

SOLVENT EFFECTS ON THE ELECTRONIC STRUCTURE OF BIS(4-DIMETHYLAMINODITHIOBENZYL) NICKEL [Ni^{II}(4-DMAB)] FROM UV-VIS AND EPR SPECTRA

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Abstract—The UV-VIS and EPR spectra of solutions of Ni^{II}(4-DMAB) in 10 solvents with donor number (DN) from 0.1 to 38.8¹ have been recorded. The changes in the spectra are explained in terms of a change in symmetry of the Ni^{II}(4-DMAB) complex on increase in donor number of the solvent. The symmetry change is from square planar to rhombic bipyramidal with corresponding change in electronic configuration of the nickel ion from d_{z²} to d_{x²-y²}. Light was observed to accelerate this structural change.

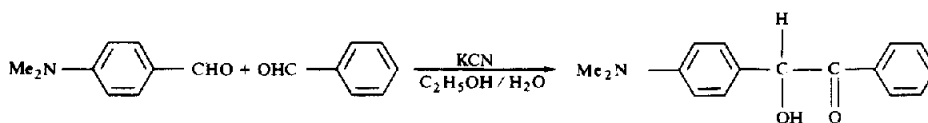
In the current literature on dithiolane complexes of nickel²⁻⁷ there is a lack of systematic studies of the effect of electron-donor properties of different solvents on the electronic structure of these complexes.

In the present work we have investigated the effect of solvents with DN from 0.1 to 38.8 on the electronic structure of the Ni^{II}(4-DMAB) complex.

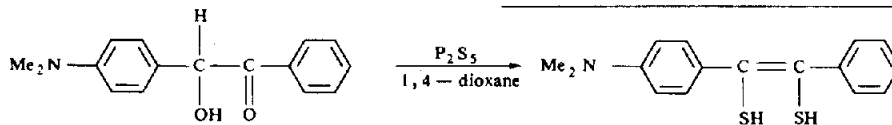
The knowledge of the mechanism of interaction of different solvents with the Ni^{II}(4-DMAB) molecule is of importance in view of the possibility of utilization of this dye as a nonlinear filter for a neodymium YAG laser.

EXPERIMENTAL

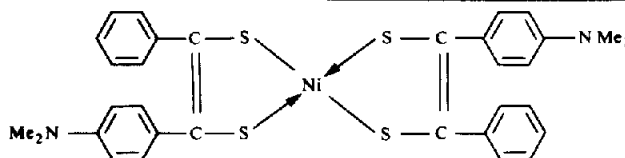
The synthesis of Ni^{II}(4-DMAB) was carried out by reacting p-N,N-dimethylaminobenzaldehyde with benzaldehyde in the presence of KCN in 1:1 water-ethanol mixture.⁹ The following reaction takes place



The unsymmetric benzoine (m.p. 162–164°) obtained is reacted with P₂S₅ to give a product with two thioalcohol groups according to



Finally the thioalcohol derivative is complexed with NiCl₂ in dioxane to give [Ni^{II}(4-DMAB)]:



A pure sample of the complex (m.p. 273°) was obtained by crystallization from dioxane followed by Soxhlet extraction, also with dioxane. The identity and purity of the complex were also confirmed by means of IR spectroscopy.

The UV-VIS spectra were recorded on Beckman Acta VII spectrometer using variable thickness cells, at room temperature. Equal concentrations of Ni^{II}(4-DMAB) (1 × 10⁻³ M dcm⁻³) were used for all solvents.

EPR spectra of identical solutions were recorded using Bruker 418-BR spectrometer working in X-band. The EPR measurements were carried out at 130 K on rapidly frozen samples owing to considerable dielectric losses of some solvents at room temperature.

RESULTS AND DISCUSSION

It is known from the literature^{2,7} that tetrathiolane nickel species of the type [Ni-S₄]_n^z are characterised by the

presence of intense electronic absorptions occurring in the visible and in the near-IR region. It has been established

that these bands are not due to d-d transitions but are charge transfer in character.

