

Remote attack by the reductant should be favored here, just as with the pentaammineterephthalate complex, and further there exists the possibility of chelation by the two remote carboxyl groups to yield the symmetric activated complex

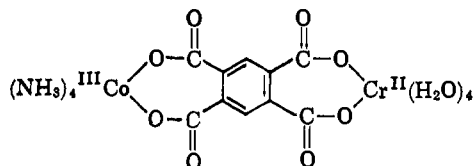


Table IV shows that only a minor fraction of reaction takes place by such a path. The rate of reduction appears to be at least as fast as that of the *p*-aldehydobenzoate complex,³ and it is not possible at the moment to establish whether chelation is an important factor in acceleration of the rate of reaction.

In summary then, it may be stated that while reductant chelation is potentially an efficient way for increasing the rate of reaction, the steric requirements are so stringent as to make reduction following attack at a single point the usual mode of reaction. The rate measured is the over-all rate of reaction, and involves the rate of combination of the reductant with the ligand, the rate for the actual electron transfer process and finally the rate of decomposition of the Co(II)-Cr(III) (or Co(II)-V(III)) intermediate. Although electron transfer is rapid, the probability for the transfer may be small, due to the requirement of energy matching at the two metal sites¹⁷; that is, the transmission coefficient for the transfer step may be very much less than one. If small enough, this probability would control the over-all rate of reaction. Chelation of the reductant should result in a more symmetric transition state for the tetraammines, resulting in easier energy matching. Seven complexes where chelation of the chromium can take place without destroying or reducing conjugated systems are the tetraammines *cis*-diacetate, 4,5-dicarboxybenzene-1,2-dicarboxylate,

(17) B. J. Zwolinski, R. J. Marcus and H. Eyring, *Chem. Rev.*, **55**, 157 (1955).

oxalate and *cis*-aquoacetate and the pentaammines oxalate, maleate and malonate. Some degree of chelation has been shown in the case of the first three, the fifth and sixth; inferred for the fourth, and not found for the malonate. Only in the cases of the tetraammine oxalate and the pentaammine oxalate and maleate is there any evidence for the rate law for an accelerating effect: none of the other tetraammines react more rapidly, and none of them show complete chelation to the chromium. Apparently the probability of electron transfer through a carboxylate system is not too small: reduction usually occurs after one bond has been formed with the reductant, before the second is formed. Oxalate is a special case since no rearrangement of the ligand is necessary to bring the oxygen into the chelating configuration.

If the tetraammine complex contains a chelate ring formed from a dibasic ligand, reduction at the remote carboxyl is no longer possible, but this is unimportant unless the ligand contains a system of conjugated double bonds. A more important loss is that of intensive rearrangement of the ligand: examination of molecular models shows this may be complete, giving an inflexible ring as in oxalate. The order of flexibility remaining is oxalate < malonate < succinate < phthalate < maleate, and it is found (Table II) that this is just the order of decreasing ΔS^\ddagger for both Cr⁺⁺ (-24 e.u. for malonate to -38 for maleate) and V⁺⁺ (-12.5 e.u. for oxalate to -43 for maleate) reductions. Aside from the values of ΔH^\ddagger and ΔS^\ddagger for the maleate, there is good agreement with the relation

$$\Delta S^\ddagger = 3.8 \times 10^{-3} \Delta H^\ddagger - 55.8$$

showing the mechanism of reduction in all cases is the same, attack at an adjacent carboxyl.

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The Occurrence of Paramagnetic Tetrahedral Forms of N-Arylsalicylaldiminonickel(II) Complexes in Solution at Elevated Temperatures

