106. *Exchange Reactions and Magnetic Susceptibilities of Complex Salts. Part IV.* Correlation with Absorption Spectra.*

By H. C. Clark and A. L. Odell.

Absorption spectra in the visible and ultraviolet regions of six nickel chelate compounds in various solvents have been determined, and correlations with magnetic measurements are suggested.

In pyridine solutions of bis-salicylaldiminenickel and bis-salicylaldehyde-*o*-phenylenedi-iminenickel, and in alcohol and dioxan solutions of bis-*N*-methylsalicylaldiminenickel, the effects of temperature changes can be correlated with the previously reported magnetic susceptibilities which indicated the presence of temperature-dependent equilibria between diamagnetic and paramagnetic forms. Absorption spectra in other solvents are discussed.

Although detailed analysis of absorption spectra of complex compounds is not yet possible, several attempts have been made to relate these spectra to their stereochemistry. McKenzie, Mellor, Mills, and Short [1] found that many paramagnetic nickel complexes show the same absorption bands as the free ligands, while for the diamagnetic complexes there appears a new band at *ca.* 410 mμ. These spectra were investigated in solution, but, as the authors point out, most of the magnetic-susceptibility determinations were made on solid samples. Willis and Mellor [2] reported that many of these complexes show a change from diamagnetism to paramagnetism on entering solution, and it has also been shown [3] that in many instances the change is incomplete and dependent on temperature. It was therefore decided to re-investigate the absorption spectra of the compounds over a temperature range.

We followed the procedure of McKenzie *et al.*[1] in tabulating results as molecular extinction coefficients (ε) at the wavelength showing absorption maxima. Tables 1 and 2 refer to measurements at 20°, and Table 3 refers to variation of maxima and to the appearance of new maxima as the temperature changes. From these Tables 1 and 2 it is clear that absorption in the region 350—450 mμ appears only when the metal ion and ligand unite to form the complex. Salicylaldehyde-ethylenedi-imine is an exception and shows a weak

Table 1. *Absorption spectra of complex compounds in various solvents at* 20°.

Complex	Solvent *	λ_1	ε_1	λ_2	ε_2	λ_3	ε_3
Bis-salicylaldehydenickel dihydrate	MeOH	385	4900	—	—	—	—
	C_5H_5N	398	7000	—	—	—	—
Bis-salicylaldehyde-ethylenedi-iminenickel	MeOH	402	5800	325	8050	—	—
	C_5H_5N	414	6400	328	8320	—	—
Bis-salicylaldiminenickel	MeOH	402	4900	322	9580	—	—
	C_5H_5N	376	6460	324	6000	—	—
Bis-salicylaldoximenickel	EtOH	383	4850	302	17,500	—	—
	$CHCl_3$	388	5350	302	17,500	—	—
	C_5H_5N	355	7650	—	—	—	—
Bis-*N*-methylsalicylaldiminenickel	EtOH	355	5900	330	6100	—	—
	$C_4H_8O_2$	410	780	315	7050	—	—
	$CHCl_3$	414	3300	325	8200	—	—
	C_6H_6	413	3500	325	8550	—	—
	C_6H_5Me	414	3400	325	8400	—	—
	m-$C_6H_4Me_2$	414	3600	325	8800	—	—
	C_6H_{12}	416	3400	328	8500	—	—
	C_5H_5N	378	8300	—	—	—	—
Bis-salicylaldehyde-*o*-phenylene-di-iminenickel	MeOH	470	8750	372	26,800	300	18,150
	$CHCl_3$	478	8600	378	27,000	300	18,300
	C_5H_5N	445	19,000	384	18,000	—	—

* $C_4H_8O_2$ = dioxan; C_6H_{12} = *cyclo*hexane.

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* Parts II and III, *J.*, 1955, 3431, 3435.

[1] McKenzie, Mellor, Mills, and Short, *J. Proc. Roy. Soc. New South Wales*, 1944, **78**, 70.

