g}(^3T_1, P)$ and $^3E_g(^3T_1, {}^3P)$ in accord with our calculated values. The assignments and calculations for complexes of $Ni(NH_3)_2Cl_2$ and $Ni(C_6H_5NH_2)_2Cl_2$ proceed in the same manner as described above.

Assigning the spectra of $Ni(H_2O)_2Cl_2$ was more difficult, since we had a very broad asymmetric band at 13,000 Å which should contain at least two spin-allowed transitions. Only three transitions could be assigned with confidence: $^3A_{2g}(^3T, F)$, $^3E_g(^3T_1, F)$, and $^3E_g(^3T_1, P)$. The assignment of the $^3B_{2g}$ transition was varied from the maximum of the asymmetric lowest energy band to values of ±200 wave numbers removed so that the calculated $^3E_g(^3T_2, F)$ transition would be at such a frequency as to cause the observed asymmetry in this low-energy band. The results obtained are reported in Table II where it is seen that the $^3B_{2g}(^3T_2, F)$ and $^3E_g(^3T_2, F)$ transitions are located together. The combination of these d–d transitions and the ir overtones gives rise to the broad band in this region.

The interpretation of the spectra of $Ni(C_5H_5N)_2X_2$ where X is chloride or bromide is most troublesome. The room-temperature reflectance spectra have been reported,[4c,5] but two different assignments have been made. The mull spectra at liquid nitrogen temperature have been reported in our previous paper and the crystal field parameters were calculated. Comparison of the spectrum of $Ni(C_5H_5N)_2Cl_2$ with that of $Ni(NH_3)_2Cl_2$ forces us to conclude that the transition at

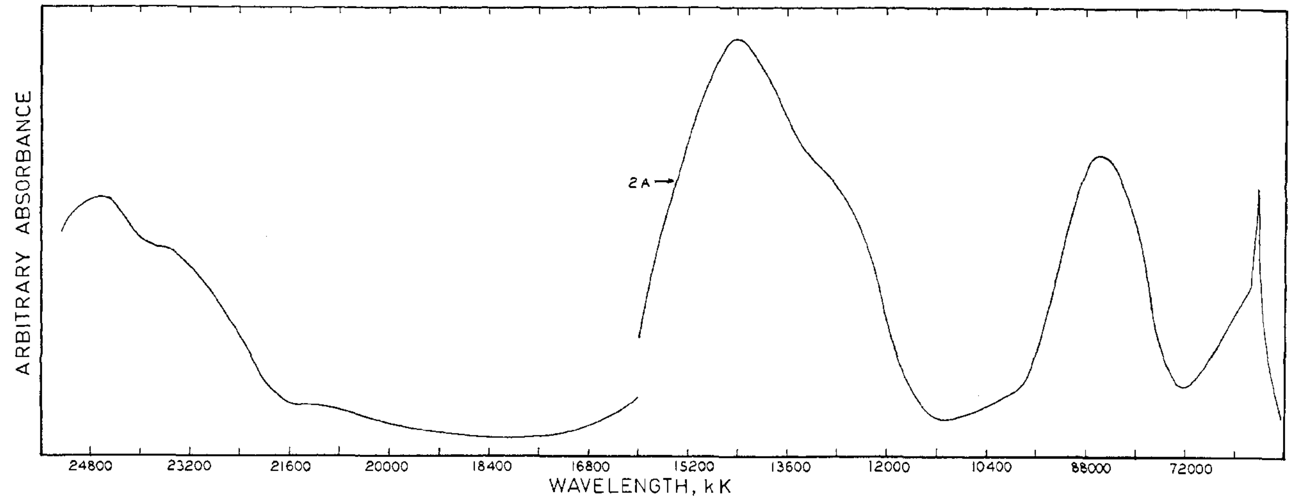

Figure 4.—Mull spectrum of $Ni(C_5H_5N)_2Cl_2$ at liquid nitrogen temperature.

TABLE IV

COMPARISON OF THE ASSIGNMENT OF THE SPECTRA OF $Ni(py)_2Cl_2$ AND CALCULATED RESULTS (CM^{-1})

Assignment of Spectra

	$^3B_{1g} \rightarrow {}^3B_{2g}$	$\rightarrow {}^3E_g$	$\rightarrow {}^3E_g$	$\rightarrow {}^1T_2(D)$	$\rightarrow {}^3A_{2g}$	$\rightarrow {}^3A_{2g}$	$\rightarrow {}^1E_g(D)$	$\rightarrow {}^3A_{2g}$
I[b]	..	8580	13,400[a]		14,360	23,850		24,650
II[c]	6270	8620	13,300		14,490	23,400		24,700
III[d]				12,500	13,990		22,000	24,100
IV[e]	6000	8400	12,200		13,900	22,200		24,100

Calculated Parameters

	B	Dq^{xy}	Ds	Dt	Dq^z	$\delta\pi$	$\delta\sigma$
I[b]	848	790	−438	−89	946	435	823
II[c]	841	629	−598	−330	1210	72	1520
III[d]	810	700			1100		
IV[e]	980	760					

[a] Shoulder. [b] This work. [c] Ref 2a. [d] Ref 4c. [e] Ref 5.

