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Ligand Field Theory of Ni(II) Complexes. II. Electronic Spectra and Structure of Some **Paramagnetic Chelates**

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An assignment of the observed absorption spectra is made for each of six paramagnetic Ni(II) chelates studied, based on the energy levels calculated for the Ni(II) ion from an electrostatic model of the complex. The best assignments, in each case, give reasonably good qualitative and quantitative agreement, explaining the number and relative intensities of the triplet-triplet and triplet-singlet transitions and giving maximum error of 30% when compared with the observed positions of maximum intensity. The consistency and relative significance of the values of the effective dipole moments used for the different coordinating oxygen and nitrogen atoms is demonstrated in several specific assignments. For the chelates of unknown structure and coordination, a comparison of various possible assignments enables structural predictions, while the chelates of known structures are given reasonable assignments with their appropriate configurations. The sensitivity of the assignments to the assumed structures allowed the general conclusion to be drawn that significantly better results are obtained if unequal effective dipole moments of different ligands are used, rather than one average value. For example, all six coordinated chelates with mixed ligands were given better assignments in tetragonal or trans-planar symmetry than octahedral symmetry. It is felt that this study demonstrates the scope of the electrostatic model of the complex ion and justifies its use to explain and predict properties of the complex molecule associated with the central ion.

I. INTRODUCTION

TN THIS paper the electronic absorption spectra of six paramagnetic Ni(II) chelates are reported. Using the electrostatic model of the complex molecule the energy levels of the central metal ion in the field of the surrounding atoms or ions can be calculated. Such a calculation was reported for Ni(II) complexes in the first paper of this series.¹ It is the purpose here to test the ligand field theory by using the central ion energy intervals calculated from it to assign appropriate observed transitions. Assignment and discussion of spectra then will be limited to those absorptions which are attributed to localized transitions between electronic states of the central metal ion perturbed and split by the effect of the attached groups in the molecule. These are low-intensity absorptions with maximum extinction coefficients of 1-300 observed in the 2000-400 m μ wavelength region. They may thus be distinguished empirically from allowed transitions involving the ligand molecules, which have maximum extinction coefficients 103 to 105 times as great and occur at wavelengths less than 400 m μ for the systems chosen. Schematic molecular structure diagrams of the particular chelates studied are given in Table I.

The energy levels calculated are functions of two field strength parameters, the effective dipole moment, and the bond distance. Since these cannot be determined independently, those values were chosen for a particular compound which gave the best over-all fit to the spectrum. However, in the set of chelates chosen, the effect of different ligand atoms on the central ion should be related. The success of the theory then, depends not only on how well a given complex spectrum is assigned, but also on whether these assignments are obtained for relatively consistent values of the parameters. Since these complexes are all paramagnetic, the assignments must also be such that a triplet state of the ion is the ground state.

In order to assign the spectrum of a given chelate, it is necessary to know the arrangement and number of attached groups about the central ion, since the relative perturbation of the free ion energy levels depends on the symmetry of the potential as well as the total field strength. While the chemical constitutions of all the compounds chosen are well known, the crystal and molecular structures of some of them are not. The spectra of compounds with unknown structures and coordination numbers were fitted to several possible symmetries. The configurations which gave the best assignments were assumed to be most probable. Information about structure and coordination of complexes can be deduced in this manner from the spectra.

The question as to whether the pure electrostatic theory is sensitive enough to detect small differences in the effective dipole moments of similar ligand atoms was also investigated. For several compounds with sets of inequivalent bonding atoms, assignments were compared for two molecular symmetries. One symmetry was used allowing for relative differences in ligand interaction, and another higher symmetry was used assuming all ligands equivalent. The results of the ligand field calculations described in I were used for all but tetrahedral symmetry for which Hartmann's² results were used.

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to as I.

² H. Hartmann and H. Fischer-Wasels, Z. physik. Chem. (Frankfurt) 4, 5/6 (1955).

Compound	
Compound	Г Ц Л
I. Ni bis o-phenylenediamine Cl2	$\begin{bmatrix} \mathbf{N}_{2} \\ \mathbf{N} \\ \mathbf{N} \\ \mathbf{N} \\ \mathbf{H}_{2} \end{bmatrix}_{2} $ Ni Cl ₂
II. Ni bis NN'-diphenylethylenediamine Cl2	$\begin{bmatrix} H_2 & H_2 \\ \phi & C - C & \phi \\ N & N \\ H & H \end{bmatrix}_2 \text{Ni } Cl_2$
III. Ni <i>bis</i> -acetylacetone·2H2O	H ₃ C OH_2 C H ₃ C = 0 $O-C$ H C $O-C$ H C $O+C$ H C $O+C$ H C $O+C$ C H O-C C H O-C
IV. Ni <i>bis</i> salicylaldehyde. 2H2O	C = O H O O H O O O H O O O H O O O H O
V. Ni <i>bis</i> glycinate: 2H2O	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$
VI. Ni <i>tris</i> ethylenediamine. Cl ₂ ·2H ₂ O	$\begin{bmatrix} C & & & & \\ C & N & H_2 & & \\ N & & N - C - H_2 & & \\ N & N & N - C - C H_2 & & \\ N & N & N - C - C H_2 & & \\ C - C & H_2 & & \end{bmatrix} Cl_2 \cdot 2H_2 O$

TABLE I. Structural formulas of Ni chelates.^a

^a The diagrams here do not necessarily imply any structural information but are meant as a visual aid. The extent of knowledge of molecular structure will be indicated for each case in context.



FIG. 1. Electronic absorption spectra of two four-nitrogen paramagnetic chelates.

II. EXPERIMENTAL

The optical absorption spectra were obtained with the Carey Model 14 recording spectrophotometer which has a wavelength range of 180-2600 m μ . All the spectra reported here were taken at room temperature with the species either in solution or powder form. The low-intensity absorptions of the six-chelates studied are shown in Figs. 1-5. The extinction coefficient



FIG. 2. Electronic absorption spectra of Ni bis acetylacetone dihydrate.