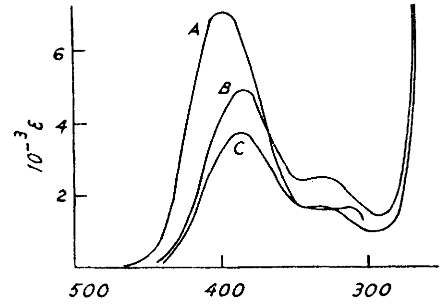
[2] Willis and Mellor, *J. Amer. Chem. Soc.*, 1947, **69**, 1237.

[3] Clark and Odell, *J.*, 1955, 3431.

absorption band at 403 mμ, which Csokan and Nyiri[4] have attributed to a hydrogen bond between the nitrogen and the oxygen atom in the *ortho*-position. It seems reasonable to conclude that the variations in intensities in the bands of this region of the spectrum are associated with changes in the mode of bonding of the metal atom rather than with changes in the structure of the ligand.

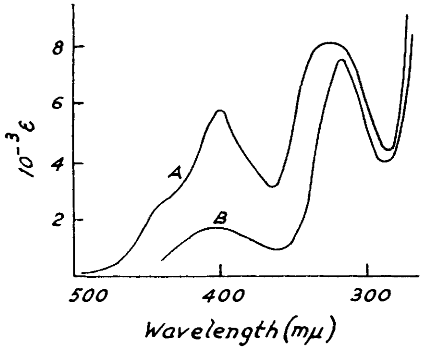
Temperature effects were observed for the solutions listed in Table 3. Other solutions showed variations with temperature only of the order of the experimental error.

FIG. 1. *Bis-salicylaldehydenickel.*



A, in pyridine; *B*, in methyl alcohol; *C*, in ethyl alcohol.

FIG. 2.



A, Bis-salicylaldehyde-ethylenedi-imine-nickel in methyl alcohol.
B, Salicylaldehyde-ethylenedi-imine in methyl alcohol.

Bis-salicylaldehydenickel (Fig. 1) has a magnetic moment of 3·2 B.M. in the solid state, and 3·26 B.M. in pyridine solution. Basolo and Matoush[5] have isolated from the pyridine solutions a derivative containing two molecules of pyridine: it is probably an octahedral complex, and the marked similarity between the absorption spectra of the pyridine and the alcohol solutions leads one to suppose that two alcohol molecules also occupy co-ordination positions.

TABLE 2. *Absorption spectra of ligands in various solvents at* 20°.

Ligand	Solvent	λ_1	ε_1	λ_2	ε_2
Salicylaldehyde-ethylenedi-imine	MeOH	403	1270	318	7000
	C_5H_5N	—	—	319	6800
Salicylaldehyde-*o*-phenylenedi-imine	MeOH	—	—	330	8700
	C_5H_5N	—	—	330	9000
Salicylaldoxime[a]	EtOH	305	4000	265	6300

[a] Sone, *J. Amer. Chem. Soc.*, 1953, **75**, 5207.

TABLE 3. *Effect of temperature on absorption spectra.*

Complex	Solvent	Positions of maxima (mμ)	ε 0°	20°	35°	45°
Bis-salicylaldiminenickel	C_5H_5N	410	2860	3110	3410	3580
		375	7650	6450	5460	5130
		340	5350	5970	6400	6790
		322	5000	5900	6700	7250
Bis-*N*-methylsalicylaldimine-nickel	EtOH	410	1490	2130	2480	2580
		358	6500	6000	5380	5100
		330	5450	6050	6550	6620
Bis-*N*-methylsalicylaldimine-nickel	$C_4H_8O_2$	410	—	780	1160	1300
		360	—	2140	2140	1880
		315	—	7050	7150	7200
Bis-salicylaldehyde-*o*-phenylene-di-iminenickel	C_5H_5N	445	22,600	19,000	15,500	14,100
		384	14,900	17,850	20,200	22,000
		348	17,800	16,800	16,600	16,000

Bis-salicylaldehyde-ethylenedi-iminenickel (Figs. 2 and 3) shows the type of spectrum

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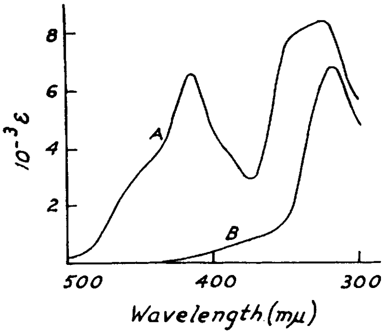
[4] Csokan and Nyiri, *Magyar Chem. Folyóirat*, 1941, **47**, 149.
[5] Basolo and Matoush, *J. Amer. Chem. Soc.*, 1953, **75**, 5663.