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Magnetic and spectrophotometric measurements on a series of N-arylsalicylaldiminonickel(II) complexes in solution in inert solvents have been carried out up to a temperature of 200°. These have shown that 2-substituted phenyl complexes, which are diamagnetic both in the solid state and in solution, retain a square-planar structure at all temperatures. For the 3- and 4-substituted phenyl complexes, the decrease in the amount of association which is observed with an increase in temperature is accompanied by the appearance of a tetrahedral species whose concentration increases with temperature. Dilution too causes a decrease in the amount of association and favors the formation of tetrahedral species. Thus in the solutions in inert solvents of these complexes there exists an equilibrium between paramagnetic polymer, diamagnetic planar and paramagnetic tetrahedral forms. Following the discovery of a tetrahedral structure for the N-*sec*-alkyl- and N-*n*-alkylsalicylaldiminonickel(II) complexes in the solid state and/or in solution, the present study confirms that a tetrahedral coordination for nickel(II) chelates is not a rare occurrence, especially at high temperatures. A comparison of the reflectance spectra of the paramagnetic solid N-aryl complexes with the spectra of the paramagnetic solid form of bis-(N-methylsalicylaldimino)-nickel(II) complex and also with the spectra of some adducts with pyridine and methanol of salicylaldiminonickel(II) complexes suggests that the paramagnetic N-aryl complexes are in some way associated even in the solid state.

Introduction

In a recent study of bis-(N-arylsalicylaldimino)-nickel(II) complexes, Holm¹ has reported that in solution in toluene and in chloroform near room tempera-

ture all of these complexes, except the 2-substituted ones, are paramagnetic and extensively associated. From a study of the temperature dependence up to 70° of the magnetic susceptibility as well as of the absorption spectra of some representative complexes it was concluded that there exists a paramagnetic polymer-

(1) R. H. Holm and K. Swaminathan, *Inorg. Chem.*, **1**, 599 (1962).

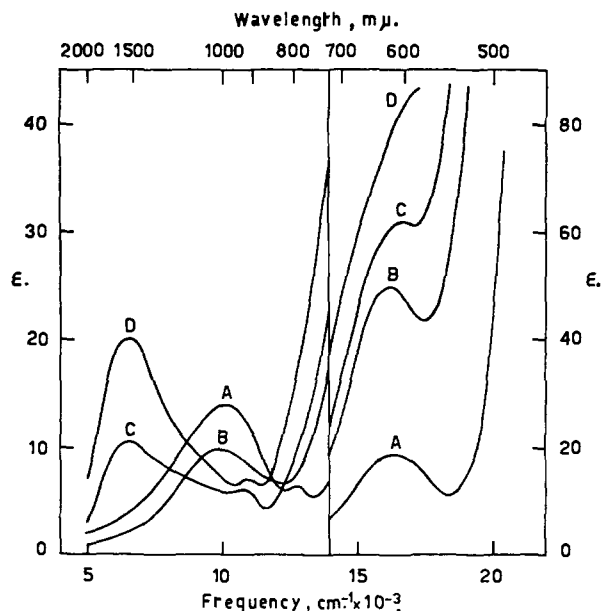


Fig. 1.—Temperature dependence of the absorption spectrum of 20 mmolal solutions of bis-(N-3-tolylsalicylaldimino)-nickel(II) complex: A, 25° in xylene; B, 80° in xylene or bibenzyl; C, 120° in bibenzyl; D, 180° in bibenzyl.

diamagnetic monomer equilibrium which is displaced to the right with increasing temperature. On the basis of such results the author reaffirms the generality of the relationship between solution paramagnetism and molecular association in nickel(II) complexes.

Our preceding discovery^{2,3} of the existence of paramagnetic pseudo-tetrahedral species of N-alkylsalicylaldiminonickel(II) complexes, especially at high temperatures, has led us to extend the magnetic and spectrophotometric investigations on the N-aryl compounds up to 200°. In addition, the reflectance spectra of a number of representative paramagnetic N-aryl complexes have been compared with those of the paramagnetic form of the N-methyl derivative⁴ as well as of other adducts with pyridine and methanol of N-substituted salicylaldiminonickel(II) complexes with the aim of getting some information about their structure.