FIG. 3. Electronic absorption spectra of Ni bis salicylaldehyde.

ordinate applies to solutions of known concentration, while the optical density ordinate applies to powders and solutions of unknown concentration. Data pertinent to these spectra, including earlier work in the literature, are listed in Table II. Positions of maximum absorption $(\lambda_{max}; \nu_{max})$ maximum extinction coefficients (ϵ_{max}) or maximum optical densities $(o.d._{max})$ and widths at half-height $(\Delta \nu_{\frac{1}{2}})$ are given whenever possible. Partially resolved or otherwise uncertain absorptions are given in parenthesis. Under the heading "Compound" is given an abbreviated name of the chelate, the form of the sample, and where applicable, the solvent, concentration of solution, and cell length used for each spectrum. If, to observe all absorptions in the intensity range $1 < \epsilon_{max} < 300$, the concentration had to be varied, this is indicated in the table by listing the several concentrations and cell lengths that were



FIG. 4. Electronic absorption spectra of Ni (glycine)₂ 2H₂O.



FIG. 5. Solid and solution spectra of Ni tris ethylenediamine chloride dihydrate.

used and indicating which bands were detectable in each.

The observation of these low-intensity absorptions was made difficult by the general insolubility of these chelates. For example, for transitions with a maximum extinction coefficient of 1-10, a minimum concentration of 2×10^{-3} mole/liter was needed for 5% absorption. Many of the chelates studied were less soluble

TABLE II. Ir visible spectra of Ni chelates. Concentration in moles/liter; 1 cm cell unless otherwise noted.

Compounds	λ_{max} (mu)	p_{max} (au)	€max or o.d. max	$(cm^{\Delta \nu_{1}})$
Ni (sal) 2H.O				
nowder	1070	4.23×10^{-2}	0.26]	
ponder	(950)	4.81	0.15	2925
	770	5.93	0.07	
	630	7.26	0.36	2010
	420	10.89	0.80}	3810
CH ₃ OH, 10 ⁻² ,	1115	3.97	6.5	2500
2 cm cell	(975)	4.69	4.3∫	2580
	(760)	6.09	4.7	3540
	645	7.08	8.0}	3340
10 ⁻² pyridine,	1000	4.57	9	2530
2 cm cell	770	5.90	≦1	
	610	7.45	13.5	2985
Ni (sal) ₂	1280	3.57	0.14	2330
dimethyl	770	5.93	0.12	
formamide	700	6.53	0.16	5350
	625	7.315	0.16{	5550
	580	7.88	0.14)	
Ni (acac) ₂ ·2H ₂ O				
powder	1125	4.06	0.21	4430
	745	6.14	0.16	
	650	7.03	0.19	4650
	400	11.43	0.28	
CHCl ₃ , 10 ⁻² N,	1125	4.06	3.2	
2 cm cell	(745)	6.14	2	
	655	6.97	3.2	

Compounds	λ _{max} (mu)	^v m s.x (au)	emax or o.d. max	(cm^{2})
CH₃OH, 5×10 ⁻²	1085 (745) 630	4.23 6.17 7.27	3.4 1.6 3.6	3295 3255
Pyridine, 5×10^{-2}	980 (765) 590	4.64 5.90 7.74	5.6 1.0 6.2	2725 3420
Ni (acac) ₂ ª benzene	1135 775 655	4.02 5.90 6.97	0.2	0120
Ni (o phen) ₂ Cl ₂ powder	1170 835	3.90 5.48	0.71 0.51	2450
	785 570 360	5.82 8.02 12.70	$0.53 \\ 0.91 \\ 1.40$	
Ni (NN'¢-en)2 Cl2 powder	1220 (1025) 850 670 (500) 415	3.74 4.46 5.38 6.82 9.144 11.02	$\begin{array}{c} 0.53 \\ 0.37 \\ 0.15 \\ 0.74 \\ 0.18 \\ 1.10 \end{array}$	7200 3495
CHCl ₃ , 10 ⁻² , 5 cm cell	1190 850 680 410	4.12 5.38 6.72 11.15	7.6 3.5 11.0 24.0	3400 3280
Ni (glycine) ₂ .2H ₂ O H ₂ O, 10 ⁻¹ M	(1150) 1005 (750) 620 370	3.97 4.55 6.09 7.37 12.36	4.2 6.1 4.2 6.8	3645 3570 3985
Ni (en) ₃ Cl ₂ ·2H ₂ O H ₂ O, 5×10 ⁻²	880 (790) 540 345	5.20 5.79 8.47 13.25	5.5 3.8 5.0 6.2	3315 3470 3740
H ₂ Oª	890 (805) 540 345	5.12 5.67 8.39 12.80	7.3 5.0 6.7 8.6	

TABLE II.—Continued.

^a See reference 11.

than this in all common inert solvents such as CCl_4 , $CHCl_3$, dimethylformamide (DMF), and benzene, and even in more interacting solvents such as methanol, ethanol, and water. Powder spectra then were an invaluable addition to the available data. The technique used by Shibata³ of equalizing the light scattering from the sample with background scattering from an appropriate material was used. The powder was deposited uniformly on a quartz plate by evaporation from a volatile solvent. Opal glass, Teflon sheets, and oil-impregnated filter paper were the materials used as scattering agents. The oil-impregnated filter paper

³ Shibata, Benson, and Calvin, UCRL 2635 (1954).

had the largest range of applicability. It gave good results in the region $380-1500 \text{ m}\mu$, whereas the others could only be used in the visible region. Under optimum conditions of thickness and uniformity of sample, and correct choice of light scattering agent, all arrived at empirically, the absorption spectra were unambiguously and reproducibly observed above the background noise level. These conditions gave the usual transmitted light spectra. Then, if there is no appreciable intermolecular interaction in the solid and no special steric constraints, powder spectra should be comparable to those in an inert solvent. This was the case for all chelates for which it was possible to obtain the spectra of the powder and an appropriate solution, as shown by curves II and III of Fig. 1; I and II of Fig. 2; II and III of Fig. 3; and the two spectra of Fig. 5. However absolute intensities cannot be obtained from powder spectra, and the relative intensities of bands at more than small frequency separations need not be significant because of the dependence of the scattering power on the frequency.

Compounds III and VI were available. The remaining four chelates were prepared by methods outlined in the thesis.⁴ In all cases chemical analysis of the compounds gave molecular formulas corresponding to the structures given in Table I.

