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A Ligand Field Approach Study of the Visible Spectra of Mono and Bis 2,2'-Dipyridyl Complexes of Ni^{II} in Non-aqueous Solvents

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The visible spectra of complex of Ni^{II} and 2,2'-dipyridil in non-aqueous solvents have been interpreted in terms of the Ligand Field Theory. A model was proposed and the obtained results are in good agreement with the spectral data.

A theoretical and experimental study of the ultraviolet spectra of 2,2'-dipyridil complexes with transition metal ions in aqueous solutions was performed in a former work of the same authors.[1]

In the present work this analysis has been extended, applying it to the particular case of the visible spectra of nickel complexes with the same ligand in non-aqueous solvents.

Besides the red complex ion $[Ni(dip)_3]^{2+}$, Ni^{II} and 2,2'-dipyridyl form the high spin ions $[Ni(dip)_2(H_2O)_2]^{2+}$ and $[Ni(dip)(H_2O)_4]^{2+}$ light-violet and light-blue colored respectively.

In some non aqueous solvents these last two ions show a broad range of colours going from deep green to deep red. In solvents of low coordinating effect, such as acetone and nitromethane, the compounds keep their original colours. In aqueous solution they are unstable and decompose giving $[Ni(dip)_3]^{2+}$.

The spectrophotometric determinations show only two absorption bands in the visible region, their energies depending on the nature of the solvent as can be seen in Figures 1 and 2. The expected third band is included in the high intensity $\pi\rightarrow\pi^*$ band due to the ligand.

The experimental data just mentioned lead to the conclusion that the solvents play a role entering the coordination sphere of the mono and bis-chelate compounds. It is possible, there fore, to build models of complex-solvent interaction allowing explanation of the spectral characteristics observed, by use of the ligand-field theory.

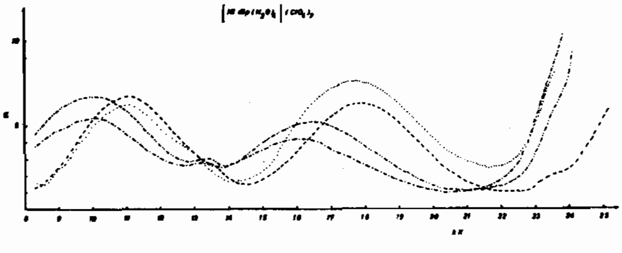

Figure 1. The absorption spectrum of $[Ni\,dip(H_2O)_4](ClO_4)_2$ in: Acetonitrile ———, Dimethylsulfoxide —.—.—; Pyridine . . . . . Dimethylformamide —..—..—..—.

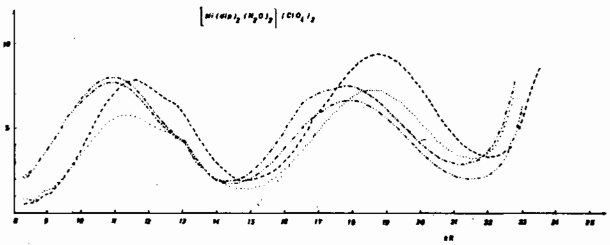

Figure 2. The absorption spectrum of $[Ni(dip)_2(H_2O)_2].(ClO_4)_2$ in: Acetonitrile ———; Dimethylsulfoxide —.—.— Pyridine . . . .; Dimethylformamide —..—..—.

Accepting that four solvent molecules are bonded to nickel in the mono-chelate compound and two in the bis-chelate one, the resulting structures exhibit a C_{2v} microsymmetry in the former complex, and C_{2v} or D_{4h} in the latter one.

The resemblance in the shape of the bands of the mono and bis-chelate compounds in solution lead us to assume the same symmetry for both.