Experimental

Preparation of Compounds.—The bis-(N-arylsalicylaldimino)-nickel(II) complexes were prepared by refluxing 0.01 mole of bis-(salicylaldehyde)-nickel(II) dihydrate with a solution of 0.03 mole of the appropriate amine in 50 ml. of ethanol until the precipitate appeared homogeneous under a microscope. After cooling, the solid was collected on a filter and recrystallized from hot xylene. The adducts of the salicylaldiminonickel(II) complexes of pyridine were obtained by adding light petroleum to the saturated pyridine solutions of the parent complexes. The light green crystals which separated were collected on a filter, washed with petroleum ether and air-dried. The bis-(N-isopropylsalicylaldimino)-nickel(II)·2MeOH adduct was obtained by cooling (to -20°) a saturated solution in methanol of the parent compound.³

Bis-(N- α -naphthylsalicylaldimino)-nickel(II): *Anal.* Calcd. for $C_{24}H_{20}O_2N_2Ni$: N, 5.08; Ni, 10.62. Found: N, 5.11; Ni, 10.42.

Bis-(N- β -naphthylsalicylaldimino)-nickel(II): *Anal.* Calcd. for $C_{24}H_{20}O_2N_2Ni$: N, 5.08; Ni, 10.62. Found: N, 5.01; Ni, 10.48.

(2) L. Sacconi, P. L. Orioli, P. Paoletti and M. Ciampolini, *Proc. Chem. Soc.*, 255 (1962); L. Sacconi, P. Paoletti and M. Ciampolini, *J. Am. Chem. Soc.*, **85**, 411 (1963). Later this result was confirmed by R. H. Holm and K. Swaminathan, *Inorg. Chem.*, **2**, 181 (1963).

(3) L. Sacconi, forthcoming article.

(4) L. Sacconi, P. Paoletti and R. Cini, Fourth International Symposium on the Chemistry of the Coordination Compounds, Rome, September, 1957; *J. Inorg. Nucl. Chem.*, **8**, 492 (1958); *J. Am. Chem. Soc.*, **80**, 3583 (1958); C. M. Harris, S. L. Lenzer and R. L. Martin, *Australian J. Chem.*, **11**, 331 (1958).

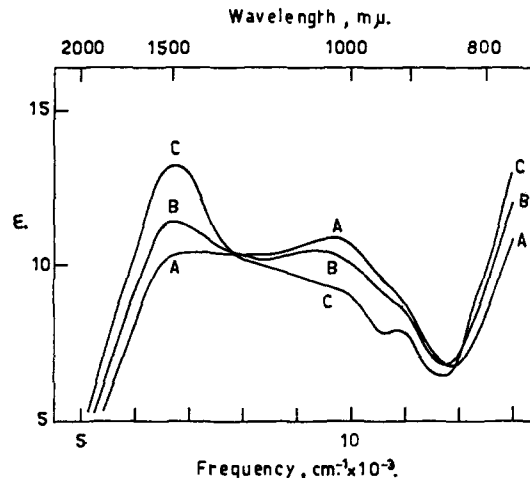


Fig. 2.—Concentration dependence of the absorption spectrum of bis-(N-3-tolylsalicylaldimino)-nickel(II) in xylene at 120°: A, 59 mmolal; B, 37 mmolal; C, 19 mmolal.

Bis-(N- m -tolylsalicylaldimino)-nickel(II)·2 pyridine: *Anal.* Calcd. for $C_{28}H_{24}O_2N_4Ni$: N, 8.79; Ni, 9.21. Found: N, 8.80; Ni, 9.18.

Bis-(N-isopropylsalicylaldimino)-nickel(II)·2 methanol: *Anal.* Calcd. for $C_{22}H_{32}O_4N_2Ni$: N, 6.27; Ni, 13.12. Found: N, 6.43; Ni, 13.15.

The identity and purity of the complexes already described in the literature^{1,5} were checked by the determination of their nitrogen content.

Magnetic and Spectrophotometric Measurements.—The apparatus and the procedure used for magnetic and spectrophotometric measurements were described in a previous paper.²

Molecular Weight Measurements.—Molecular weights were measured at 37° on solutions in benzene or toluene using a Mechrolab osmometer. The solvents were dried over sodium and distilled through a Todd column packed with glass helices. The instrument was calibrated with benzil for both solvents.