III. THE NATURE OF THE OBSERVED ABSORPTIONS. PREDICTED POLARIZATION BEHAVIOR

A. Symmetry Forbidden Transitions

An electronic transition between two states m and nwill be allowed by electric dipole radiation if there is a nonzero transition moment between them, i.e.,

$$\langle m | e \mathbf{r} | n \rangle \pm 0.$$

Then the direct product of the irreducible representations of the two states and of the electric vector must contain the totally symmetric representation of the group of the molecule. From this condition many specific selection rules can be derived.

Since all the functions arising from a $3d^n$ configuration are even, i.e., remain invariant under inversion through the origin of the coordinate system, and since the electric vector is odd, transition between these central ion states are forbidden. However this is precisely the origin postulated for the low-intensity transitions observed in these complexes, which are about 10⁻⁴ as intense as dipole allowed transitions. Several ideas have been advanced to explain the nonzero intensities of these transitions⁵ and these have been recently discussed.6-8 It is now generally felt9 that they are made allowed by asymmetric distortions in

the molecule which destroy the center of symmetry and thus invalidate the inversion operation. This allows a mixing of odd excited electronic states of the ion from such configurations as $3d^{n-1}4p$ with the even states arising from the $3d^n$ configuration with a resulting nonzero value of the transition moment. These hemihedral distortions can arise in two ways: (a) odd vibrational modes momentarily distort the nuclei from their equilibrium configurations, and (b) the local geometry about the central ion does not have a center of symmetry. The observed absorptions in systems with a static center of symmetry are therefore simultaneous electronic and vibrational transitions. These so-called vibronic transitions are not resolved in general and any one broad band observed is the envelope of many such transitions between two electronic states; i.e., all possible $0-1_i$ transitions, plus some combinations $0-1_i+1_j$, plus some transitions from excited vibrational modes in the ground electronic state. For each molecular configuration with a center of symmetry used, the odd modes available for mixing with the even electronic states were determined from an analysis of the symmetry of the pure vibrational modes. For complexes of four-coordinated tetragonal symmetry there are four odd vibrational modes available: the A_{2u} and B_{2u} bending modes and the E_u stretching modes. For the six-coordinated tetragonal complex there are six modes: odd stretching modes of A_{2u} and E_u symmetry, and odd bending modes of B_{2u} , A_{2u} , and E_u symmetry. Since more odd modes are available a general increase in intensity in going from four to six coordinated complexes would be expected. For the trans-planar symmetry the odd vibration modes are B_{1u}, B_{2u} , and B_{3u} .

B. Spin-Forbidden Transitions

If the electron spin angular momentum is preserved as a good constant of the motion in the complex, then all electronic and vibronic transitions must take place between states of the same multiplicity. However, the coupling of the spin and orbital angular momentum mixes states with different values of L and S, preserving only the total angular momentum J. Then in the presence of the ligand field those singlet and triplet states will interact which have the same transformation

200	TTT	a					•		
'ADTE		States	which	con	mit	under	CDIN	Arbit.	compling
TADLE	TTT*	SLATES	which	uan	ma	under	SOM-	ULUIL.	coupling.
									·· I 0.

Octahedral (Oh)	Tetragonal (D _{4h})	Cis-planar (C2v)	Trans-planar (D_{2h})
${}^{3}A_{1} - {}^{1}T_{1}; {}^{3}A_{2}, {}^{1}T_{2}$	${}^{3}A_{2g}$; ${}^{1}A_{1g}$, ${}^{1}E_{g}$	${}^{3}A_{1}; {}^{1}A_{1}, {}^{1}B_{1}, {}^{1}B_{2}$	${}^{3}A_{g}; {}^{1}B_{1g}, {}^{1}B_{2g}, {}^{1}B_{3g}$
${}^{3}E - {}^{1}T_{1}, {}^{1}T_{2}$	³ B _{1g} ; ¹ B _{2g} , ¹ E _g	${}^{3}A_{2}; {}^{1}A_{2}, {}^{1}B_{1}, {}^{1}B_{2}$	${}^{3}B_{1g}; {}^{1}A_{g}, {}^{1}B_{2g}, {}^{1}B_{3g}$
${}^{3}T_{1} - {}^{1}A_{1}, {}^{1}E_{1}, {}^{1}T_{1}, {}^{1}T_{2}$	${}^{3}B_{2g}$, ${}^{1}B_{1g}$, ${}^{1}E_{g}$	${}^{3}B_{1}; {}^{1}A_{1}, {}^{1}A_{2}, {}^{1}B_{1}$	${}^{3}B_{2g}; {}^{1}A_{g}, {}^{1}B_{1g}, {}^{1}B_{3g}$
${}^{3}T_{2} - {}^{1}A_{2}, {}^{1}E_{1}, {}^{1}T_{1}, {}^{1}T_{2}$	${}^{3}E_{g}; {}^{1}A_{1g}, {}^{1}A_{2g}, {}^{1}B_{1g}, {}^{1}B_{2g}, {}^{1}E_{g}$	${}^{3}B_{2}; {}^{1}A_{1}, {}^{1}A_{2}, {}^{1}B_{2}$	${}^{3}B_{3g}; {}^{1}A_{g}, {}^{1}B_{1g}, {}^{1}B_{2g}$

⁴ G. Maki, Ph.D. thesis, University of California (1957).

J. H. Van Vleck, J. Phys. Chem. 41, 67 (1937).
 C. J. Ballhausen, Acta Chem. Scand. 9, 821 (1955).
 O. Holmes, Ph.D. thesis, University of California, 1955.

⁸ W. Moffitt and C. J. Ballhausen, Ann. Rev. Phys. Chem. 7,

^{107 (1956)}

⁹ A. D. Liehr and C. J. Ballhausen, Phys. Rev. 106, 1161 (1957).

TABLE IV. Polarization of absorptions in D_{4h} symmetry.