In this way, an ideal approximation consists in assuming a nickel ion immersed in a field of symmetry C_{2v} where the nitrogen atoms of the 2,2'-dypiridyl and the donating atoms of the solvents would be orthoaxially located.[2]

Under these assumptions the potential operator derived[3,4] for the bis complex is:

$$V_{C2v} = r^2\,\frac{2\sqrt{5\pi}}{5}\left(\frac{Q_N}{R_N^3}-\frac{Q_X}{R_X^3}\right)Y_2^\circ +$$
$$\frac{r^4\sqrt{\pi}}{2}\left(\frac{Q_N}{R_N^5}+\frac{Q_X}{R_X^5}\right)Y_4^\circ + r^4\,\frac{4\sqrt{\pi}}{3}\,\frac{Q_N}{R_N^5}\,Y_4^\circ +$$
$$\frac{r^4\sqrt{70\pi}}{12}\left(\frac{Q_N}{R_N^5}+\frac{Q_X}{R_X^5}\right)\left\{Y_4^4+Y_4^{-4}\right\}$$

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[1] L. Gil, E. Moraga, and S. Bunel, *Mol. Phys.*, *12*, 333 (1967).

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where R is the metal-ligand distance and Q is the charge on the ligand atom bonded to nickel.

The potential corresponding to the mono-chelate compound is easily obtained by permutation of the subindices N and X.

Applying the potential thus obtained, the mono-electronic matrix elements for the bis-chelate compound with octahedral functions as a base are:

$$<z^2/V/z^2> = 2(Ds^N-Ds^X)+33/7\ Dq^N+\ 9/7\ Dq^X$$
$$<x^2-y^2/V/x^2-y^2> = 2(Ds^X-Ds^N)+23/7\ Dq^N+19/7\ Dq^X$$
$$<xy/V/xy> = 2(Ds^X-Ds^N)-12/7\ Dq^N-16/7\ Dq^X$$
$$<yz/V/yz> = (Ds^N-Ds^X)-22/7\ Dq^N-\ 6/7\ Dq^X$$
$$<xz/V/xz> = (Ds^N-Ds^X)-22/7\ Dq^N-\ 6/7\ Dq^X$$

where:

$$Dq = \frac{1}{6}\frac{Q}{R^5}r^{-4}$$

and:

$$Ds = \frac{1}{7}\frac{Q}{R^3}r^{-2}$$

In these expressions it is seen that the effect of the solvent is separated from the dipyridyl effect.

Permutation of the superindices gives the matrix elements for the mono-chelate complex.

The determinantal wave functions of symmetry C_{2v} used appear below in «hole»[4] formalism:

$$\Psi{}^3B_1{}^0 = \quad |(x^2-y^2)z^2|$$
$$\Psi{}^3A_1{}^a = \quad |xy\ z^2|$$
$$\Psi{}^3A_2{}^a = \frac{1}{\sqrt{2}}|xz\ z^2|+|yz\ z^2|$$
$$\Psi{}^3B_2{}^a = \frac{1}{\sqrt{2}}|xz\ z^2|-|yz\ z^2|$$
$$\Psi{}^3A_2{}^b = \frac{1}{\sqrt{2}}|xz(x^2-y^2)|-|yz(x^2-y^2)|$$
$$\Psi{}^3B_2{}^b = \frac{1}{\sqrt{2}}|xz(x^2-y^2)|+|yz(x^2-y^2)|$$
$$\Psi{}^3B_1{}^b = \quad |xy(x^2-y^2)|$$
$$\Psi{}^3A_2{}^c = \frac{1}{\sqrt{2}}|xz\ xy|+|yz\ xy|$$
$$\Psi{}^3B_2{}^c = \frac{1}{\sqrt{2}}|xz\ xy|-|yz\ xy|$$
$$\Psi{}^3B_1{}^c = \quad |xz\ yz|$$

The superindices 0, a, b, c appearing in the representations correspond to states derived from $^3A_2$ (F), $^3T_2$ (F), $^3T_1$ (F) and $^3T_1$ (P) respectively of nickel in octahedral surroundings.

Table I shows the configuration matrices built up for the triplet states of the bis complex. The corresponding matrices of the mono complex are obtained from these.