Results and Discussion

As was shown by Holm,¹ the spectra of the paramagnetic solutions of these complexes present bands at 10,000 and 12,800 cm^{-1} at room temperature which are considered characteristic of the associated forms. In addition, these spectra have another crystal field band at 16,300 cm^{-1} in a region where the tetrahedral and planar species also absorb.² A typical spectrum, that for the 3-tolyl compound, is shown in Fig. 1. On increasing the temperature the heights of such bands decrease, showing that the percentages of the associated forms decrease with temperature. Above 80°, however, bands at 6,700 and 11,100 cm^{-1} commence to be perceptible and these were found to be characteristic of the tetrahedral forms of the N-alkylsalicylaldiminonickel(II) complexes.^{2,3} The intensity of the latter bands increases steadily with the temperature. In particular, the molar absorptance at the peak at 6,700 cm^{-1} reaches values of about 20 at 180°. Such a value may be considered as indicative of the presence of about 50% of the tetrahedral form. In fact, previous spectrophotometric measurements combined with measurements of the electric and magnetic moments of the "reference" compound bis-(N-*t*-butylsalicylaldimino)-nickel(II)² lead to a calculated value of *ca.* 42 for the molar absorptance at the peak at 6,700 cm^{-1} for the pure tetrahedral form. The same temperature dependence is shown by the spectra of other paramagnetic N-aryl complexes. The essential spectral data at 180° are shown in Table I. The Cl-substituted phenyl derivatives exhibit the least tendency to form tetrahedral species.

The variation in the concentration of the solutions of the N-aryl complexes also influences the relative pro-

(5) F. Basolo and W. R. Matoush, *J. Am. Chem. Soc.*, **75**, 5663 (1953).

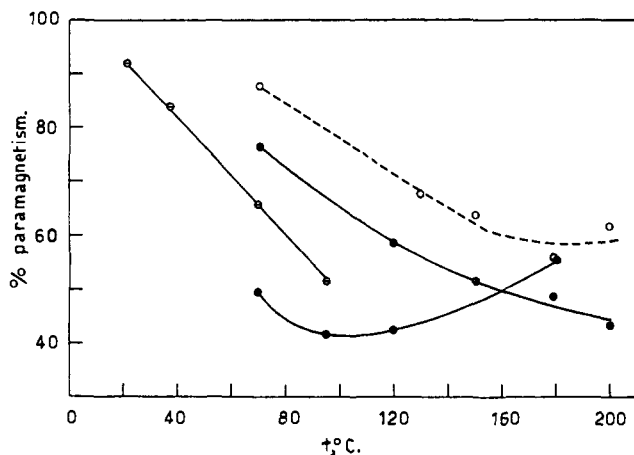


Fig. 3.—The percentages of paramagnetic forms of some N-arylsalicylaldiminonickel(II) complexes as a function of temperature; N-phenyl complex: \ominus , 24.9 mmolal in xylene; \bullet , 24.9 mmolal in bibenzyl; \oplus , 68.1 mmolal in bibenzyl; N-3-tolyl complex: \circ , 59.7 mmolal in bibenzyl.

portions of the tetrahedral and associated forms. In the spectrum of the 3-tolyl derivative in xylene at 120° (Fig. 2), for example, the height of the peak at 6,700 cm^{-1} due to the tetrahedral form decreases with increasing concentration while that of the peak at 10,000 cm^{-1} due to the associated form increases. Similarly, the degree of association, \bar{n} , of such complexes measured at 37° by the osmometric method increases with the concentration. Inspection of Table II

TABLE I
SPECTROPHOTOMETRIC DATA FOR BIS-(N-ARYLSALICYLALDIMINO)-NICKEL(II) COMPLEXES IN BIBENZYL AT 180°

Aryl	Concn., mmolal	ν_{max} , cm^{-1}	ϵ_{max}	Tetrahed., % ^a
C_6H_5	21.5	6,600	17	40
3- $\text{CH}_3\text{C}_6\text{H}_4$	19.8	6,900	20	48
4- $\text{CH}_3\text{C}_6\text{H}_4$	21.6	6,900	14	33
3- ClC_6H_4	19.8	6,900	10	24
4- ClC_6H_4	19.1	6,700	11	26
$\beta\text{-C}_{10}\text{H}_7$	19.5	6,500	16	38

^a Calculated from the formula: % tetrahed. = $100 \times \epsilon_{\text{max}}/42$.

