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Complexes of Nickel (II) with Schiff Bases Formed from Salicylaldehydes and N-Substituted Ethylenediamines. I[1]

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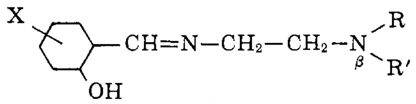
Schiff bases formed from ring-substituted salicycaldehydes and N-substituted ethylenediamines form four types of complex with nickel(II) with a general formula $[X\text{–}SALen\text{–}N(R)R']_2Ni$. When R = H, R′ = *n*-alkyl, benzyl, the ligands are tridentate and their nickel complexes are six-coordinate, octahedral, and mononuclear both in the solid state and in noncoordinating solvents. They do not form adducts with pyridine. When R = H, R′ = *ortho*-substituted phenyl, the complexes are all square-planar and diamagnetic. When R′ = phenyl or *para*-substituted phenyl the complexes are either square-planar or octahedral depending on the ring substituent X. In "inert" solvents compounds with any substituted N-phenyl group exist as octahedral and square-planar forms in equilibrium, with a greater proportion of the square-planar form at higher temperatures. In pyridine the compounds are converted into octahedral pyridine adducts. When R = phenyl, R′ = methyl, phenyl, these Schiff bases function as bidentate ligands and form *trans*-planar complexes both in the solid state and in "inert" solvents, and the complexes form adducts with pyridine.

Introduction

The complexes of nickel(II) with N-substituted salicylaldimines exhibit varied stereochemistry,[2] with conformational equilibria often existing in solution between polymeric,[3] square-planar, and tetrahedral species.[4] Of interest also is the fact that the first inner complexes of nickel(II) to be shown to have the tetrahedral structure were Schiff base complexes.[4a]

We have now investigated the nickel(II) Schiff base complexes of the general formula



I

where R, R′ are H, *n*-alkyl, aryl, benzyl; X is H, 3-Cl, 5-Cl, 3-methyl, 5-methyl, 5-ethyl, 5-NO_2, 3,4-benzo, 5,6-benzo. It is found that these complexes, which will be referred to as $[X\text{–}SALen\text{–}N(R)R']_2Ni$, may be four- or six-coordinate according to environmental factors and the substituents X, R, and R′. The magnetic and dipole moments and electronic spectra were measured and information was thus obtained about the stereochemistry of the complexes both as solids and in solution.

Molecular weight measurements of all compounds included in the present investigation revealed no evidence for association, so that the possibility of a polymeric structure for the paramagnetic compounds can be excluded.

Experimental

Preparation of the Compounds.—The complexes were prepared by refluxing 0.01 mole of the substituted bis(salicylaldehyde)-nickel(II) dihydrate with a solution of 0.022 mole of the appropriate N-substituted ethylenediamines in *ca.* 50 ml. of ethanol until the precipitate appeared homogeneous under a microscope. In some cases a few ml. of water was added to facilitate the precipitation of the compound. After cooling the precipitate was collected and recrystallized. Those N-substituted ethylenediamines which were not commercially available were prepared according to the literature.[5] In the case of the N,N-diphenylethylenediamine a pure product could not be isolated. The crude mixture of the diamine and diphenylamine, as it results from the reaction synthesis, was used as such. The complexes were prepared by allowing an excess of this mixture to react with bis(salicylaldehyde)nickel(II) dihydrate. Analytical and physical data of these compounds are summarized in Table I.

Spectrophotometric Measurements.—The absorption spectra were recorded with a Beckman DK2 spectrophotometer. The solvents were purified by the standard procedures used for spectrophotometric measurements. The reflectance spectra were recorded using the standard Beckman reflectance attachment and magnesium oxide as a reference. Concentrations of the solutions were in the range 0.01–0.02 *M*.