It is possible to verify that, giving the same value to the parameters representing the dipyridyl and the solvent, the diagonal elements of matrices are transformed into those corresponding to the octahedral field.

In the numerical solution of the secular equations, the Dq values given in the literature[5,6] were directly used.

The same was done with the repulsion parameter B. But in this case intermediate values were taken proportional to the number of 2,2'-dipyridyl and solvent molecules present in the corresponding model (Table IV).

In the estimation of Ds^N and Ds^X, the ratio Ds/Dq $=K$[7,8,9] was used, K changing from 0 to 0·8 thus covering the range of published values.

In the present study a value of 0.2 was given to K since this gives the best correspondence between the calculated and experimental values of the absorption maxima.

It has been found that the energy levels are affected little by the variation of K. This is due to the fact that the Ds terms always appear as differences between the Ds values of the dipyridyl and of the solvent. These differences are small compared to the remaining terms appearing in the diagonal of each matrix.

For $K=0$ the ligand field diagonal perturbation elements are expressed only in terms of the Dq values of the dipyridyl and of the solvents. They are not made equal to the diagonal perturbation terms obtained with Dq average (except for the fundamental state) as can be seen in Table V for the «bis compound».

The energy levels obtained with $K=0$ do not give a better agreement with the experimental bands. On comparing the energy levels obtained with $K=0$ and with $K=0.2$, it is observed that the differences are not bigger than 0.17 kK as in the case of the $^3B_1$ state of the $[Ni(dip)_2(H_2O)_2]^{2+}$ ion in dimethylsulfoxide.

In this case a value of 17,473 kK is obtained. The result obtained with $K=0.2$ agrees better with the experimental values.

On performing numerical calculations the authors have kept in mind the criticism some authors[10,11,12] have made regarding the application of parameters obtained from octahedral complexes to structures of low symmetry. Nevertheless the satisfactory results obtained give support to this approach.

Tables II and III show a summary of the maximum values together with extinction coefficients of the band observed, and the calculated values with their corresponding representations in C_{2v} symmetry.

Ligand field calculations show only two components under each band. The states $^3A_2$ and $^3B_2$ have the same energy, they are accidentally degenerate.

The energy difference between the states $^3A_2$ and $^3A_1$ corresponding to the components of the first band

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Table I.

	$^3A_2^a$	$^3A_2^b$	$^3A_2^c$
$^3A_2^a$	$-3\,Ds^N+3\,Ds^X-11/7\,Dq^N-3/7\,Dq^X$ $+28\,A-41\,B+21\,C$	$-3\sqrt{3}\,B$	$-3\sqrt{3}\,B$
$^3A_2^b$		$Ds^N-Ds^X-1/7\,Dq^N-13/7\,Dq^X$ $+28\,A-47\,B+21\,C$	$3/2\,B$
$^3A_2^c$			$Ds^N-Ds^X+34/7\,Dq^N+22/7\,Dq^X$ $+28\,A-47\,B+21\,C$
	$^3B_1^0$	$^3B_1^b$	$^3B_1^c$
$^3B_1^0$	$-8\,Dq^N-4\,Dq^X$ $+28\,A-50\,B+21\,C$		
$^3B_1^b$		$4Ds^N-4Ds^X-11/7\,Dq^N-3/7\,Dq^X$ $+28\,A-38\,B+21\,C$	$6\,B$
$^3B_1^c$			$-2\,Ds^N+2\,Ds^X+44/7\,Dq^N+12/7\,Dq^X$ $+28\,A-47\,B+21\,C$
	$^3A_1^a$		
$^3A_1^a$	$-3\,Dq^N+Dq^X$ $+28\,A-50\,B+21\,C$		

Table II. [Ni dip$(H_2O)_4$]$(ClO_4)_2$ [a]