TABLE II
MOLECULAR WEIGHT DATA FOR BIS-(N-ARYLSALICYLALDIMINO)-NICKEL(II) COMPLEXES AT 37°

Solvent	Aryl	Concn., mmolal	\bar{n}
Toluene	C_6H_5	16.4, 22.7	1.49, 1.57
		30.2, 39.6	1.60, 1.73
	3- $\text{CH}_3\text{C}_6\text{H}_4$	17.6, 24.5	1.94, 2.06
		31.7, 37.7	2.13, 2.17
Benzene	C_6H_5	14.3, 27.7	1.48, 1.60
		23.3, 32.7	1.95, 2.12
	3- $\text{CH}_3\text{C}_6\text{H}_4$	23.3, 26.8	1.78, 1.84
	4- $\text{CH}_3\text{C}_6\text{H}_4$	8.0, 27.6	1.48, 1.57
	4- ClC_6H_4	16.2, 24.9	1.40, 1.38
	2- $\text{CH}_3\text{C}_6\text{H}_4$	16.8	0.99
	$\alpha\text{-C}_{10}\text{H}_7$	8.3	0.98
	$\beta\text{-C}_{10}\text{H}_7$	20.8	1.41

shows that the value of \bar{n} for the 3-tolyl derivative diminishes from 2.17 to 1.94 while the concentration decreases from 37.7 to 17.6 mmolal. For the phenyl derivative \bar{n} goes from 1.73 to 1.49 for the same amount of dilution. The same trend is also shown by the other complexes of the series in benzene solution. It must be noted that the present values of \bar{n} , both in benzene and toluene solutions, are in every case lower than those obtained by Holm in toluene.¹

The results of the measurements of magnetic susceptibility made on solutions of the phenyl and *m*-tolyl derivatives in bibenzyl and xylene at various temperatures (Table III) furnish further information on the equilibria which occur in these systems. On increasing the temperature the μ_{eff} values decrease less and less. For the most diluted solution the plot of μ_{eff} vs. temperature has a minimum at about 100°. Since an increase in the molecular association with rising temperature is necessarily excluded, the trend of paramagnetism above 100° confirms the formation at high temperatures of paramagnetic tetrahedral species which equals or even overcompensates for the effects of the disappearance of the associated forms.

TABLE III
MAGNETIC DATA FOR BIS-(N-ARYLSALICYLALDIMINO)-NICKEL(II) COMPLEXES

Aryl	Solvent	Concn., mmolal	t , °C.	χ_{Ni} 10 ⁶	μ_{eff} (B.M.)	Param. % ^a
C_6H_5	Xylene	24.9	21	4220	3.16	92
			37	3652	3.02	84
			70	2593	2.68	66
			95	1900	2.32	52
			120	1468	2.16	43
			180	1661	2.46	56
	Bibenzyl	24.9	21	4409	3.23	96
			70	1882	2.34	50
			95	1536	2.14	42
			120	1468	2.16	43
			180	1661	2.46	56
			200	1319	2.24	46
3- $\text{CH}_3\text{C}_6\text{H}_4$	Bibenzyl	68.1	70	3029	2.90	77
			120	2032	2.54	59
			150	1671	2.39	52
			179	1459	2.31	49
			200	1319	2.24	46
			200	1724	2.60	62
	Bibenzyl	59.7	70	3457	3.09	88
			130	2269	2.72	68
			150	2048	2.64	64
			179	1684	2.48	56
			200	1724	2.60	62
			200	1724	2.60	62
$\alpha\text{-C}_{10}\text{H}_7$	Solid		21	0		
$\beta\text{-C}_{10}\text{H}_7$	Solid		21	4230	3.18	

^a Calculated from the formula: % param. = $100 \times \mu_{\text{eff}}^2/3.3^2$.

^b Diamagnetic susceptibility not accurately determined.