I. Triplet states					
z allowed transitions	xy allowed transitions				
${}^{3}B_{2g} {-}^{3}B_{2g}$ allowed by A_{2u} ${}^{5}B_{2g} {-}^{3}A_{2g}$ allowed by B_{2u} ${}^{3}B_{2g} {-}^{3}E_{g}$ allowed by E_{u}	${}^{3}B_{2g} \longrightarrow {}^{3}E_{g}$ allowed by A_{2u} and B_{2u} ${}^{3}B_{2g}$ —to all four other symmetries allowed by E_{u}				
II.	Singlet states				
z allowed transitions	xy allowed transitions				
$\begin{array}{c} \hline A_{1g} - A_{1g} \text{ allowed by } A_{2u} \\ A_{1g} - B_{1g} \text{ allowed by } B_{2u} \\ A_{1g} - E_g \text{ allowed by } E_u \end{array}$	$A_{1g} - E_g$ allowed by A_{2u} and B_{2u} A_{1g} - all four remaining symmetries allowed by E_u				

properties under all operations which preserve only the total angular momentum. The sets of interacting singlet and triplet states were determined for the four symmetries used in the energy calculations and are given in Table III. Because of this partial mixing of the singlet and triplet states, spin-forbidden transitions are made allowed. This is another order of forbiddenness on top of the g-g prohibition and such triplet-singlet transitions are weaker and sharper than those that are spin-allowed. There are then two types of absorptions possible in the wavelength range under consideration, empirically distinguishable by form and intensity.

C. Polarization Behavior

A knowledge of the irreducible representations of the odd vibrational modes, the x, y, and z components of the electric vector and the ground state of the molecule, enables the prediction of the polarization of the observed transitions. Different vibrational modes make the transition allowed for radiation polarized in different directions. In tetragonal symmetry, the lowest triplet state was found to be a B_{2g} state, and the lowest singlet state A_{1g} . The molecule is considered to be in its ground vibrational state A_{1g} , z transforms like A_{2u} ,

TABLE V. Polarization of absorptions in six-coordinated tetragonal complexes.

m . . . tat . .

Polarization

Transition	10111241101
${}^{3}B_{2g} - A_{1g}$ $B_{2g} - A_{2g}$ $B_{2g} - B_{1g}$ $B_{2g} - B_{2g}$ $B_{2g} - E_{g}$	Completely in xy plane Mainly in xy plane Completely in xy plane Almost equally in xy plane and normal to it Almost equally in xy plane and normal to it
$ \begin{array}{c} {}^{1}A_{1g} - A_{1g} \\ A_{1g} - A_{2g} \\ A_{1g} - B_{1g} \\ A_{1g} - B_{2g} \\ A_{1g} - B_{2g} \\ A_{1g} - E_{g} \end{array} $	About equally in xy plane and normal to it Completely in xy plane Mainly in xy plane Completely in xy plane About equally in xy plane and normal to it

and x and y belong to E_u . Table IV lists those transitions allowed by the electric vector parallel and perpendicular to the xy molecular plane of a four-coordinated complex. If the stretching mode E_u provides the major interaction then for both singlet and triplet systems, transitions to E_q would be predominantly z polarized, and all other transitions would be mostly xy polarized. For six-coordination, two new modes are added but no new symmetries. If the two types of stretching modes A_{2u} and E_u provide the dominant interaction, Table V lists the predicted polarization of the transitions. For the trans-planar symmetry, a B_{3q} state is the lowest triplet and an A_q state the lowest singlet. The three odd vibrational modes make all possible transitions allowed with the polarization behavior given in Table VI. Single crystal spectra of molecules whose structures are known, would be needed to see if the polarization behavior predicted for these symmetries is correct.

TABLE VI. Polarization of absorptions in trans-planar complexes.

I. Singlet states

 $A_g - A_g$ in all three directions $A_g - B_{1g}$ polarized in xy plane, not seen along the z axis $A_g - B_{2g}$ polarized in xz plane, not seen along the y axis $A_g - B_{3g}$ polarized in yz plane, not seen along the x axis

II. Triplet states

 $B_{\delta q}$ — A_q polarized in yz plane, not seen along x axis $B_{\delta q}$ — B_{1q} polarized in xz plane, not seen along y axis $B_{\delta q}$ — B_{2q} polarized in xy plane, not seen along z axis $B_{\delta q}$ — B_{2q} seen in all three directions

IV. CRITERIA FOR AGREEMENT AND LIMITATIONS IN THE ACCURACY OF THE CALCULATED AND OBSERVED SPECTRA

If the ligand field model of the complex molecule is to be at all useful, the energy intervals calculated from it should reproduce at least the qualitative aspects of the observed spectra. On the basis of the data presented here, there are two main criteria for qualitative agreement. In each case the number of transitions predicted in the observable range must be correct and the absorptions assigned to spin forbidden (T-S)transitions should be less intense than the spin allowed (T-T) ones.[†]

In this study then, for those symmetries for which

 $[\]dagger$ Investigations of the relative intensities of the different T-T transitions such as the recent one of Liehr and Ballhausen,⁹ and of the polarization behavior of single crystal spectra analogous to that done by Holmes and McClure⁷ would give two more qualitative checks on the correctness of the assignments.

more transitions are possible than observed, the unobserved ones must be explained. For the T-T transitions there are only two possible explanations, the energy interval is out of the observable range or there is an accidental near-degeneracy of states. Transitions to singlet states will be observed however, only if the singlet state lies close to a triplet state with which it can interact. The absence of such a condition, or the masking of these weaker transitions by neighboring spin-allowed ones, are two plausible reasons why all T-S transitions in the observable range are not seen.

The severest limitations to the definitiveness of the assignments and the information derived therefrom are the ambiguities in the spectra themselves. The shape of the envelope of vibronic transitions which constitutes a broad absorption band depends on the relative intensities of each transition in the band and it is not a priori expected to have a regular form. For partially resolved bands it is difficult to decide how many electronic transitions are involved. Also the position of maximum intensity does not correspond to the 0-0 pure electronic absorption which is forbidden in these cases. The energies calculated from the ligand field potential assume fixed nuclei and are purely electronic. They are compared with the position of maximum intensity simply for convenience. The maximum error in this position taken as the 0-0 transition should be about 2000 cm⁻¹, which is within the expected accuracy of the theoretical calculations. The effect of vibrational motion, considered from the crystal field approach is to change the effective field strength. The position and shape of the absorption band should then be temperature-dependent. No study of the temperature dependence was made. In each case then, the observed bands are given a plausible but not infallible

interpretation. Within the framework of these limitations, it is believed that the simple electrostatic model of the complex is useful and the structural inferences and differences in ligand effect derived from the spectral assignments significant, if the proposed assignments give qualitative agreement with a reasonable interpretation of the observed bands and qualitative agreement in the position of the absorption maximum to within 30%, with a self-consistent set of field parameters.