Solvent	First band cm^{-1} observed	First band cm^{-1} Calculated	Second band cm^{-1} observed	Second band cm^{-1} Calculated
Dimethylsulfoxide	10,101(5.45)	9,007 $^3A_2$ $(^3B_2)$ 10,175 $^3A_1$	16,065(4.15)	15,250 $^3B_1$ 16,303 $^3A_2$ $(^3B_2)$
Dimethylformamide	10,153(6.70)	9,500 $^3A_2$ $(^3B_2)$ 10,500 $^3A_1$	16,529(5.13)	15,870 $^3B_1$ 16,870 $^3A_2$ $(^3B_2)$
Pyridine	11,111(6.19)	10,367 $^3A_2$ $(^3B_2)$ 11,075 $^3A_1$	17,799(7.56)	16,970 $^3B_1$ 17,829 $^3A_2$ $(^3B_2)$
Acetonitrile	11,000(6.66)	10,854 $^3A_2$ $(^3B_2)$ 11,400 $^3A_1$	17,921(6.20)	17,626 $^3B_1$ 18,438 $^3A_2$ $(^3B_2)$

[a] Figures in brackets correspond to extinction values.

Table III. [Ni(dip)$_2$$(H_2O)_2$]$(ClO_4)_2$

Solvent	First band cm^{-1} observed	First band cm^{-1} calculated	Second band cm^{-1} observed	Second band cm^{-1} calculated
Dimethylsulfoxide	10,869(7.75)	10,175 $^3A_1$ 11,065 $^3A_2$ $(^3B_2)$	17,974(7.57)	17,644 $^3B_1$ 18,039 $^3A_2$ $(^3B_2)$
Dimethylformamide	10,989(8.08)	10,500 $^3A_1$ 11,242 $^3A_2$ $(^3B_2)$	17,921(6.74)	17,896 $^3B_1$ 18,301 $^3A_2$ $(^3B_2)$
Pyridine	11,363(5.80)	11,075 $^3A_1$ 11,571 $^3A_2$ $(^3B_2)$	18,622(7.27)	18,343 $^3B_1$ 18,797 $^3A_2$ $(^3B_2)$
Acetonitrile	11,627(7.84)	11,400 $^3A_1$ 11,731 $^3A_2$ $(^3B_2)$	18,727(9.41)	18,567 $^3B_1$ 19,088 $^3A_2$ $(^3B_2)$

Table IV.

Ligands / * Parameters	Dipyridyl	Dimethyl sulfoxide	Dimethyl formamide	Pyridine	Acetonitrile
Dq	1,230	805	870	985	1,050
B (ave) «mono» compound		893	883	867	877
B (ave) «bis» compound		866	861	853	858

* All values are given in cm^{-1}.

in less than 1,168 cm^{-1} in all cases. A similar difference occurs between the components of the second band. It is easy to understand then why none of the bands show splitting, even though those having a higher difference between the components are the more deformed.

This result allows one to understand why hexacoordinated complexes of low symmetry, such as C_{2v}, formed by mixed ligands exhibit spectral curves of shape similar to the curves shown by octahedral complexes.

The shoulders appearing in the first band or at the base of the band near 13,000 cm^{-1} correspond to spin forbidden transitions $^3B_1 \rightarrow {}^1A_1$ and $^3B_1 \rightarrow {}^1B_1$.

Table V.

State O_h Symmetry	Diagonal perturbation elements Dq average	State C_{2v} symmetry	Diagonal perturbation elements K = 0
$^3T_1$ (P)	$16/3\ Dq^N+8/3\ Dq^X$	$^3A_2$ ($^3B_2$)	$34/7\ Dq^N+22/7\ Dq^X$
$^3T_1$ (F)	$-4/3\ Dq^N-2/3\ Dq^X$	$^3B_1$	$44/7\ Dq^N+12/7\ Dq^X$
		$^3A_2$ ($^3B_2$)	$-1/7\ Dq^N-13/7\ Dq^X$
$^3T_2$ (F)	$-4/3\ Dq^N-2/3\ Dq^X$	$^3B_1$	$-11/7\ Dq^N-3/7\ Dq^X$
		$^3A_2$ ($^3B_2$)	$-11/7\ Dq^N-3/7\ Dq^X$
$^3A_2$ (F)	$-8\ Dq^N-4\ Dq^X$	$^3A_1$	$-3\ Dq^N+Dq^X$
		$^5B_1$	$-8\ Dq^N-4\ Dq^X$