Table 1. UV-VIS data of the complex $Ni^{II}(4-DMAB)$ in various solvents

No.	Solvent	DN	λ_1 nm	$\epsilon_1 \times 10^3$	λ_2 nm	$\epsilon_2 \times 10^3$	λ_3 nm	$\epsilon_3 \times 10^3$	λ_4 nm	$\epsilon_4 \times 10^3$	λ_5 nm	$\epsilon_5 \times 10^3$	λ_6 nm	$\epsilon_6 \times 10^3$	λ_7 nm	$\epsilon_7 \times 10^3$	λ_8 nm	$\epsilon_8 \times 10^3$
1	Methylene chloride	0.1			315	21,000	375	10,200	450	3600					1072	10,800	1140	19,600
2	Nitromethane	2.7			325	48,200									1080	19,200	1140	19,600
3	Nitrobenzene	4.4													1088	27,200	1124	29,400
4	Chlorobenzene	9.0			320	16,900	350	9600	425	5400	455	2700			1068	49,200	1128	43,200
5	Acetonitrile	14.1	265	33,000	315	58,500									1075	29,400		
6	Dioxane	14.8	250	17,400	305	18,000	350	14,700										
7	Tetrahydrofuran	20.0	275	35,000	320	45,000			450	5400	460	10,800	978	7550	1058	22,800	1172	2150
8	Tetrahydrofuran + NaH		255	37,200	320	38,400									1096	31,200	1130	18,600
9	Dimethylformamide	27.0			317	12,600												
10	Dimethylsulfoxide	29.8	263	10,500	320	18,400												
11	Hexamethylphosphoric triamide	38.8	275	14,000					450	2400	520	720	985	3480				

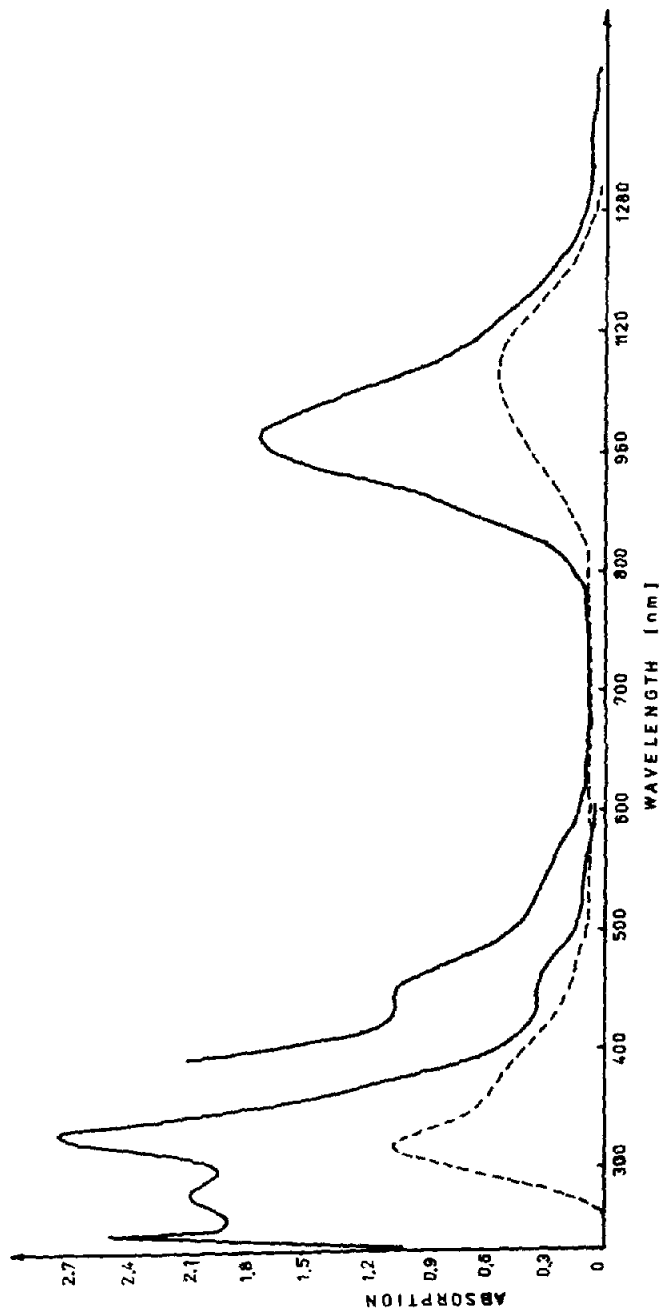


Fig. 1. UV-VIS spectra of $\text{Ni}^{\text{II}}(\text{4-DMAB})$ in — HMPA, --- CH_2Cl_2 .