V. ASSIGNMENT AND DISCUSSION OF SPECTRA AND STRUCTURE

A. Ni $(o-phenylenediamine)_2Cl_2$ (I) and Ni $(NN'-di-phenylethylenediamine)_2Cl_2$ (II)

These two chelates are examples of paramagnetic complexes with four exactly equivalent nitrogen ligands bound to the Ni(II) ion. Their spectra are shown in Fig. 1. The absorption bands are interpreted in the following way. For compound I, one of the sharp peaks at 835 and 785 m μ is assumed to be a T-S transition and the other four are taken as the usual g-g forbidden T-T transitions. For compound II, the partial resolution of the lowest energy band is assumed real, corresponding to two separate electronic states, giving a total of four T-T transitions, the weak sharp peaks at 850 and 500 m μ being taken as T-S absorptions. These decisions about the spectra form the experimental basis for the assignments made.

Nothing is known about the structure of these molecules. The Ni(II) ion was first assumed four-coordinated, with the effect of the Cl ion negligible, and assignment of the spectra in tetrahedral and tetragonal symmetry was made. The possible coordination of the Cl ions was then considered, and a six-coordinated

	Four-cool	dinated	Six-coo	ordinated	
Exptl. ΔE	ΔE tetrahedral	ΔE tetragonal	ΔE tetragonal	ΔE octahedral	
	${}^{3}T_{1} \rightarrow^{\mathrm{b}}$	${}^{3}B_{2g} \rightarrow {}^{b}$ ${}^{3}E_{c} 1.9 \times 10^{-2}$	${}^{3}B_{2g} \rightarrow b$	${}^{3}A_{2g} { ightarrow} {}^{\mathrm{b}}$	
3.9×10^{-2} 5.5×10^{-2}	${}^{3}T_{2}$ 4.43 $\times 10^{-2}$ ${}^{1}E$ 6.8 $\times 10^{-2}$	${}^{3}A_{g} {}^{3}.8 \times 10^{-2} {}^{3}B_{1g} 6.6 \times 10^{-2}$	${}^{3}E_{g} 3.9 \times 10^{-2}$ ${}^{3}A_{2g} = 6.2 \times 10^{-2}$	${}^{3}T_{2g}$ (3.9×10 ⁻²)	
5.8×10^{-2} (f) ° 8.0×10^{-2}	${}^{1}T_{2} 6.9 \times 10^{-2}$ ${}^{3}A_{2} 9.33 \times 10^{-2}$	${}^{1}B_{2g}$ 7.7×10 ⁻² ${}^{3}E_{g}$ 8.1×10 ⁻²	$^{3}B_{1g}$ $^{1}A_{1g}$ 6.8×10 ⁻² $^{3}E_{g}$ 7.9×10 ⁻²	${}^{1}E_{g}$ 7.6×10 ⁻²	
12.7×10 ⁻²	³ <i>T</i> ₁ 11.4×10 ^{−2}	${}^{3}A_{2g}^{}13.7 \times 10^{-2}$ ${}^{3}E_{g}16.0 \times 10^{-2}$	${}^{3}A_{2g}^{}$ 12.7×10 ⁻² ${}^{3}E_{g}^{}$ 14.8×10 ⁻²	${}^{3}T_{1g}$ 12.6	
rameters used	u=1	u = 0.6	u = 0.55 $R = 1.5$	u = 0.36 = u'	

TABLE VII. Assignments of spectrum of Ni (o-phenylenediamine)₂ Cl₂ (I).^a

^a All energy differences are in atomic units 1 au= 2.187×10^5 cm⁻¹. u is also in atomic units 1 au=2.54 D and R is in angstroms.

^b This is the symmetry of the ground state. Transitions and energy intervals are between the ground state and states listed below. The same convention is folowed for all subsequent assignments.

^c (f) means spin-forbidden (T-S) transition.

	Four-co	ordinated	Six-coordinated			
Exptl. ΔE	ΔE tetrahedral	ΔE tetragonal	ΔE tetragonal	ΔE octahedral		
		³ E ₂ 1.3×10 ⁻²	${}^{3}E_{a} 2.2 \times 10^{-2}$			
3.75×10 ⁻²	³ T ₂ 4.4×10 ⁻²	${}^{3}A_{2g}$ 3.6×10 ⁻²	${}^{3}B_{1g}$ 3.65×10 ⁻²	${}^{3}T_{2g}$ (3.75×10 ⁻²)		
4.5×10^{-2}		$^{3}B_{1g}$ 4.4×10 ⁻²	${}^{3}A_{2g}$ 4.65 $\times 10^{-2}$			
$5.4 \times 10^{-2}(f)$	${}^{1}E 6.8 \times 10^{-2}$	${}^{1}A_{1g} 5.1 \times 10^{-2}$	${}^{1}B_{2g}$ 5.2×10 ⁻²	${}^{3}T_{1g}$ 6.5×10 ⁻²		
6.8×10^{-2}	${}^{1}T_{2} 6.9 \times 10^{-2}$	${}^{3}E_{g}$ 5.6×10 ⁻²	${}^{3}E_{g}$ 5.6×10 ⁻²	${}^{1}E_{q}$ 7.5×10 ⁻²		
		${}^{1}B_{g}$ 8.0×10 ⁻²	${}^{1}A_{1g} 6.6 \times 10^{-2}$	-		
$9.1 \times 10^{-2}(f)$	${}^{3}A_{2} 9.3 \times 10^{-2}$	${}^{1}E_{a}$ 8.7×10 ⁻²	${}^{1}E_{q}9.2\times10^{-2}$	${}^{1}T_{2a}$ 11.0×10 ⁻²		
Q /		${}^{1}A_{2a}$ 9.1×10 ⁻²	• • •			
		${}^{1}B_{1a}$ 9.9×10 ⁻²				
11.0×10^{-2}	${}^{3}T_{1}$ 11.4×10 ⁻²	${}^{3}A_{2a}$ 10.4×10 ⁻²	${}^{3}A_{2a}$ 11.0×10 ⁻²	${}^{3}T_{2a}$ 12.2×10 ⁻²		
•••		${}^{3}E_{g}$ 13.1×10 ⁻²	· · · · · · · · · · · · · · · · · · ·	- 20		
Parameters used (au:	u=1	u=0.4	u = 0.35 p = 1	u = 0.35 = u'		
A)	R = 1.5	R = 1.5	R = 1.5 Z = 1.9	R = 1.5 = Z		
·						

TABLE VIII. Assignment of spectrum of Ni (NN'-diphenylethylenediamine)₂Cl₂ (II).

assignment made in tetragonal and octahedral symmetry. The assignments for all of these cases are given in Table VII for compound I and Table VIII for compound II. In all cases, the point dipole approximation was the only possible one, and a value for the chelate-Ni distance of 1.5 A best. The axial charges were placed at a distance of 1.9 A and this was not varied. The assignments were made for the best values of the nitrogen dipole moment u, and the Cl ion charge p or moment u'.