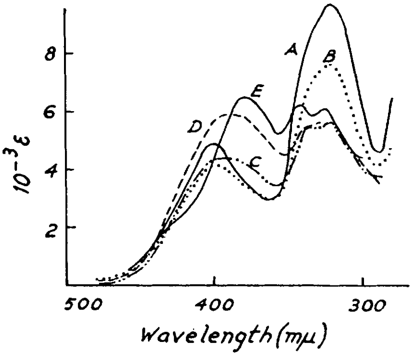
regarded by McKenzie *et al.*[1] as typical of diamagnetic nickel complexes, having an intense band at 402 mμ in methanol, and shifted to 414 mμ in pyridine. (This shift appears to be general for these nickel complexes in this solvent.) This complex is diamagnetic in the solid state and also in pyridine solution; it has a negligible rate of ligand exchange.[6] This behaviour may be explained [3] in terms of a dsp^2 planar configuration, or alternatively a d^2sp^3 disolvated octahedral structure involving the promotion of two electrons to a $5s$ orbital. The high energy increment involved in such a promotion renders the second explanation unlikely, especially in view of the weak co-ordinating properties of ethanol.

FIG. 3.



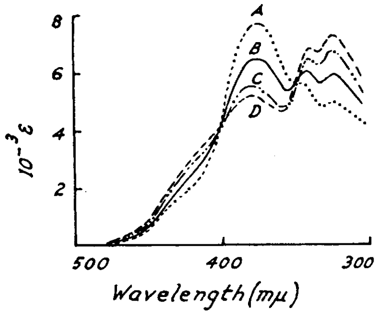
A, Bis-salicylaldehyde-ethylenedi-iminenickel in pyridine.
B, Salicylaldehyde-ethylenedi-imine in pyridine.

FIG. 4. *Bis-salicylaldiminenickel.*



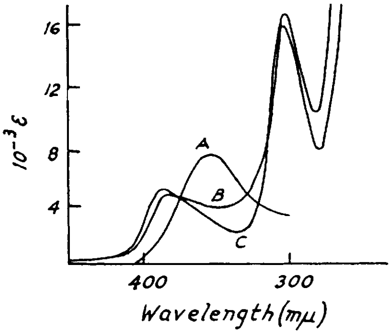
A, in methyl alcohol;
B, in 99% methyl alcohol–1% pyridine;
C, in 95% methyl alcohol–5% pyridine;
D, in 90% methyl alcohol–10% pyridine;
E, in pyridine.

FIG. 5. *Bis-salicylaldiminenickel in pyridine.*



A, at 0°; *C*, at 35°;
B, at 20°; *D*, at 45°.

FIG. 6. *Bis-salicylaldoximenickel.*



A, in pyridine; *B*, in ethyl alcohol;
C, in chloroform.

The similarity of the spectra in ethanol and in pyridine leads us to suppose that in each of these solvents the complex has a dsp^2 square configuration. In neither solvent was a change in magnetic moment or in absorption spectrum observed with changing temperature.