Magnetic Measurements.—The magnetic measurements were performed by the Gouy method, with the apparatus and the experimental technique described in a previous paper.[6] The sample tube was calibrated with $Hg[Co(NCS)_4]$ and freshly boiled distilled water.[7]

Dielectric Polarization Measurements.—The apparatus and the procedures used have been previously described.[8] The molar refraction for the sodium D-line, R_D, of the complexes was calculated by adding the proper values of bond refractions to the measured molar refraction of the bis(N-methylsalicylaldimino)nickel(II) complex.[9] Values of the orientation polarization,

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[1] This work was supported by the U. S. Department of the Army through its European Research Office, under Contract No. DA-91-591-EUC-2965, and by the Italian "Consiglio Nazionale delle Ricerche."

[2] L. Sacconi, *Experientia, Suppl.*, **9**, 148 (1964).

[3] R. H. Holm and T. M. McKinney, *J. Am. Chem. Soc.*, **82**, 5506 (1960); R. H. Holm, *ibid.*, **83**, 4683 (1961); R. H. Holm, Proceedings of the Sixth International Conference on Coordination Chemistry, S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p. 341; R. H. Holm and K. Swaminathan, *Inorg. Chem*, **1**, 599 (1962); L. Sacconi, P. Paoletti, and R. Cini, *J. Am. Chem. Soc.*, **80**, 3583 (1958).

[4] (a) L. Sacconi, P. L. Orioli, P. Paoletti, and M. Ciampolini, *Proc. Chem. Soc.*, 255 (1962); (b) L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Am. Chem. Soc.*, **85**, 411 (1963); (c) L. Sacconi and M. Ciampolini, *ibid.*, **85**, 1750 (1963); (d) L. Sacconi, *J. Chem. Soc.*, 4608 (1963); (e) M. R. Fox, E. C. Lingafelter, P. L. Orioli, and L. Sacconi, *Nature*, **197**, 1104 (1963); (f) L. Sacconi, M. Ciampolini, and N. Nardi, *J. Am. Chem. Soc.*, **86**, 819 (1964).

[5] G. H. Coleman and J. E. Callen, *ibid.*, **68**, 2006 (1946).

[6] L. Sacconi, R. Cini, M. Ciampolini, and F. Maggio, *ibid.*, **82**, 3487 (1960).

[7] B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and L. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960, p. 415.

[8] L. Sacconi, M. Ciampolini, F. Maggio, and F. P. Cavasino, *J. Inorg. Nucl. Chem.*, **19**, 73 (1961).

[9] L. Sacconi, P. Paoletti, and G. Del Re, *J. Am. Chem. Soc.*, **79**, 4062 (1957).