The data in Table III and Fig. 3 show that the percentage of the paramagnetic forms at 180° for the two complexes considered lie between 46 and 48% at the same temperature. Considering the errors involved in the magnetic and spectrophotometric measurements at high temperatures and the unavoidable arbitrary choice of limiting values for μ_{eff} and ϵ which have been used to calculate the percentages, such values are to be considered very close. This demonstrates that the presence of the tetrahedral species is predominantly responsible for the paramagnetism of the solutions of the complexes above 100°.

In conclusion, it may be stated that three forms of the N-aryl complexes (aryl = phenyl, 3- and 4-substituted phenyl, β -naphthyl, *i.e.*, 3,4-benzophenyl) can exist in solution: the paramagnetic polymeric, the diamagnetic planar and the paramagnetic tetrahedral. At room temperature the percentage of the first forms is greater than 80% while the percentage of the last is negligible. With an increase in temperature, while the proportion of the paramagnetic polymeric forms decreases, the percentage of the paramagnetic tetrahedral forms increases. The same shift in the equilibrium can be achieved, at constant temperature, by diluting the solutions.

The 2-derivatives, the α -naphthyl (2,3-benzophenyl) complex included, which in solution are diamagnetic monomers, have absorption in the crystal field region, at room temperature, identical with that of the planar

n-alkylsalicylaldiminonickel(II) complexes^{2,6} *i.e.*, no absorption in the interval 5–13,000 cm^{-1} and a single crystal field band at 16,000 cm^{-1} with $\epsilon \approx 90$. No significant change is observed in the spectra on increasing the temperature from 25 to 180°. These complexes, therefore, in this range of temperature, retain a square planar configuration.

Spectra of the Solid Compounds.—The diamagnetic solid *N*-aryl complexes, namely, the phenyl, 4-*F*-phenyl, 2-substituted phenyl¹ and α -naphthyl complexes, have reflectance spectra characteristic of a planar configuration (Fig. 4).

The spectra of the paramagnetic solids, namely of the 3- and 4- CH_3 and Cl-phenyl derivatives,¹ have bands at 7,500, 10,000, 12,800, and 16,800 cm^{-1} . The close resemblance between these spectra and those of the solutions of the same complexes at room temperature seems to indicate that they are associated to some extent even in the solid state. A tetrahedral structure on the other hand must be excluded because of the great difference between these spectra and those of the tetrahedral salicylaldiminonickel(II) complexes.² To get further information on the nature of such association, the reflectance spectra of other paramagnetic salicylaldiminonickel(II) complexes in the solid state have been recorded. In particular the paramagnetic insoluble form of the bis-(*N*-methylsalicylaldimino)-nickel(II) complexes (for which a polymeric octahedral structure has been proposed⁴), the adducts of the *N*-methyl⁶ and *N*-aryl complexes with two molecules of pyridine and the adduct of the *N*-isopropyl complex with two molecules of methanol have been examined. Some of these spectra are shown in Fig. 4.

The pyridine adducts, like the parent compounds dissolved in pyridine, show two crystal field bands, at 10,000 and 16,700 cm^{-1} for the aryl derivatives and at 11,200 and 18,000 cm^{-1} for the *N*-methyl derivative. In these compounds the nickel atom can be definitely considered as being octahedrally coordinated. If therefore we take the rule of average environment as being valid,⁷ we can use the scheme of energy levels for d^8 -configuration in an octahedral field proposed by Liehr and Ballhausen.⁸ The assignment of the two bands turns out to be in excellent quantitative agreement with the theory if a Dq value equal to 1,000 cm^{-1} is used for the aryl complexes and a value equal to 1,120 cm^{-1} is used for the *N*-methyl compound. The higher value for the latter compound is not surprising in view of the greater electron-releasing power of the methyl group with respect to the aryl group. The first band corresponds to the transition ${}^3A(F) \rightarrow {}^3T_{2g}(F)$ ($\nu_1 \approx 10Dq$ *ca.*) and the second to the transition ${}^3A_{2g}(F) \rightarrow T_{1g}(F)$ ($\nu_2 \approx 18Dq$ *ca.*). A third band corresponding to the spin-allowed transition ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ ($\nu_3 \approx {}^3P - {}^3F + 12Dq$ *ca.*) should occur at about 27,000 cm^{-1} , but it is probably hidden by the more intense charge transfer bands. A weaker spin-forbidden band at 12,500 cm^{-1} is also expected for both kinds of adduct. This band may be obscured by the more intense ν_1 band; in fact in some cases, especially in the spectra of the pyridine solutions, the ν_1 band is slightly asymmetric with a shoulder on the high wave-number side.

