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Five-Coordination in Some Complexes of Nickel(II) with Schiff Bases, Formed from Salicylaldehydes and N,N-Substituted Ethylenediamines. II[1,2]

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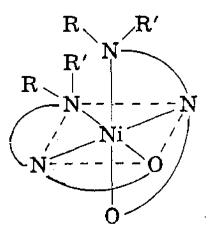
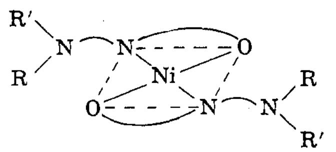
Further studies on the complexes of nickel(II) with Schiff bases formed from ring-substituted salicylaldehydes and N,N-disubstituted ethylenediamines are presented. The compounds have a general formula $[X\text{–}SALen\text{–}NR_2]_2Ni$; when $-NR_2$ is a dimethylamino group or pyrrolidino group the ligands are tridentate and all the complexes formed from them are paramagnetic and have distorted octahedral configuration. The complexes where $-NR_2$ is a piperidino group are all diamagnetic and have the square-planar configuration. When $-NR_2$ is a diethylamino group the configuration of the complex is square-planar or octahedral depending on the substituent X, except for X = 3-Cl, 5-Cl, and 3,4-benzo when the complexes are paramagnetic and five-coordinate with $\mu_{eff} \approx 3.3$ B.M. The configuration of the five-coordinate complex most resembles that of a distorted square pyramid; the complexes are the first reported examples of high-spin five-coordinate complexes of nickel(II).[3] Most compounds of the present study exist in solution as mixtures of planar, five-coordinate, and octahedral forms.

Introduction

Complexes to which the structures I and II were assigned were described in the first paper of this series.



I



II

In this group of compounds, given the formula $[X\text{–}SALen\text{–}N(R)R']_2Ni$, R and R′ were hydrogen, *n*-alkyl, or aryl groups and X was 3-CH_3, 5-CH_3, 5-C_2H_5, 3-Cl, 5-Cl, 5-NO_2, 3,4-benzo (compound derived from 2-hydroxy-1-naphthaldehyde), or 5,6-benzo (compound derived from 1-hydroxy-2-naphthaldehyde). In the solid compounds it was found that the terminal (β) nitrogen atoms were sometimes involved in coordination, giving octahedral complexes of type I, and sometimes were not, giving square-planar complexes of type II, depending on the nature of R, R′, and X. Both forms usually existed in equilibrium together where the compounds were dissolved in "inert" solvents. The present paper describes the preparation and properties of the analogous complexes where R = R′ and $-NR_2$ is $-N(CH_3)_2$, $-N(C_2H_5)_2$, $-N(CH_2)_4$ (pyrrolidino), or $-N(CH_2)_5$ (piperidino). The compounds were investigated by the same methods as before.

Experimental

Preparation of Compounds.—The complexes were prepared by heating together the substituted bis(salicylaldehydo)nickel(II) dihydrate (10 mmoles) with the appropriate N,N-substituted ethylenediamine (22 mmoles) and ethanol (*ca.* 50 ml.) under reflux until the precipitate was homogeneous. In some cases a little water was added to facilitate the precipitation. After cooling the reaction mixture, the precipitate was collected and recrystallized. Substituted ethylenediamines not commercially available were prepared by the method of Coleman and Callen.[4] The analytical and physical data for the compounds are summarized in Table I.

Spectrophotometric Measurements.—The absorption spectra were recorded on a Beckman DK2 spectrophotometer using a 1-cm. stoppered silica cell. Temperatures from 20 to 80° were obtained by circulating paraffin oil from a thermostat regulated to ±0.5° through a cell housing designed and constructed in this institute. Allowance was made for the temperature variation of solution density when calculating extinction coefficients. Solvents for spectroscopy were purified by the standard procedures. The reflectance spectra were measured with the standard Beckman reflectance attachment using magnesium oxide as reference.