TABLE I

SUMMARY OF PHYSICAL AND ANALYTICAL DATA OF [X–SALen–N(R)R′]$_2$Ni COMPLEXES

						Calcd., %		Found, %	
R	R′	X	Crystallization	Formula[a]	M.p., °C.	N	Ni	N	Ni
H	CH_3	H	CH_3OH	$C_{20}H_{26}N_4O_2Ni$	235–238	13.56	14.21	13.27	14.35
		3-Cl	*m*-Xylene	$C_{20}H_{24}N_4O_2Cl_2Ni$	220–223	11.63	12.18	11.85	12.02
		3,4-Benzo	$CHCl_3$	$C_{28}H_{30}N_4O_2Ni$	>242	10.92	11.44	10.69	11.61
		5,6-Benzo	CH_3OH	$C_{28}H_{30}N_4O_2Ni$	>240	10.92	11.44	10.91	11.32
H	C_2H_5	H	C_6H_6	$C_{22}H_{30}N_4O_2Ni$	190–191	12.70	13.31	12.79	12.89
		5,6-Benzo	C_2H_5OH	$C_{30}H_{34}N_4O_2Ni$	235–238	10.35	10.85	10.26	10.53
H	*n*-C_3H_7	H	$CHCl_3$ + pet. ether	$C_{24}H_{34}N_4O_2Ni$	201–202	11.94	12.51	11.82	12.90
		3-CH_3	C_6H_6 + cyclohexane	$C_{26}H_{38}N_4O_2Ni$	197–199	11.27	11.81	11.47	11.60
		5-CH_3	$CHCl_3$ + pet. ether	$C_{26}H_{38}N_4O_2Ni$	221–224	11.27	11.81	11.24	12.07
		5-C_2H_5	$CHCl_3$ + pet. ether	$C_{28}H_{42}N_4O_2Ni$	205–208	10.67	11.18	10.66	11.53
		5-Cl	C_6H_6 + cyclohexane	$C_{24}H_{32}N_4O_2Cl_2Ni$	187–190	10.41	10.91	10.39	10.66
		5,6-Benzo	C_6H_6 + pet. ether	$C_{32}H_{38}N_4O_2Ni$	143–145	9.84	10.31	9.58	10.70
H	*n*-C_4H_9	H	$CHCl_3$ + pet. ether	$C_{26}H_{36}N_4O_2Ni$	222–225	11.27	11.86	11.28	11.92
H	$CH_2C_6H_5$	H	*m*-Xylene	$C_{32}H_{34}N_4O_2Ni$	223–225	9.91	10.39	9.73	10.58
		3,4-Benzo	C_6H_6	$C_{40}H_{38}N_4O_2Ni$	251–254	8.42	8.83	8.32	8.68
		5,6-Benzo	C_5H_5N + *m*-xylene	$C_{40}H_{38}N_4O_2Ni$	254–256	8.42	8.83	8.41	8.75
H	C_6H_5	H	$CHCl_3$ + ligroin	$C_{30}H_{30}N_4O_2Ni^a$	211–212	10.42	10.93	10.58	11.00
		3-CH_3	$CHCl_3$ + ligroin	$C_{32}H_{34}N_4O_2Ni^a$	215–216	9.91	10.39	9.99	10.19
		3-Cl	$CHCl_3$ + pet. ether	$C_{30}H_{28}N_4O_2Cl_2Ni$	234–236	9.24	9.68	9.35	9.42
		5-Cl	$CHCl_3$ + pet. ether	$C_{30}H_{28}N_4O_2Cl_2Ni$	232–234	9.24	9.68	9.32	9.80
		3,4-Benzo	Toluene	$C_{38}H_{34}N_4O_2Ni$	227–229	8.79	9.21	8.48	9.40
		5,6-Benzo	$CHCl_3$ + ligroin	$C_{38}H_{34}N_4O_2Ni^a$	239–241	8.79	9.21	8.81	9.36
H	*o*-$CH_3C_6H_5$	H	$CHCl_3$ + ligroin	$C_{32}H_{34}N_4O_2Ni^a$	217–218	9.91	10.39	10.05	10.21
		3-Cl	$CHCl_3$ + pet. ether	$C_{32}H_{32}N_4O_2Cl_2Ni^a$	175–176	8.83	9.26	8.81	9.62
		5-Cl	$CHCl_3$ + pet. ether	$C_{32}H_{32}N_4O_2Cl_2Ni^a$	167–168	8.83	9.26	8.82	9.44
		3,4-Benzo	$CHCl_3$ + pet. ether	$C_{40}H_{38}N_4O_2Ni^a$	202–204	8.42	8.83	8.46	8.79
		5,6-Benzo	$CHCl_3$ + pet. ether	$C_{40}H_{38}N_4O_2Ni^a$	222–223	8.42	8.83	8.43	8.51
H	*p*-$CH_3C_6H_4$	H	$CHCl_3$ + cyclohexane	$C_{32}H_{34}N_4O_2Ni^a$	217–219	9.91	10.39	9.96	10.12
		3-Cl	$CHCl_3$ + pet. ether	$C_{32}H_{32}N_4O_2Cl_2Ni$	>240	8.83	9.26	8.86	9.05
		5-Cl	$CHCl_3$ + pet. ether	$C_{32}H_{32}N_4O_2Cl_2Ni$	>240	8.83	9.26	8.76	9.41
		3,4-Benzo	$CHCl_3$ + pet. ether	$C_{40}H_{38}N_4O_2Ni$	202–204	8.42	8.83	8.60	8.91
		5,6-Benzo	$CHCl_3$	$C_{40}H_{38}N_4O_2Ni^a$	233–236	8.42	8.83	8.43	8.65
H	α-$C_{10}H_7$	H	C_6H_5	$C_{38}H_{34}N_4O_2Ni^a$	231–234	8.79	9.22	8.58	9.12
CH_3	C_6H_6	H	$CHCl_3$	$C_{32}H_{34}N_4O_2Ni^a$	171–173	9.91	10.39	9.93	10.10
		5-CH_3	C_6H_6 + cyclohexane	$C_{34}H_{38}N_4O_2Ni^a$	200–202	9.44	9.90	9.53	9.61
		3-Cl	$CHCl_3$ + pet. ether	$C_{32}H_{32}N_4O_2Cl_2Ni^a$	199–200	8.83	9.26	9.02	9.49
		5-Cl	$CHCl_3$ + pet. ether	$C_{32}H_{32}N_4O_2Cl_2Ni^a$	178–180	8.83	9.26	8.85	9.01
		3,4-Benzo	$CHCl_3$ + cyclohexane	$C_{40}H_{38}N_4O_2Ni^a$	191–193	8.42	8.83	8.56	8.75
		5,6-Benzo	C_6H_6	$C_{40}H_{38}N_4O_2Ni^a$	>240	8.42	8.83	8.27	9.06
C_6H_6	C_6H_6	H	$CHCl_3$	$C_{42}H_{38}N_4O_2Ni^a$	239–240	8.12	8.52	8.16	8.34
		3-Cl	*m*-Xylene	$C_{42}H_{36}N_4O_2Cl_2Ni^a$	>242	7.39	7.74	7.40	8.02
		5-Cl	*m*-Xylene	$C_{42}H_{36}N_4O_2Cl_2Ni^a$	>242	7.39	7.74	7.31	7.60
		3,4-Benzo	$CHCl_3$ + C_2H_5OH	$C_{50}H_{42}N_4O_2Ni^a$	198–199	7.10	7.44	7.08	7.51
		5,6-Benzo	$CHCl_3$ + ligroin	$C_{50}H_{42}N_4O_2Ni^a$	241–242	7.10	7.44	6.89	7.72