Bis-salicylaldiminenickel (Figs. 4 and 5) has in methanol solution an absorption spectrum of the form expected for a diamagnetic complex, although the magnetic susceptibility in this solvent could not be determined because of the low solubility. In Part II [3] it was shown that this compound in pyridine solution exhibits a temperature-dependent equilibrium between diamagnetic and paramagnetic forms, and it was suggested that the latter form was an octahedral bispyridine adduct. Absorption maxima were observed for the pyridine solution at 375, 343, and 324 mμ. A strong absorption at 322 mμ, with a pronounced "shoulder" in the 340 mμ region, was also observed in methanol

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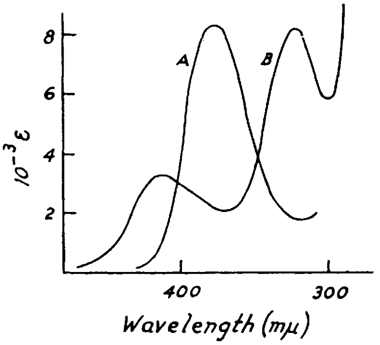
[6] Clark and Odell, *J.*, 1955, 3435.

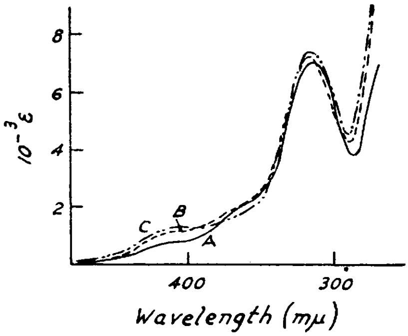
solution, in which the material is presumably diamagnetic. On the other hand, the 376 mμ band can reasonably be compared with the 378 mμ band observed in the absorption spectrum of bis-*N*-methylsalicylaldiminenickel in pyridine, where extreme paramagnetic behaviour is observed, which is ascribed to the presence of a bispyridine adduct. Curves in Fig. 4 show the rise of the 376 mμ peak, and the fall of the 342 and 324 mμ peaks, with increasing pyridine concentration in methanol solutions. On increase of temperature from 0° to 45°, the pyridine solution showed a decrease in the intensity of the 376 mμ band, and an increased absorption in the 400—415 mμ and 320—330 mμ regions (see Fig. 5).

FIG. 7. *Bis-*N*-methylsalicylaldiminenickel.*



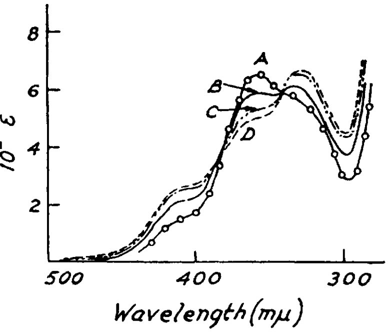
A, in pyridine; *B*, in chloroform.

FIG. 8. *Bis-*N*-methylsalicylaldiminenickel in dioxan.*



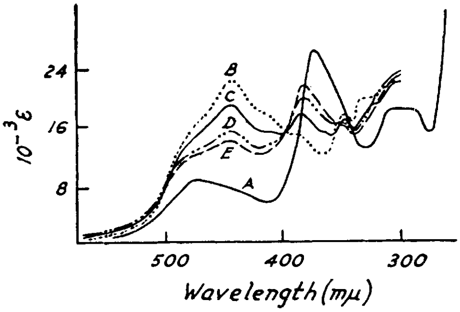
A, at 20°; *B*, at 35°; *C*, at 45°.

FIG. 9. *Bis-*N*-methylsalicylaldiminenickel in ethyl alcohol.*



A, at 0°; *B*, at 20°; *C*, at 35°; *D*, at 45°.

FIG. 10. *Bis-salicylaldehyde-*o*-phenylenediiminenickel.*



A, in methyl alcohol; *B*, *C*, *D*, *E*, in pyridine at 0°, 20°, 35°, and 45°, respectively.

This change is in agreement with the presence of a temperature-dependent equilibrium favouring the diamagnetic form at higher temperatures.