Magnetic Measurements.—The magnetic measurements were performed by the Gouy method with the apparatus and experimental technique described previously.[5] The sample tube was calibrated with $Hg[Co(NCS)_4]$[6] and freshly distilled water.[6]

Molecular Weight Determination.—Molecular weights in benzene at 37° were measured on a Mechrolab osmometer. Benzene was distilled from phosphorus pentoxide through a Todd column packed with glass helices. The instrument was calibrated with benzil.

Results and Discussion

Compounds in the Solid State. Series 1. $-NR_2$ = $-N(CH_3)_2$.—The 3,4-benzo derivative is ochre but all the other compounds of this series are green. The compounds are paramagnetic with $\mu_{eff} \approx 3.2$ B.M. (see Table II). The reflectance spectra (Figure 1) show one band at *ca.* 16,700 cm.$^{-1}$, another in the region 9500–11,100 cm.$^{-1}$, and a shoulder at *ca.* 6500 cm.$^{-1}$. These spectra are very similar to those of compounds of series 1 of the previous paper[1] (R = H, R′ = *n*-alkyl).

(1) Part I: L. Sacconi, P. Nannelli, and U. Campigli, *Inorg. Chem.* **4**, 818 (1965).

(2) 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."

(3) *Cf.* A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, London, 1962, pp. 918, 919.

(4) G. H. Coleman and J. E. Callen, *J. Am. Chem. Soc.*, **68**, 2006 (1946).

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

(6) B. N. Figgis and L. Lewis, "Modern Coordination Chemistry," J. Lewis and L. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p. 415.

Table I

Summary of Physical and Analytical Data for Substituted [X–SALen–NR_2]$_2$Ni Complexes

	X	–NR_2	Crystallization	Formula	M.p., °C.	Calcd., % N	Calcd., % Ni	Found, % N	Found, % Ni
I	H	$-N<^{CH_3}_{CH_3}$	$CHCl_3$ + petr. ether	$C_{22}H_{30}N_4O_2Ni$	174–176	12.70	13.30	12.82	13.85
II	3,4-Benzo		$CHCl_3$ + petr. ether	$C_{30}H_{34}N_4O_2Ni$	230–233	10.35	10.84	10.47	10.62
III	5,6-Benzo		$CHCl_3$ + ligroin	$C_{30}H_{34}N_4O_2Ni$	224–228	10.35	10.84	10.70	10.90
IV	H	$-N<$ CH_2-CH_2 / CH_2-CH_2 (ring)	$CHCl_3$ + petr. ether	$C_{26}H_{34}N_4O_2Ni$	169–171	11.36	11.90	11.58	11.61
V	5-CH_3		$CHCl_3$ + petr. ether	$C_{28}H_{38}N_4O_2Ni$	184–186	10.75	11.26	10.82	11.02
VI	5-Cl		$CHCl_3$ + petr. ether	$C_{26}H_{32}N_4O_2Cl_2Ni$	225–227	9.97	10.44	9.91	10.30
VII	5,6-Benzo		$CHCl_3$ + cyclohexane	$C_{34}H_{38}N_4O_2Ni$	239–241	9.44	9.89	9.35	9.97
VIII	H	$-N<^{C_2H_5}_{C_2H_5}$	Petr. ether	$C_{26}H_{38}N_4O_2Ni$	56–58	11.26	11.80	11.38	11.50
IX	3-CH_3		Petr. ether	$C_{28}H_{42}N_4O_2Ni$	76–78	10.66	11.17	10.70	11.28
X	5-CH_3		Petr. ether	$C_{28}H_{42}N_4O_2Ni$	99–101	10.66	11.17	10.68	11.23
XI	3-Cl		$CHCl_3$ + petr. ether	$C_{26}H_{36}N_4O_2Cl_2Ni$	150–151	9.90	10.37	10.06	10.41
XII	5-Cl		$CHCl_3$ + petr. ether	$C_{26}H_{36}N_4O_2Cl_2Ni$	167–170	9.90	10.37	10.01	10.35
XIII	5-C_2H_5		Petr. ether	$C_{30}H_{46}N_4O_2Ni$	81–82	10.13	10.60	10.00	10.91
XIV	5-NO_2		C_6H_6	$C_{26}H_{36}N_6O_6Ni$	185–187	14.31	9.99	14.57	10.15
XV	3,4-Benzo		$CHCl_3$ + petr. ether	$C_{34}H_{42}N_4O_2Ni$	158–160	9.38	9.82	9.45	9.75
XVI	5,6-Benzo		Petr. ether	$C_{34}H_{42}N_4O_2Ni$	130–132	9.38	9.82	9.48	9.65
XVII	H	$-N<^{CH_2-CH_2}_{CH_2-CH_2}>CH_2$	$CHCl_3$ + petr. ether	$C_{28}H_{38}N_4O_2Ni$	149–151	10.71	11.26	10.80	11.05
XVIII	3-CH_3		$CHCl_3$ + petr. ether	$C_{30}H_{42}N_4O_2Ni$	156–157	10.20	10.68	10.45	10.60
XIX	5-CH_3		$CHCl_3$ + cyclohexane	$C_{30}H_{42}N_4O_2Ni$	178–179	10.20	10.68	10.55	10.52
XX	3-Cl		$CHCl_3$ + petr. ether	$C_{28}H_{36}N_4O_2Cl_2Ni$	133–135	9.49	9.94	9.56	9.80
XXI	5-Cl		$CHCl_3$ + cyclohexane	$C_{28}H_{36}N_4O_2Cl_2Ni$	184–186	9.49	9.94	9.53	10.03
XXII	5-C_2H_5		$CHCl_3$ + petr. ether	$C_{32}H_{46}N_4O_2Ni$	177–179	9.70	10.16	9.89	10.20
XXIII	5,6-Benzo		$CHCl_3$ + cyclohexane	$C_{36}H_{42}N_4O_2Ni$	208–210	9.02	9.44	9.07	9.30