[a] Diamagnetic.

P_0, were calculated by assuming a value of 20% R_D for the atom polarization.

Molecular Weight Determinations.—Molecular weights were measured at 37° on benzene solutions using a Mechrolab osmometer. Benzene was distilled over phosphorus pentoxide through a Todd column packed with glass helices. The instrument was calibrated with benzyl. Weight fractions were in the range 0.002–0.006.

Results and Discussion

Series 1: R = H, R′ = *n*-alkyl, benzyl.—All these compounds are mustard-colored and paramagnetic with values of μ_{eff} varying from 3.05 to 3.30 B.M. (Table II). In the range of wave numbers from 6000 to 20,000 cm.$^{-1}$ the spectra of the solids or of solutions in "inert" solvents such as chloroform or benzene are similar to those of other octahedral nickel(II) complexes,[4c,10] but quite different from those of tetrahedral complexes (Figure 1).[4a,4b] There are two crystal field transitions, with maxima at 11,500 to 11,800 cm.$^{-1}$ (ν_1, ϵ_1 ~35) and 17,900 to 18,300 cm.$^{-1}$ (ν_2, ϵ_2 ~20) (the molar extinction coefficients ϵ are given in l. mole^{-1} cm.$^{-1}$). The ratio ν_2/ν_1 is approximately 1.6, as predicted and found for octahedral nickel(II) complexes.[10] Compounds of series 1 may be assigned an octahedral structure on this basis. The octahedron is notably distorted since ϵ_1 and ϵ_2 are rather higher than those found in known regular octahedral structures[10] and the distortion is easily justified in terms of the geometry of the ligands. Also, the dipole moments of representative compounds of the series, chosen as the most soluble in benzene, are very high at 8–10 D. (Table III), indicating considerably asymmetric structures. It will be remembered that the dipole moments of tetrahedral salicylaldimino nickel(II) complexes are about

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[10] C. K. Jørgensen, *Acta Chem. Scand.*, **10**, 887 (1956).