6000 kK in $Ni(C_5H_5N)_2Cl_2$ cannot be assigned as a d–d spin-allowed transition because ammonia and pyridine have almost the same ligand field strength. If pyridine-d_5 is substituted for pyridine in the complex, the transition is still observed at the same frequency. As shown by Figures 4 and 5, the C–H stretching vibration overtones disappear. The mull spectrum of $Cd(C_5H_5N)_2Cl_2$ at liquid nitrogen temperature has been studied. It is found that there is no transition around 6000 kK except for the C–H vibration overtones. The assignment of this band as a low-lying spin-forbidden transition was attempted, but the value of C/B calculated from this assignment is 3.0, much smaller than the value of 4.71 generally found for nickel(II) complexes. In order to fit the spectra and at the same time obtain spectrochemical parameters which are reasonable when compared with other complexes with similar configurations, we conclude that the $^3B_{2g}(^3T_2, F)$ transition is hidden under the $^3E_g(^3T_2, F)$ band. As can be seen in Tables II and III, the agreement between calculated and observed frequencies with the new assignment is even better than that reported previously.[2a]

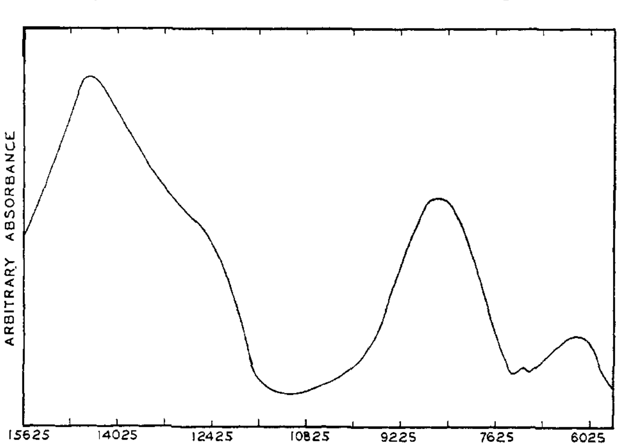

Figure 5.—Mull spectrum of $Ni(C_5D_5N)_2Cl_2$ at liquid nitrogen temperature.

Discussion

The electronic spectrum of the complexes $Ni(C_5H_5N)_2Cl_2$ and $Ni(C_5H_5N)_2Br_2$ have been previously studied[4c,5] by the reflectance technique. The reported interpretations differ because the spin-forbidden transitions are assigned differently leading to two different sets of ligand field parameters. The shoulders on the main bands were assigned as spin-allowed transitions by Goodgame, Goodgame, and Weeks[5] and Drago and Rowley.[2a] The parameters were calculated with the consideration of all off-diagonal elements[2a] with a modest fit of the experimental data. On the other hand, Nelson and Shepherd[5] suggested that the shoulders on the higher energy bands were spin-forbidden transitions, as did Hathaway and Holah.[10] When all off-diagonal elements are included in the analysis of these data, a set of parameters which reproduce the experimental data cannot be obtained. Our assignments, I, and those of Rowley and Drago, II, Lever, Nelson, and Shepherd, III, and Goodgame, Goodgame, and Weeks, IV, are summarized in Table IV, and spectrochemical parameters evaluated at different levels of approximations for these assignments are also summarized. In order to resolve the problem of the assignment of the transitions in $Ni(C_5H_5N)_2X_2$, the calculated ligand field parameters for both assignments for this complex are compared with the parameters from $Ni(C_5H_5N)_4X_2$ and with those from $Ni(NH_3)_2X_2$. The parameters from both the old and new assignment are shown in Table IV. Using the previously reported assignment, the calculated ligand field strength of pyridine, Dq^z, is much larger than that for ammonia in the complex $Ni(NH_3)_2X_2$. Generally, in related complexes, the ligand field strengths of pyridine and ammonia are similar. Even though the potential existence of steric effects complicates the interpretation of $10Dq$ for pyridine, the 300-cm^{-1} difference between $Dq^z(C_5H_5N)$ and $Dq^z(NH_3)$ required by the earlier assignment[2a] is not likely. The complete X-ray analysis of $Ni(C_5H_5N)_2X_2$ has not been done yet, but the structure of $Co(C_5H_5N)_2Cl_2$ has been published,[11] and $Ni(C_5H_5N)_2Cl_2$ and $Co(C_5H_5N)_2Cl_2$ are found to be isomorphorous.[5a] The cobalt–nitrogen distance in $Co(C_5H_5N)_2Cl_2$ is 2.14 Å. The structures of $Ni(C_5H_5N)_4Cl_2$ and $Co(C_5H_5N)_4Cl_2$ have been published by Porai-Koshits and Autsishkina.[12] The nitrogen–nickel bond length is 2.00 Å and the cobalt–nitrogen bond length is 1.99 Å. Assuming that the nickel–nitrogen bond length in $Ni(C_5H_5N)_2Cl_2$ is at least 2.1 Å, the calculated Dq^z for pyridine in $Ni(C_5H_5N)_2Cl_2$ should be smaller than that in $Ni(C_5H_5N)_4Cl_2$. The assignments reported earlier[2a] lead to the opposite results. The new assignments (in Table IV) lead to spectrochemical parameters which are consistent with the X-ray results. The transition at 6000 cm^{-1} in $Ni(C_5H_5N)_2X_2$ is still a problem but could result from interactions between the chains or from the presence of some impurities such as $NiCl_3^-$ fragments in the chain.