Assignment in tetrahedral symmetry can only explain three T-T transitions and two T-S transitions in this region. Then to assign the spectrum for I the two peaks at 0.055 and 0.058 atomic units (au) would both have to be taken as spin-forbidden. For II, the large absorption at 0.068 au would have to be taken as spin-forbidden, the small one at 0.0091 au as spinallowed and the resolution in the first transition ignored. Thus this assignment has several important discrepancies.

Assignments in both four- and six-coordinated symmetries accounts for the four T-T transitions seen and for the absence of the other two, one being at too high and the other at too low a frequency to be observed. The one T-S transition in compound I and the two in compound II are two singlet states which can interact with their two nearest triplet neighbors. In each case there is no possibility of other spin-forbidden transitions. Thus, this analysis gives good qualitative agreement and the quantitative agreement is within 20%.

Assuming an average effect of the ligands and making an assignment in octahedral symmetry, only accounts for three T-T and one T-S transition in this region. Then in compound I the absorption at 0.080 au is unexplained and for compound II, the resolution in the first band must again be ignored and the weak band at 0.054 au is attributed to a T-T transition while the strong one at 0.068 au to a spin-forbidden one.

The results indicate then, that if the chelate is fourcoordinated, square planar symmetry gives a better unexplanation of the spectra than tetrahedral. If they are six-coordinated, tetragonal symmetry is superior to octahedral. A particularly direct illustration that an axial distortion does give a more accurate description of the six-coordinated complex, is the assignment for compound II. By coincidence, the two six-coordinated assignments were made for the same value of the nitrogen dipole moment, u=0.35 au. Since the value in octahedral symmetry was chosen for the best fit, no gain in accuracy can be obtained by varying the field strength, but a tetragonal distortion can be applied. There is then a real symmetry effect and the pure ligand field calculation seems capable of distinguishing fairly small differences in the effect of the neighboring atoms. Comparing the two tetragonal assignments, the numerical agreement with the observed peak positions is better with the inclusion of the Cl⁻ ions. Then a comparison of all four assignments allows the inference that these chelates are two six-coordinated tetragonal Ni(II) complexes.

Differences in the appearance and position of the absorption bands of these two related compounds and assignments of each have been made with reasonable relative values of the dipole moment of the nitrogens. The u parameter may be associated with the electron distribution localized about the ligand nitrogen atom. Since there is a reduction in the interaction of the nitrogen electrons with the benzene ring, an orthodiamine nitrogen such as in compound I should have a larger localized electron density than a nitrogen of the substituted aniline type of compound II. The difference in the values of u assigned to these two compounds is then in the right direction.

B. Ni bis Acetylacetone Dihydrate (III)

This compound may serve as an example of a paramagnetic chelate with four equivalent oxygen ligands. The spectra of the dihydrate in the solid and in various solvents is shown in Fig. 2. Nothing is known about the structure of the dihydrate. It may reasonably be assumed that together with the two molecules of chelating agent, the two water molecules form a sixcoordinated complex with tetragonal symmetry. The anhydrous chelate is believed to be a trimer in the solid.¹⁰ It is not known whether it dissociates in solution. The spectra of the dihydrate in powder form and inert solvents and the reported11 spectrum of the anhydrous chelate in benzene are all the same.[‡] This indicates that the local molecular symmetry in the dihydrate remains intact upon solution. The similarity

TABLE IX. Assignment of spectrum of Ni (acetylacetone)₂.

In inert solvent or solid dihydrate					
Exptl. $\Delta E^{\mathbf{a}}$	$\Delta E: 4\text{-coordinated} \\ \text{tetragonal } {}^{s}B_{2g} \rightarrow$	$\Delta E: 6\text{-coordinated} \\ \text{octahedral } {}^{3}A_{2g} \rightarrow$			
4.02×10 ⁻²	${}^{3}E_{g}$ 1.65×10 ⁻² ${}^{3}A_{2g}$ 3.65×10 ⁻²	³ T ₂₀ 4.0×10 ⁻²			
5.90×10^{-2} 6.90×10^{-2} 11.4×10^{-2}	${}^{1}A_{1g} 4.35 \times 10^{-2}$ ${}^{3}B_{1g} 5.55 \times 10^{-2}$ ${}^{3}E_{g} 6.75 \times 10^{-2}$ ${}^{3}A_{2g} 11.7 \times 10^{-2}$	${}^{3}T_{1g} 6.9 \times 10^{-2}$ ${}^{1}E_{g} 7.0 \times 10^{-2}$ ${}^{3}T_{1g} 12.6 \times 10^{-2}$			
Parameters used (au; A)	u = 0.5 R = 1.5	u = 0.37 = u' R = 1.5 = Z			

^a The first three transitions are observed in all inert solution spectra, the numbers are taken from the anhydrous form, the fourth transition is seen only in the powder dihydrate.

in the spectra of the anhydrous and hydrated species may be explained by the assumption that in both cases the axial perturbation is small compared to the effect of the chelate oxygen atoms. This is exactly opposite to Jorgensen's opinion¹¹ that the anhydrous chelate in benzene is octahedral.

For comparison the published spectrum of the anhydrous compound was assigned with the assumption of both four- and six-coordination. A tetrahedral assignment was not possible. Assignments in square planar and octahedral symmetry are given in Table IX. They are also applicable to the hydrate since observed differences between the spectra are smaller than the accuracy of any assignment.