Table II

Magnetic Susceptibility Data of [X–SALen–N(R)R′]$_2$Ni Complexes

R	R′	X	T, °C.	$\chi_g \times 10^6$	$\delta^a \times 10^6$	$\chi^{Ni} \times 10^6$	μ_{eff}, B.M.
H	CH_3	H	24	9.31	248	4095	3.13
		3-Cl	18	7.74	282	4015	3.08
		3,4-Benzo	22	7.26	305	4030	3.10
		5,6-Benzo	24	7.38	306	4095	3.13
H	C_2H_5	H	21	8.46	272	4005	3.10
		5,6-Benzo	21	7.10	329	4170	3.13
H	n-C_3H_7	H	21	7.43	296	4140	3.13
		3-CH_3	19	7.42	319	4015	3.08
		5-CH_3	22	7.44	319	4020	3.10
		5-C_2H_5	21	7.20	343	4125	3.13
		5-Cl	23	7.11	330	4155	3.16
		5,6-Benzo	17	7.10	353	4395	3.21
H	n-C_4H_9	H	20	7.63	319	4115	3.12
H	$CH_2C_6H_5$	H	25	7.19	344	4410	3.28
		3,4-Benzo	22	5.41	404	4005	3.09
		5,6-Benzo	24	5.64	404	4155	3.16
H	C_6H_5	3-Cl	21	6.48	367	4295	3.19
		5-Cl	22	6.08	367	4050	3.10
		3,4-Benzo	22	4.66	392	3360	2.83
H	p-$CH_3C_6H_4$	3-Cl	19	5.85	390	4095	3.11
		5-Cl	18	6.07	390	4235	3.15
		3,4-Benzo	23	5.56	416	4115	3.13

[a] δ = diamagnetic corrections calculated from Pascal's constants.[4f]

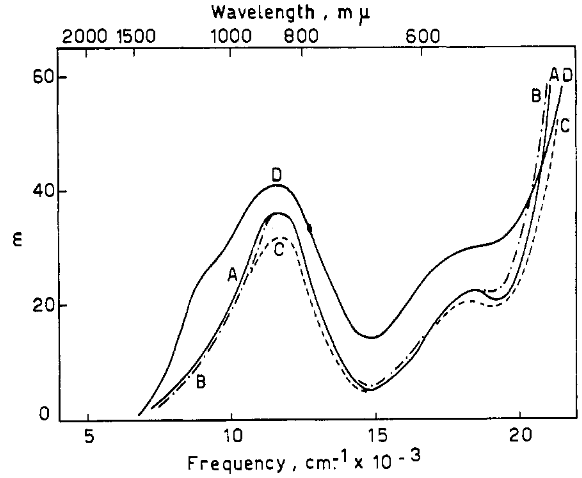


Figure 1.—Absorption and reflectance spectra of [SALen–NHCH$_3$]$_2$Ni complex at room temperature: A, in benzene; B, in pyridine; C, in chloroform; D, reflectance spectrum.

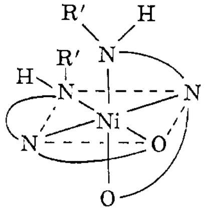
Table III

Dielectric Polarization Data for Some [X–SALen–N(R)R′]$_2$Ni Complexes in Benzene at 25°

R	R′	X	$P_{2\infty}$, cc.	R_D, cc.	P_0, cc.	μ, D.
H	CH_3	H	1729	125	1579	8.78
H	n-C_3H_7	H	1515	144	1342	8.09
H	n-C_3H_7	5-Cl	2256	154	2071	10.05
H	n-C_3H_7	5-CH_3	1599	153	1415	8.31
CH_3	C_6H_5	H	237	167	37	1.34
C_6H_5	C_6H_5	H	276	206	29	1.19