The calculated Dq^{xy} for the halides is higher than the Dq^z values of terminal halides in complexes such as $Ni(C_5H_5N)_4X_2$. The cause of this discrepancy can be seen in the magnitude of the $\delta\pi$ values. As shown in Table III, the calculated $\delta\pi$ is 435 cm^{-1} for $Ni(C_5H_5N)_2Cl_2$, while that in $Ni(C_5H_5N)_4Cl_2$ is -10 cm^{-1}. By definition, $\delta\pi$ is $*\pi_z - *\pi_{xy}$,[6] so in $Ni(C_5H_5N)_2Cl_2$, $\delta\pi$ is $*\pi_{py} - *\pi_{Cl}$, while in $Ni(C_5H_5N)_4Cl_2$, it is $*\pi_{Cl} - *\pi_{py}$. Assuming $*\pi_{py}$ is similar in both complexes, the decrease in $\delta\pi$ of 400 wave numbers can be attributed mainly to the difference in $*\pi$ for a terminal and bridging chloride. This is reasonable for there is less lone-pair electron density on a bridging chloride to participate in the antibonding interaction and consequently $10Dq$ would be greater for a bridging compared to terminal halide.

The calculated Dq^{xy} values for chloride or bromide remain practically constant as the axial ligand is changed in this series of complexes except for $Ni(H_2O)_2Cl_2$, where a smaller Dq^{xy} is obtained for chloride. This exception is due to a significant change in the polymeric structure from hydrogen-bonding interactions. The detailed argument will be presented shortly using Dq^{xy}, Dq^z, $\delta\pi$, and $\delta\sigma$ parameters.

The order calculated for Dq^z is $NH_3 >$ pyridine $>$ aniline $> H_2O$ for the chloride series and pyridine $> NH_3 >$ aniline for the bromide series. As might be expected from the inductive effect of the four bridging chlorides, all Dq^z values are smaller than the values for the same ligand in octahedral complexes except for Dq^z of water in $Ni(H_2O)_2Cl_2$. In all the nitrogen ligand complexes, the nickel–nitrogen bond length in the NiL_2X_2 complexes are longer than those in the octahedral complexes.

Morosin[4b] indicated that the structure of $Ni(H_2O)_2Cl_2$ is different from that of $Co(H_2O)_2Cl_2$ or $Ni(amine)_2Cl_2$; in the former, the plane consisting of nickel and the four halides is bent relative to the similar plane in an adjacent nickel atom so as to form an angle of 167.94° between two planes. The hydrogen bonds appear to be bi- and trifurcated, a given proton interacting with the bridging chloride and the neighboring water molecule. The effect of this hydrogen bonding is to make the halides poorer donors and the water molecules stronger donors (Table III). The hydrogen bonding to chloride weakens the nickel–chlorine bond increasing both $\delta\sigma$ and $\delta\pi$ ($\delta_{H_2O} - \delta_{Cl^-}$ or $\pi_{H_2O} - \pi_{Cl^-}$).

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