The four-coordinated assignment accounts with very good numerical agreement for the three transitions reported in the solution spectra both here and by Jorgensen,¹¹ and also for the fourth observed in the solid. The first and the last of the possible absorptions are too low and too high to be observed. The doublet in the visible is assigned to two spin-allowed transitions

Table	X.	Assignment	of	spectrum	of	Ni	(acetylacetone) ₂
		-	in	nuridina			
			11	i pynume.			

Exptl. ΔE	Six-coordinated ΔE tetragonal: ${}^{3}B_{2g} \rightarrow$	ΔE octahedral: $^{3}A_{2g} \rightarrow$
	3E 0 0 10-9	
	$^{6}E_{g} 2.2 \times 10^{-2}$	
4.6×10^{-2}	$^{3}B_{1g} 4.8 \times 10^{-2}$	${}^{3}T_{2a}$ 4, 75×10 ⁻²
1.0/(10	${}^{3}A_{2a}$ 5.2×10 ⁻²	1 20 1110/(10
$6.0 \times 10^{-2}(f)$	${}^{1}B_{2a}$ 6.6×10 ⁻²	$^{1}E_{a}$ 7.88×10 ⁻²
7.7×10^{-2}	${}^{3}E_{q}^{-3}7.5 imes10^{-2}$	${}^{3}T_{2q}^{2}$ 8 2×10 ⁻²
Parameters used	$u = 0.5$ $u^1 = 0.7$	u = 0.44 = u'
(au; A)	R = 1.5 Z = 1.9	R = 1.5 = Z

which interact differently with the available odd vibrational modes. Slight resolution of the first band, observed in the solid spectrum, may be accounted for by the mixing of the ${}^{3}A_{2q}$ and the ${}^{1}A_{1q}$ states. The octahedral assignment has the qualitative discrepancy that the weaker of the visible doublets is assigned to a spin-allowed and the stronger to a spin-forbidden transition. Also the numerical accuracy is not as good. The, of the two extreme possibilities, making the axial ligands equivalent to the chelate oxygens or considering their effect to be negligible, the assumption of the fourcoordination gives a better assignment. It might be concluded then that the axial perturbation is rather weak.

The small shifts that occur in the spectrum of Ni bis acetylacetone dihydrate in methanol and the larger ones in pyridine indicate that the solvent replaces the water as a coordinating agent in these solutions. To explain a solvent effect in octahedral symmetry, the effective point dipole used has to be "reaveraged" as the axial perturbation gets larger. This was done to assign the spectrum of Ni bis (ac ac) in pyridine allowing free range of parameters. For comparison, an assignment was also made in tetragonal symmetry. Here a value of u = 0.5 for the chelate oxygens was used to be consistent with the four-coordinated assignment in Table IX. Also an independently determined value of 0.7 for the effective dipole moment of pyridine was used. This is a value consistent with magnetic data

TABLE XI. Assignment of anhydrous Ni (salicylaldehyde)₂ in D_{2h} symmetry.

$u_1=0.35; u_2=0.85$				
Transition	$\Delta E_{\mathrm{calc}} {}^{3}B_{3g} \rightarrow$	ΔE_{obs}		
${}^{3}B_{3a}$ ${}^{3}A_{a}$	4.3×10 ⁻²	3.6×10-2		
${}^{3}B_{3g} - {}^{1}A_{g}$	5.4×10^{-2}	$5.9 \times 10^{-2} (f)$		
${}^{3}B_{3g} - {}^{3}B_{1g}$	6.3×10^{-2}	6.5×10^{-2}		
${}^{3}B_{3g} - {}^{3}B_{2g}$	6.8×10^{-2}	7.3×10^{-2}		
${}^{3}B_{3g} - {}^{3}B_{2g}$ ${}^{3}B_{2g} - {}^{1}B_{2g}$	6.8×10^{-2} 7.1 × 10^{-2}	7.3×10^{-7} 7.9×10^{-7}		

 ¹⁰ G. J. Bullen, Nature 177, 537 (1956).
 ¹¹ C. K. Jorgensen, Acta. Chem. Scand. 9, 1362 (1955). See data in Table II.

[‡] This is true except for the resolution of the band at 400 m μ in the solid.

for some diamagnetic chelates in pyridine. Thus all the parameters for the tetragonal assignment were predetermined. The two assignments are given in Table X. Three transitions are observed in this spectrum, the one labeled spin-forbidden (f) being much weaker than the other two. Octahedral symmetry describes the qualitative aspects of the spectra, but the numerical fit to the singlet transition is quite poor. The assignment in tetragonal symmetry explains the shifting to the violet of the two principal bands in going from the benzene to the pyridine solution and places them with reasonable accuracy. It also explains the reduced intensity and increased sharpness of the weaker band as a change from a spin-allowed to a spin-forbidden transition. Also less apparent resolution and increased intensity in the first band is accounted for, since here it is attributed to three nearly degenerate states. Assignment then in tetragonal symmetry where predetermined parameters place the pyridines further away than the in-plane ligands and give them a larger effective dipole moment, compares favorably with the octahedral one, where a value of u was chosen more freely. This illustrates that maintaining small differences in ligands can be significant and that a reasonable explanation of solvent effect can be obtained with consistent values of the field parameter u.

C. Ni bis Salicylaldehyde (IV)

The absorption spectra of the dihydrate in powder form and in solutions of methanol and pyridine are shown in Fig. 3. In solution there are two main absorption bands each appearing to be of a composite nature. In addition, in powder form, there is another shoulder at 420 m μ . There may then be from three to five separate electronic transitions observed. It is also difficult to tell which if any are spin-forbidden. In order to separate the effect of an axial perturbation, an attempt

TABLE XII. Assignment of spectrum of Ni (salicylaldehyde)₂ 2H₂O (powder or inert solvent).