4 D.[4b] The high dipole moments of compounds of this series are thus consistent with a *cis*-octahedral structure.

The bonds between the β nitrogen atoms and the central nickel atom are particularly strong in series 1 compounds. This is shown by the strength of the crystal field, with 10Dq varying from 11,500 to 11,800 cm.$^{-1}$. This value should be compared with the values for other nickel(II) ions surrounded by a N_4O_2 set of donor atoms: 10,000 cm.$^{-1}$ for adducts of the type bis(N-arylsalicylaldimino)nickel(II)–2-pyridine[4c] and bis(N-alkylsalicylaldimino)nickel(II)–2-pyridine,[11] 10,500 cm.$^{-1}$ for the ion [Ni(tren)(H$_2$O)$_2$]$^{2+}$,[10] and also 11,200 and 11,500 cm.$^{-1}$ for the ions containing a N_6 set of donor atoms, [Ni(en)$_3$]$^{2+}$ and [Ni(den)$_2$]$^{2+}$.[10] The strength of these bonds is also shown by the fact that the donor groups cannot be replaced by pyridine. The spectra of the complexes in pyridine are virtually identical with those of the complexes in "inert" solvents, both as far as the crystal field transitions are concerned and also the charge-transfer and intra-ligand transitions (Figure 1). It may be concluded that the groups R′ = n-alkyl, benzyl exert a strong electron-releasing influence and no determining steric hindrance.



II

Series 2: R = H, R′ = *o*-tolyl, α-naphthyl.—The solid compounds of this series are all olive-green and diamagnetic regardless of the nature of the ring substituent X. Their reflectance spectra are characteristic of square-planar complexes[4c] with no appreciable absorption below 13,000 cm.$^{-1}$ and are altogether similar to the spectra of compounds of series 4 (see below), so

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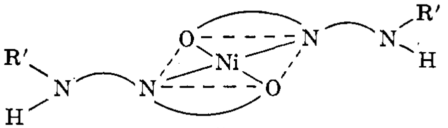
(11) Unpublished results from this laboratory.

TABLE IV

SPECTROPHOTOMETRIC ABSORPTION DATA OF SOME $[X\text{-SALen-N(H)R'}]_2Ni$ COMPLEXES IN CHLOROFORM AND BENZENE SOLUTION

R	X	Solvent	ϵ_1	ν_1	ϵ_2	ν_2	ϵ_1/ϵ_2
C_6H_5	H	$CHCl_3$	47	10,750	33	17,000	1.4
		C_6H_6	44	10,750	41	16,900	1.1
	3-CH_3	$CHCl_3$	44	10,700	40	17,900	1.1
C_6H_5	3-CH_3	C_6H_6	40	10,650	43	16,800	0.9
	3-Cl	$CHCl_3$	50	10,850	32	17,200	1.6
	5-Cl	$CHCl_3$	52	10,900	30	17,200	1.7
	3,4-Benzo	$CHCl_3$	37	10,500	26	17,500	1.4
	5,6-Benzo	$CHCl_3$	32	10,400	...	...	...
p-$CH_3C_6H_4$	H	$CHCl_3$	52	10,870	31	17,250	1.7
		C_6H_6	56	10,800	45	17,100	1.2
	3-Cl	$CHCl_3$	53	11,000	30	17,400	1.8
	5-Cl	$CHCl_3$	53	11,050	28	17,050	1.9
	3,4-Benzo	$CHCl_3$	56	10,800	34	17,450	1.7
	5,6-Benzo	$CHCl_3$	54	10,800	42	17,450	1.3
o-$CH_3C_6H_4$	H	$CHCl_3$	8	10,800	68	16,250	0.12
	3-Cl	$CHCl_3$	3.5	10,800	66	16,050	0.05
		C_6H_6	3	10,800	67	15,850	0.05
	5-Cl	$CHCl_3$	21	10,800	58	16,200	0.4
	3,4-Benzo	$CHCl_3$	10	10,600	88	15,650	0.11
		C_6H_6	10	10,600	88	15,650	0.11
	5,6-Benzo	$CHCl_3$	...	...	136	16,650	...

that we may by analogy assign to the compounds of this series a *trans*-planar structure of the type



III

The spectra of these compounds differ from their nickel complex analogs with *cis*-planar configuration.[12] A *cis* structure thus seems unlikely.