TABLE II
MAGNETIC SUSCEPTIBILITY DATA FOR SUBSTITUTED [X–SALen–NR_2]$_2$Ni COMPLEXES IN THE SOLID STATE

Compound	Temp., °C.	$10^6\chi_g$	$10^6\chi_{Ni}$[a]	μ_{eff}, B.M.
I	22	9.09	4298	3.20
II	22	7.40	4239	3.21
III	22	7.31	4280	3.19
IV	21	8.64	4557	3.29
V	23	7.43	4192	3.16
VI	23	6.82	3917	3.05
VII	18	6.41	4155	3.12
VIII	20	7.25	3976	3.06
IX	21	Diamagnetic		
X	22	Diamagnetic		
XI	21	7.39	4589	3.30
XII	23	7.35	4566	3.30
XIII	20	Diamagnetic		
XIV	20	Diamagnetic		
XV	22	6.76	4410	3.24
XVI	21	Diamagnetic		
XVII	23	Diamagnetic		
XVIII	21	Diamagnetic		
XIX	22	Diamagnetic		
XX	25	Diamagnetic		
XXI	23	Diamagnetic		
XXII	22	Diamagnetic		
XXIII	21	Diamagnetic		

[a] Corrected for diamagnetic contribution as calculated from Pascal's constants (P. W. Selwood, "Magnetochemistry," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1956).

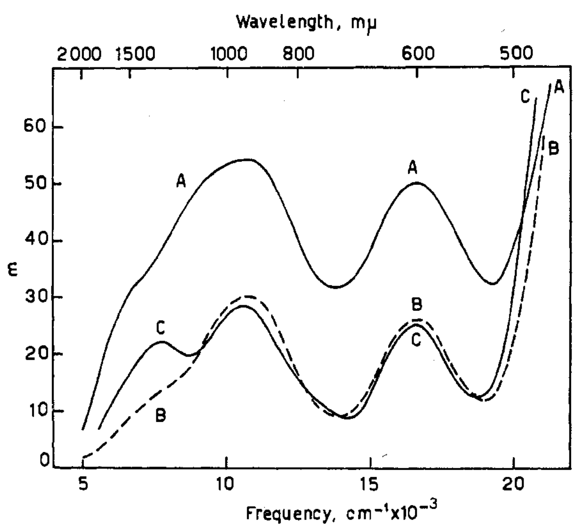


Figure 1.—Absorption and reflectance spectra of [H–SALen–$N(CH_3)_2$]$_2$Ni complex at room temperature: A, by reflectance absorption, scale arbitrary; B, in benzene; C, in chloroform.