ΔE exptl.	Six-coordinated $\Delta E \ irans$ -planar ${}^{3}B_{3g} \rightarrow$	ΔE octahedral ${}^{3}A_{2g} \rightarrow$	
$\begin{array}{c} 4.2 \times 10^{-2} \\ (4.8) \times 10^{-2} (f_{7}^{2}) \\ 5.9 \times 10^{-2} (f_{7}^{2}) \\ 7.3 \times 10^{-2} \\ 10.9 \times 10^{-2} \end{array}$	${}^{3}A_{g} 3.2 \times 10^{-2}$ ${}^{1}A_{g} 4.8 \times 10^{-2}$ ${}^{3}B_{1g} 6.2 \times 10^{-2}$ ${}^{3}B_{2g} 7.0 \times 10^{-2}$ ${}^{3}B_{2g} 10.6 \times 10^{-2}$	${}^{3}T_{2g} 4.2 \times 10^{-2}$ ${}^{3}T_{1g} 7.4 \times 10^{-2}$ ${}^{1}E_{1g} 7.6 \times 10^{-2}$ ${}^{3}T_{1g} 13.0 \times 10^{-2}$	
Parameters used	$u_1 = 0.35$ $u_2 = 0.85$ u' = 0.5 R = 1.5 $Z = 1.9$	u = 0.4 = u' R = 1.5 = Z	

TABLE XIII. Assignment of the spectrum of Ni bis glycinate $2H_2O$ in six-coordinated D_{2h} symmetry.

$u_1=0.6, u_2=1.1, u'=0.5, R=1.5, Z=1.9$				
Transition	$\Delta E_{e al e}$	ΔEobs	% error	
${}^{3}B_{3a} - {}^{3}A_{a}$	2.5×10^{-2}			
${}^{3}B_{3g} - {}^{1}A_{g}$	3.7×10^{-2} 5.9 × 10 ⁻²	$4.0 \times 10^{-2}(f)$	8% 30%	
${}^{3}B_{3g} - {}^{1}B_{3g}$	7.6×10^{-2}	$6.1 \times 10^{-2}(f)$	25%	
${}^{3}B_{3g} - {}^{3}B_{2g}$ ${}^{3}B_{3g} - {}^{3}B_{2g}$	8.8×10^{-2} 12.3×10 ⁻²	$7.4 imes 10^{-2}$ $12.4 imes 10^{-2}$	$20\% \\ 1\%$	
			,,,	

was made to prepare anhydrous Ni *bis* salicylaldehyde using anhydrous NiCl₂ and salicylaldehyde in dimethyl formamide. The spectrum of this species formed *in situ* is also shown in Fig. 3. It differs from the hydrate in that the first band appears to be only one transition while the visible absorption is resolved into a quartet of peaks and shoulders.

Nothing is known about the structure of the anhydrous chelate. A fairly complete x-ray diffraction study of the hydrated compound has recently been made.¹² The local symmetry about the Ni ion was found to be a distorted octahedron with a *trans*-planar arrangement (D_{2h}) of the chelate oxygens at approximately equal distances from the Ni. The distance to the water molecules was not determined.

Assignment of the spectrum of the anhydrous species in D_{2h} four-coordinated symmetry as shown in Table XI gives a remarkably good explanation and numerical fit of the observed absorptions. A difference in the effect of the two kinds of ligand oxygens then is manifest. The phenolic oxygen has a formal point charge and the carbonyl bond in the simple valence bond model is 40% ionic. Then a ratio in the neighborhood of 2.5/1 for the electrostatic effect of these two oxygens on the Ni ion would be expected. The assigned ratio of 2.41 is close enough to this value to give relative meaning to the *u* parameters used.

The dihydrate spectra were assigned in *trans*-planar symmetry using the values of the chelate oxygen dipole moments from the anhydrous four-coordinated assignment and a value for the water molecules of 0.5 au. An assignment was also made in octahedral symmetry, for the best value of an average dipole moment for all six oxygens. These assignments are given in Table XII. The octahedral assignment does not account for any possible resolution of the lowest energy band and also assigns the stronger peak of the visible doublet to a spin-forbidden transition. The *trans*-planar assignment then, with consistent values of chelate parameters, gives a better explanation of the spectrum.

 $^{^{12}}$ J. D. Breazeale, Ph.D. thesis, University of Washington (1955).

TABLE	XIV.	Assignr	nent of	the	spectrum	ı of Ni	tris	ethylene-
	diar	nine Cl ₂	$2H_2O$	in oc	tahedral	symm	etry	

u=0.5, R=1.5					
Transition	ΔE_{calc} ΔE_{obs}		% error		
${}^{3}A_{2a}$ ${}^{3}T_{2a}$	5.3×10 ⁻²	5.2×10 ⁻²	2%		
${}^{3}A_{2q} - {}^{1}E_{q}$	7.6×10^{-2}	$(5.8) \times 10^{-2}$	30%		
${}^{3}A_{2a} - {}^{3}T_{1a}$	9.1×10 ⁻²	8.5×10^{-2}	8%		
${}^{3}A_{2a} - {}^{3}T_{1a}$	13.9×10 ⁻²	13.3×10^{-2}	4%		

D. Ni bis Glycinate Dihydrate (V)

The spectrum of the water solution of this compound is shown in Fig. 5. There are three main bands with definitely weaker shoulder on the low-energy side of the first two. The molecular structure is known to be *trans*-planar in the solid.¹³ A plot of the energies *versus* u_1 with $u_2=0.5+u_1$ with D_{2h} symmetry was used to assign this spectrum, without an exhaustive search for the best combination of parameters. An assignment was obtained at $u_1=0.6$ as shown in Table XIII. This assignment interprets the two shoulders as mainly spin-forbidden transitions. The numerical fit is adequate. Assignment in octahedral symmetry is completely unsatisfactory here. Then by going to slightly higher values of the in-plane effective dipole moments than that used for compound IV, the spectrum of an entirely different *trans*-planar chelate has been explained. This may serve as an example of one general use to which the calculations for D_{2h} symmetry can be put.

E. Ni *tris* Ethylenediamine $Cl_2 2H_2O$ (VI)

The spectra in the solid form and in aqueous solution are shown in Fig. 5 and are identical. Therefore, the tris complex must remain intact in solution and it is not likely that either the Cl ions or the water molecules are directly coordinated to the Ni ion. Though the molecular structure is unknown, the six nitrogens are equivalent and assignment in octahedral symmetry seemed most plausible. This is shown in Table XIV and is seen to give excellent numerical agreement with the three main T-T peaks and explains the weaker fourth transition quite reasonably as a spin-forbidden one to the ${}^{1}E_{g}$ state which can interact with its two nearest triplet neighbors. Then only for this case of six truly equivalent ligands does assumption of octahedral symmetry explain all the transitions consistently and give a reasonable numerical assignment.

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¹³ A. J. Stosick, J. Am. Chem. Soc. 67, 365 (1945).