Table VI. [a]

Solvent	* $[Ni\ dip(H_2O)_2(NO_3)_2]\ .\ H_2O$		* $[Ni(dip)_2(NO_3)_2]\ .\ 2H_2O$	
	First band cm^{-1} observed	Second band cm^{-1} observed	First band cm^{-1} observed	Second band cm^{-1} observed
Dimethylsulfoxide	10,101(5.52)	16,393(4.47)	10,949(8.83)	17,730(7.62)
Dimethylformamide	10,101(6.64)	16,598(6.01)	10,989(9.71)	17,986(8.79)
Pyridine	10,810(6.10)	17,065(7.91)	11,235(7.75)	18,416(9.10)
Acetonitrile	10,526(7.29)	16,892(13.66)	11,235(8.95)	18,182(13.56)

[a] Figures in brackets correspond to extinction values. * Proposed formulae.

They have their origin in the $^3A_2 \rightarrow {}^1E$ transition in octahedral symmetry.

In the ion, $[Ni(dip)(H_2O)_4]^{2+}$, the $^1B_1$ state has higher energy than the $^3A_1$ state, the difference being 8B+2C. Therefore under C_{2v} symmetry, the $^3A_1$ state will never intersect the $^1B_1$ state as in the case with the states $^3T_2$ and ^1E in octahedral symmetry.

In the ion, $[Ni(dip)_2(H_2O)_2]^{2+}$, the $^3A_2$ state is placed in between the $^3A_1$ and $^1B_1$ states, thus reducing the distance between the spin allowed and spin forbidden bands.

On the other hand, the energy of the $^1A_1$ state cannot be expressed in a simple form since it comes from a sixth degree equation. The numerical solutions to this equation, for C/B values fluctuating between 3.5 and 4.0,[13] show that the energy of the $^1A_1$ states in always less than that of the $^1B_1$ state. The difference between them is never greater than 0.5 kK.[14]

Both the shift and the position of the bands calculated for the assumed model agree well with the observed values, considering that the maxima observed correspond to intermediate values of two transitions.

The results are not so good for the spectra of solution of the same complexes, where the anion perclorate is replaced by nitrate and the difference between the calculated and observed value increases with the increase of the Dq value of the solvent (Table VI).

It is possible to ascribe this difference to the structure of the complex. The nitrate ion would be covalently bonded to nickel and the solvents would not be able to displace it under the conditions existing when the measurements were performed.

In order to analyze this situation, the I.R. spectra of the nitrates of the mono, bis and tris complexes of nickel and 2,2'dipyridyl have been measured.

The possibility has been proposed that the nitrate ion covalently bonded to a metal reduces its local symmetry from D_{3h} to C_{2v} allowing for the separation of the E' components of the I.R. band placed near 1,380 cm^{-1}.[15,16]

Our determinations of the I.R. spectrum of the compound $[Ni(dip)_3](NO_3)_2$ show a strong and sharp-pointed band at 1,385 cm^{-1} and another band of medium strength at 825 cm^{-1}, assigned to E' and A$_2''$ in D_{3h} symmetry, which are equivalent to the bands present in the ionic nitrates.[17]

In the species $[Ni(dip)_2(NO_3)_2]2H_2O$ and $[Ni(dip)(NO_3)_2(H_2O)_2]H_2O$ the I.R. spectra are a bit different. The first complex shows the E' band separated in two components located at 1,385 cm^{-1} and 1,360 cm^{-1} and the second also split into two components placed at 830 cm^{-1} and 806 cm^{-1}.