Bis-salicylaldoximenickel (Fig. 6) in ethanol solution showed absorption maxima at 383 and 302 mμ, the former not being observed for an ethanol solution of the ligand. These results agree with those of Sone.[7] It seems reasonable to suppose that the band at 383 mμ is analogous to the " nickel " band abserved in the 410 mμ region for diamagnetic complexes, the entire spectrum having been shifted some 20 mμ to shorter wavelengths. The spectrum of the chloroform solution of this complex is very similar to that of the ethanol solution. This was unexpected, in view of the magnetic moment of 1·7 B.M. found at 25° in chloroform,[3] which indicated a temperature-dependent equilibrium between paramagnetic and diamagnetic forms. The absorption spectra in both ethanol and chloroform showed no variation with temperature over the range 0—45°. In pyridine a single absorption maximum was observed at 355 mμ. With allowance for the shift of some 20 mμ (which

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[7] Sone, *J. Amer. Chem. Soc.*, 1953, **75**, 5207.

corresponds to 4·3 kcal./mole) observed with this complex in other solvents, this band may be compared with the 378 mμ band of the octahedral complexes. The isolation of a bispyridine adduct [3] of magnetic moment 3·2 B.M. supports this view.

Bis-*N*-methylsalicylaldiminenickel, although diamagnetic as a solid, was paramagnetic in all the solvents studied. In pyridine solution the formation of a bispyridine adduct has been established,[3] and the absorption spectrum of this solution (Fig. 7) shows only one band with a maximum at 378 mμ, suggesting again that this type of spectrum indicates octahedral configuration. In ethanol and dioxan solutions (Figs. 8 and 9), the observed magnetic susceptibilities indicate temperature-dependent equilibria. The spectra observed at 20° were different from those of typical diamagnetic complexes such as bis-salicylaldehyde-ethylenedi-iminenickel, and showed considerable variation with temperature. At higher temperatures, absorption increases in the 410 and 320 mμ regions, which are the typical bands of diamagnetic forms, while at lower temperatures these peaks become smaller and an intense band appears at 358 mμ. These results are thus correlated with the magnetic measurements. Similarity in the form of the absorption peak at 358 mμ in methanol at 0° to that at 378 mμ in pyridine (after allowance for the usual displacement to longer wavelengths in pyridine) suggests that the paramagnetic form is a disolvated octahedral adduct.

Absorption spectra of the complex in chloroform and in methylbenzenes do not fit into the pattern outlined above. Magnetic measurements have indicated the presence of equilibria between paramagnetic and diamagnetic forms in these solvents. The absorption spectra, however, showed typical " diamagnetic " bands at 415 and 325 mμ, and moreover, temperature changes caused no variation in intensity of these bands. Whether the paramagnetic form is octahedral or tetrahedral in these cases in not clear. Chloroform and the methylbenzenes are not likely to form strong bonds with the nickel atom, but the possibility of some solvation cannot be ruled out, as Rundle and Goring [8] have found evidence for a silver perchlorate–benzene complex.

Bis-salicylaldehyde-*o*-phenylenedi-iminenickel (Fig. 10). Magnetic measurements have shown that a temperature-dependent equilibrium between paramagnetic and diamagnetic forms exists in pyridine solutions of this complex. Absorption spectra in methanol and in chloroform solutions were identical and of the same general type as typical " diamagnetic " spectra, but with peaks at 470, 372—378, and 300 mμ. These bands were of high intensity. In comparing these spectra with those of other nickel complexes, it is convenient to regard the intense 372—378 mμ band as analogous to the 410 mμ " nickel " band, shifted 30 mμ to shorter wavelengths. This shift may be associated with the necessarily planar configuration of this ligand which would require *trans*-addition of the pyridine molecules. The absorption spectrum of the pyridine solution was different, and showed maxima at 442, 382, and 348 mμ. At higher temperatures, absorption increased in the 380 and the 470 mμ region, and decreased at 442 mμ; *i.e.*, at high temperatures, the absorption maxima occurred at approximately those wavelengths which showed strong absorption in the chloroform solution. This supports the observed increasing proportion of the diamagnetic form at higher temperatures.

The absorption spectra and magnetic susceptibilities of these complexes in solution can thus be correlated by using the postulate of an equilibrium between paramagnetic and diamagnetic forms in cases where the magnetic moments have intermediate values. Solutions in chloroform and hydrocarbon solvents do not, at present, fit this interpretation.

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[8] Rundle and Goring, *ibid.*, 1950, **72**, 5337.