These considerations allow us to discuss the reflect-

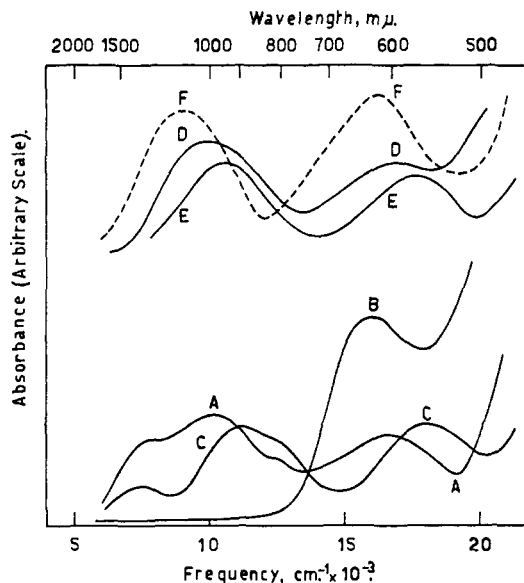


Fig. 4.—Reflectance spectra of some salicylaldiminonickel(II) complexes and adducts: A, bis-(*N*-3-tolylsalicylaldimino)-nickel(II); B, bis-(*N*-2-tolylsalicylaldimino)-nickel(II); C, bis-(*N*-methylsalicylaldimino)-nickel(II), paramagnetic form; D, bis-(*N*-3-tolylsalicylaldimino)-nickel(II)·2 pyridine; E, bis-(*N*-methylsalicylaldimino)-nickel(II)·2 pyridine; F, bis-(*N*-isopropylsalicylaldimino)-nickel(II)·2 methanol.

ance spectra of the paramagnetic *N*-aryl compounds and of the paramagnetic bis-(*N*-methylsalicylaldimino)-nickel(II) complex. In the spectra of all these compounds the two ν_1 and ν_2 bands, found in the respective octahedral adducts, are still present. In addition there are, as has already been stated, two weaker bands which occur practically at the same frequencies for both types of compounds, *i.e.*, at 7,500 and 12,800 cm^{-1} . These spectral data can be tentatively explained by supposing that the nickel(II) atoms are not all equivalent from the point of view of coordination. Some of them may be subjected to a crystal field similar to that acting in the pyridine adducts thus attaining octahedral coordination by association, while others may be subjected to a field of a different kind. If these latter atoms also were octahedrally coordinated the two bands at 7,500 and 12,800 cm^{-1} would be assigned as ν_1 and ν_2 , respectively, with an average Dq of about 750 cm^{-1} . Otherwise, it may be that these nickel atoms exhibit a different type of coordination. For instance, they may be five-coordinated as suggested¹ for the dimers present in the solution in inert solvents.

It must be noted, however, that if association occurs through intermolecular sharing of oxygen atoms, as previously postulated,⁴ the Dq values of 1,000 and 1,120 cm^{-1} appear to be surprisingly high. In fact for the bis-(*N*-isopropylsalicylaldimino)-nickel(II)·2MeOH adduct, in which a N_2O_4 set of donor atoms is present, a Dq value of 910 cm^{-1} is found (Fig. 4).

The fact that the 2-substituted aryl complexes are planar diamagnetic in the solid state can be attributed, as has already been done for the solutions,¹ to some kind of steric hindrance to association exerted by the groups in the *o*-position.

Acknowledgment.—Thanks are expressed to Dr. M. J. Campbell and Dr. N. Nardi for assisting with some of the measurements, and to the Italian "Consiglio Nazionale Ricerche" for financial assistance.

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(8) A. D. Liehr and C. J. Ballhausen, *Ann. Phys. (New York)*, **6**, 134 (1959).