The latter compound presents a spectrum similar to the former, the E' band having a shoulder at 1,408 cm^{-1} and a maximum at 1,385 cm^{-1}, the second band being split in two at 825 and 813 cm^{-1}. The E' band near 724 cm^{-1}, which is of low strength in the ionic compounds, is not observed in the complexes studied.

The observed characteristics of the infrared spectra of both the mono and bis-chelate make it possible to propose a covalent bond between nickel and the nitrate ion even though there is not sufficient basis to predict at this moment whether the nitrate ion is behaving as a mono or a bis-chelate ligand.

Experimental Section

Spectrophotometric measurements were performed in a Beckman DU-2 spectrophotometer with 0.1 *M*

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solutions of the complexes.

Solvents used were Merck, Matheson-Colleman and Bell, spectral quality.

Magnetic moment measurements were performed in a Gouy balance calibrated with trisethilenediamine Ni^{II} thiosulfate at 293°K.

The infrared spectra were obtained with a Leitz Wetzlar G III spectrophotometer in a KBr disc.

Preparation of the Compounds. $[Ni(dip)(H_2O)_4](ClO_4)_2$. It was prepared at room temperature by mixing a 0.1 *M* solution of $Ni(ClO_4)_2 \cdot 6H_2O$ in acetone with an equal volume of 0.1 *M* solution of 2,2'-dipyridyl in the same solvent. The solution turned pink and crystals of the same colour precipitated. After 24 hours the solution changed from pink to blue and the crystals dissolved. This solution was concentrated to a third of its volume and the solvent was evaporated in a vacuum chamber. Light-blue microcrystals were thus obtained.

Anal. Calcd. Ni, 12.08; C, 24.70; N, 5.70; H, 3.30; Obtained Ni, 12.03; C, 25.00; N, 5.80; H, 3.20; μ, 3.35.

$[Ni(dip)_2(H_2O)_2](ClO_4)_2$. It was prepared by mixing a 0.1 *M* solution of $Ni(ClO_4)_2 \cdot 6H_2O$ in acetone with an equal volume of 0.2 *M* solution of 2,2'-dipyridyl in acetone. The solution turned pink-violet and abundant pink crystals precipitated. It was set aside until the solution changed to violet and was then refluxed to dissolve the crystals. This solution was concentrated to a third of its volume and the solvent was evaporated in a vacuum chamber. Light-violet microcrystals were thus obtained.

Anal. Calcd. Ni, 9.68; C, 39.64; N, 9.24; H, 3.32; Obtained, Ni, 9.40; C, 39.50; N, 9.50; H, 3.20; μ, 3.24.

$[Ni(dip)(NO_3)_2(H_2O)_2] \cdot H_2O$. It was prepared at room temperature by adding a 0.1 *M* solution of 2,2'-dipyridyl in acetone, drop by drop and with continous stirring, to an equal volume of 0.1 *M* solution of $Ni(NO_3)_2 \cdot 6H_2O$ in acetone. This operation took about 40 minutes at the end of which time small blue crystals appeared on the walls of the flask. The solvent was slowly evaporated at room temperature (24 hours). Rosette blue crystals were thus obtained.

Anal. Calcd. Ni, 14.94; C, 30.50; N, 14.20; H, 3.59; Obtained, Ni, 14.81; C, 30.70; N, 14.00; H, 3.60; μ, 3.25.

$[Ni(dip)_2(NO_3)_2] \cdot 2H_2O$. It was obtained by mixing a 0.1 *M* solution of $Ni(NO_3)_2 \cdot 6H_2O$ in acetone with an equal volume of 0.2 *M* solution of 2,2'-dipyridyl in the same solvent. The red crystals that appeared were refluxed for 3 hours. After this time they turned from red to violet. They were vacuum filtered and washed several times with acetone.

Anal. Calcd. Ni, 11.86; C, 48.50; N, 16.90; H, 3.25; Obtained, Ni, 11.89; C, 48.10; N, 16.50; H, 3.30; μ, 3.23.

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