Series 3: R = H, R' = phenyl, *p*-tolyl.—In this series the solid compounds with X = H, 3-methyl, 5-NO_2, or 5,6-benzo are green and diamagnetic (Table I) with reflectance spectra characteristic of planar complexes (Figure 2). When X = 3-Cl, 5-Cl, or 3,4-benzo the solids are green and paramagnetic, μ_{eff} varying from 2.83 to 3.20 B.M. (Table II). There are two bands in the reflectance spectra, at 10,500 and 17,000 cm.$^{-1}$, indicating, as in the first series, a distorted octahedral structure.

When the N-aryl group is *ortho*-substituted (series 2) both the electron-attracting and steric effects of this group hinder the β nitrogen atom from coordinating, and square-planar complexes result in the solid state. When, as in the third series, the aryl group is *para*-substituted the steric repulsions are less and the β nitrogen atom can, in suitable circumstances, be bound to the central nickel atom, giving an octahedral complex. The nature of the group X is here the determining circumstance, presumably through an electronic effect, so that 3-Cl, 5-Cl, and 3,4-benzo substituents cause the octahedral structure to be preferred, whereas the other substituents favor the planar structure.

All the compounds of series 2 and 3 (except one *o*-tolyl derivative) give two absorption bands in non-coordinating solvents, at *ca.* 10,000 and 16,000–18,000 cm.$^{-1}$. The ratio between the apparent maximum extinction coefficients of the two bands (ϵ_1/ϵ_2) is less than that observed in compounds of series 1 and varies with solvent. It will be remembered that the planar complexes of nickel(II) have no absorption below 13,000 cm.$^{-1}$ but have a relatively intense band at 15,000–18,000 cm.$^{-1}$ (ϵ 80–120).[4b,12] The presence of two crystal field bands with an intensity ratio ϵ_1/ϵ_2 less than that found in the octahedral complexes of series 1 seems to indicate the existence of an equilibrium of planar and octahedral forms. This means that when lattice forces are removed the β nitrogen atoms are able to coordinate to a greater or lesser extent to the nickel atom. The value of ϵ_1/ϵ_2 gives some measure of the relative proportion of the two species in equilib-

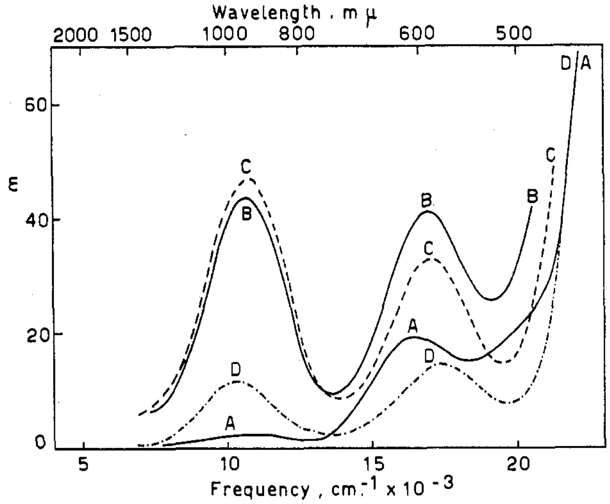


Figure 2.—Reflectance and absorption spectra of $[\text{SALen-NHC}_6H_5]_2Ni$ complex: A, reflectance spectrum; B, in benzene; C, in chloroform; D, in pyridine.

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[12] G. Maki, *J. Chem. Phys.*, **29**, 1129 (1958).