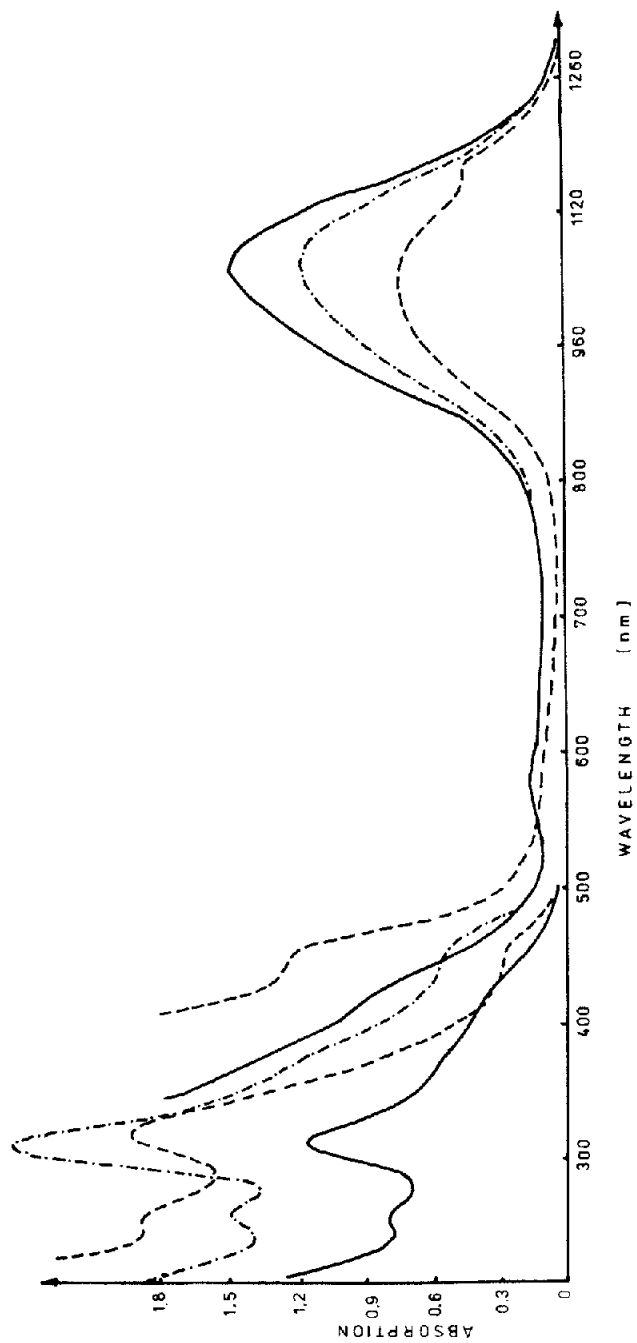


Fig. 2. UV-VIS spectra of Ni^{II}(4-DMAAB) in THF — freshly prepared, - - - after 10 days, - · - · freshly prepared + NaH.

Schrauzer and Mayweg² have determined for the complexes of the type [NiS₄C₄R₄]^{0 or 1} that these low energy absorption bands are the result of π - π charge transfer transitions and the remaining bands were described as M = π or n = s \rightarrow M or π type.

Ni^{II}(4-DMAB) had an intense band in the near-IR with ν_{\max} dependent on the solvent as shown in Table 1. Two more bands in the UV region, a strong one with $\lambda_{\max} = 325$ nm, and a somewhat weaker one with $\lambda_{\max} = 370$ nm were also observed. In solvents with low DN (0.1~9) such as methylene chloride (Fig. 1), chlorobenzene and nitrobenzene the electronic spectra of Ni^{II}(4-DMAB) were found to be stable with the time. In solvents with higher donor numbers (9~20) however, such as acetonitrile, dioxane and tetrahydrofuran (THF) the electronic spectrum of Ni^{II}(4-DMAB) was observed to exhibit changes with time (Fig. 2).

The electronic spectra of freshly prepared solutions of the complex in the above mentioned solvents were identical with the spectrum in methylene chloride. With time, the longest wavelength band in the electronic spectrum exhibited an increasing blue shift and a new weaker band with an even longer wavelength was formed. A second new band with $\lambda_{\max} = 450$ nm was also formed in the short wavelength part of the spectrum.

For solvents with high DN such as dimethylformamide (DMF), pyridine, dimethylsulfoxide (DMSO) and hexamethylphosphoric triamide (HMPA) a blue shift in position of the band falling in the near-IR, as well as the formation of a new band in the 450 nm region were also observed (Table 1 and Fig. 1). In order to gain a fuller understanding of solvent effects on Ni^{II}(4-DMAB) an analysis of EPR spectra of the various solutions was carried out. The results are summarized in Table 2 and show how the EPR spectrum of Ni^{II}(4-DMAB) changes with the donor number of the solvent (Table 2, Fig. 3). The EPR spectrum of the complex was not observed for solvents with low DN (Fig. 3). Irradiation of samples with white light or Nd-YAG laser output did not yield a spectrum either. With increase in DN the formation of the radical signal ($\Delta H \sim 11$ G, $g = 2.003$) (Fig. 3) is observed after a few days. Exposure of the sample to white light or Nd-YAG laser output results in an acceleration of this process. For solvents with DN approximately higher than 26 the formation of an anisotropic EPR spectrum with components g_1, g_2, g_3 is observed (Fig. 3). In addition, for solutions of Ni^{II}(4-DMAB) in DMF and DMSO, the spectrum is formed with time and the formation can again be accelerated with white light or Nd-YAG laser output. For solutions of Ni^{II}(4-DMAB) in pyridine or HMPA a strong EPR signal appears immediately on dissolving the complex.

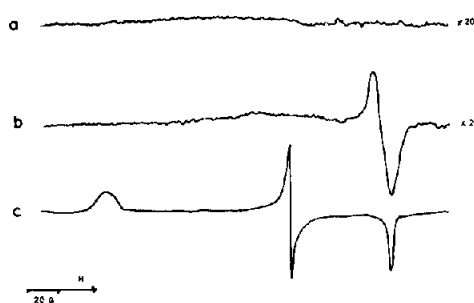


Fig. 3. EPR spectra of Ni^{II}(4-DMAB) in (a) CH₂Cl₂, (b) THF, (c) HMPA.

On the basis of our results it is possible to distinguish three mechanisms of interaction between the solvent and the complex Ni^{II}(4-DMAB) the classification being made in terms of DN of the solvent. In the first group of solvents (DN from 0.1 to 9) the interaction is thought to be very weak, such that the resulting perturbation in the electron density distribution in the molecule of the complex is not manifested in the UV-VIS and EPR spectra.

The absence of the EPR signal suggests that the complex is diamagnetic with square planar structure and the associated d_{z^2} electronic configuration of the nickel ion.

Increase in DN of the solvent (up to 20) leads to an increase in the interaction with the complex resulting in a change in electron density distribution on the ligand and in the appearance of a radical signal in the EPR spectrum and of new bands in the electronic spectrum. These changes can be attributed to the formation of a monoanionradical system of the complex.

Additional proof for the formation of monoanionradicals is provided by the comparison of UV-VIS and EPR spectra of freshly made up solution of Ni^{II}(4-DMAB) in THF which was reduced with NaH with spectra of a solution of Ni^{II}(4-DMAB) in THF which was allowed to stand for a few days. These two sets of spectra are identical although the intensive bands with $\lambda_{\max} = 450$ nm and $\lambda_{\max} = 1172$ nm and a radical signal in EPR appear immediately on reduction with NaH while without NaH these appear spontaneously after a period of a few days. This yields support to our supposition since it is known from the literature² that identical reduction of many metallorganic complex including nickel complexes of type [Ni-S₄]₂ⁿ in solvents with medium DN (9-20) leads to the formation of monoanion radicals.

The analysis of the EPR results suggests that solvents with high DN (from 26 to 40) lead to a change in the

Table 2. EPR data of the complex Ni^{II}(4-DMAB) in various solvents

No.	Solvent	DN ¹	g_1	g_2	g_3	g radical
1	Methylene chloride	0.1				
2	Nitromethane	2.7				
3	Acetonitrile	14.1				2.003
4	Dioxane	14.8				2.003
5	Tetrahydrofuran	20.0				2.003
6	Dimethylformamide	26.6	1.999	2.040	2.118	
7	Dimethylsulfoxide	29.8	1.999	2.040	2.119	
8	Pyridine		1.999	2.040	2.119	
9	Hexamethylphosphoric triamide	38.8	1.999	2.040	2.119	

electron configuration of the central ion from $d_{z^2}^2$ to $d_{x^2-y^2}^2$. This is connected with the transition of the complex from square planar to rhombic bipyramidal symmetry, resulting from the coordination of solvent molecules at positions 5 and 6 of the central ion. The analogous effect of the coordination of the solvent to the central ion was observed by Cox *et al.*⁸ for the nickel complexes with salicylaldoxime in pyridine-benzene mixtures.

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