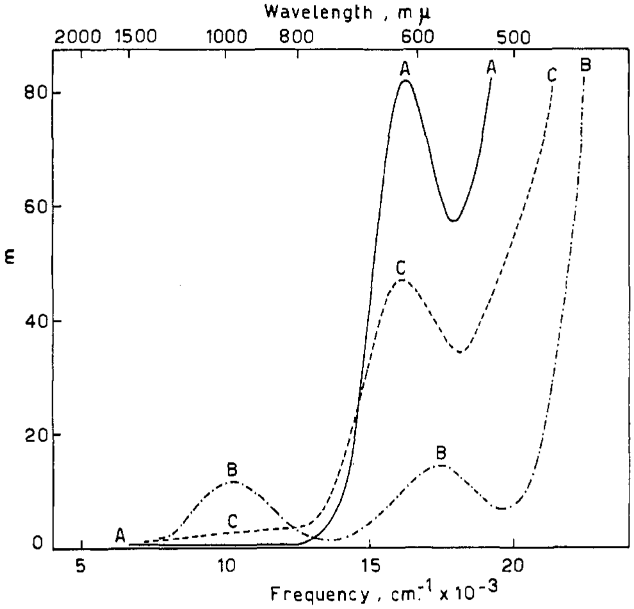

Figure 3.—Absorption and reflectance spectra of [SALen–N(CH_3)C_6H_5]$_2$Ni complex: A, in benzene; B, in pyridine; C, reflectance spectrum.

rium, being greater the higher the proportion of the octahedral form.

Data concerning the solution spectra of the complexes of the second and third series are given in Table IV. Only the complex R′ = *o*-tolyl, X = 5,6-benzo remains substantially planar in solution. The percentage of the octahedral form in chloroform solution appears to vary according to the ring substituent X in approximately the order 5,6-benzo < 3,4-benzo ≈ H < 3-Cl < 5-Cl, except where R′ = *o*-tolyl: 3-Cl < 3,4-benzo. The square-planar configuration is thus most strongly induced by the 5,6-benzo substituent. It is significant that the same holds true in equilibria between tetrahedral and square-planar forms of N-isopropylsalicylaldimino nickel(II) complexes.[4f] Table IV also shows that the octahedral form is present to a greater extent in chloroform than in benzene.

On the other hand, for a given substituent X the percentage of a complex in the octahedral form increases as R′ is varied in the order *o*-tolyl < phenyl < *p*-tolyl. This implies the existence of competition between steric hindrance due to the methyl substituent and its inductive effect which should make the tolyl-substituted nitrogen atoms stronger donors than the phenyl-substituted ones. This effect of methyl substitution in the aryl group finds a parallel in the order *o*-methylpyridine < pyridine < *p*-methylpyridine in the adducts of these bases with bis(benzoylhydrazone)-nickel(II) (NiDBH).[13]

The reduced donor power of the β nitrogen atoms in series 2 and 3 compounds as compared with series 1 is also shown by the following considerations. First, the octahedral crystal fields are weaker by about 1000 cm.$^{-1}$ in $10Dq$, and second bis adducts are formed in all cases in pyridine solution, giving spectra with the characteristic low-intensity bands at 10,500 ($\epsilon \sim 12$) and 17,000 cm.$^{-1}$ ($\epsilon \sim 15$). Magnetic measurements on compounds of series 2 and 3 in solution at room temperature are not possible due to low solubility.

Nevertheless the magnetic moment of the [3,4-benzo–SALen–NH(phenyl)]$_2$Ni complex dissolved in bibenzyl has been found to decrease with increasing temperature from 80 to 170°. This fact indicates an endothermic rearrangement from the octahedral to the planar form.

Series 4: R = phenyl, R′ = methyl, phenyl.—All compounds of this series are olive-green and diamagnetic both as solids or in "inert" solvents (Table I). Reflectance and solution spectra give one absorption band at *ca.* 16,000 cm.$^{-1}$ (ϵ 85–95), showing that these complexes have the square-planar structure (Figure 3). Values of dipole moments in benzene are given in Table III. The very small values indicate a *trans*-planar arrangement.

In pyridine the complexes are transformed into octahedral adducts, giving the two characteristic bands in the absorption spectra. It is evident that the steric repulsion of the group attached to the β nitrogen atom and the electron-withdrawing effect of the phenyl substituents do not permit these Schiff bases to act as tridentate ligands.

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(13) L. Sacconi, G. Lombardo, and P. Paoletti, *J. Chem. Soc.*, 848 (1958).