Series 2. $-NR_2 = -N(CH_2)_4$.—The 5,6-benzo derivative is ochre but again all other compounds of this series are green. The value of μ_{eff} (Table II) varies from 3.05 to 3.29 B.M. The reflectance spectra (Figure 2), apart from a shoulder at 7100–7700 cm.$^{-1}$, are similar to those of the preceding series. One must therefore assign to compounds of both groups a distorted octahedral structure of the type I, as previously established[1] for the complexes where R = H, R′ = *n*-alkyl.

Series 3. $-NR_2 = -N(C_2H_5)_2$.—These compounds are found to possess three types of configuration in the

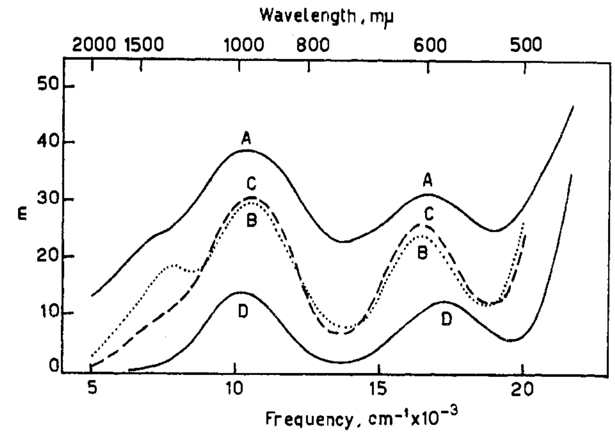


Figure 2.—Reflectance and absorption spectra of [H–SALen–$N(CH_2)_4$]$_2$Ni complex at room temperature: A, by reflectance absorption, scale arbitrary; B, in benzene; C, in chloroform; D, in pyridine.

solid state, the substituent X being the factor which determines which is adopted by any particular compound. When X = H, the complex is paramagnetic and octahedral, having μ_{eff} = 3.06 B.M. and having a reflectance spectrum (Figure 3) familiar from compounds in the previous series of the paper. When X =

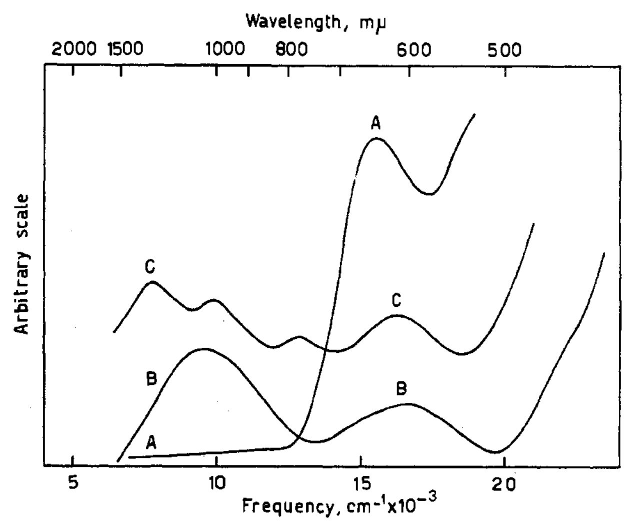


Figure 3.—Reflectance spectra of [3-CH_3–SALen–$N(C_2H_5)_2$]$_2$Ni complex (curve A), [H–SALen–$N(C_2H_5)_2$]$_2$Ni complex (curve B), [5-Cl–SALen–$N(C_2H_5)_2$]$_2$Ni complex (curve C).

3-CH_3, 5-CH_3, 5-C_2H_5, 5-NO_2, or 5,6-benzo the complexes are planar and diamagnetic, with reflectance spectra accordingly. But, when X = 3-Cl, 5-Cl, or 3,4-benzo the reflectance spectra of the paramagnetic compounds (μ_{eff} between 3.24 and 3.30 B.M., Table II) show four bands at *ca.* 7700, 9800, 12,800, and 16,200 cm.$^{-1}$. These spectra are not compatible with either a tetrahedral or regular or distorted octahedral configuration for the complex. The absorption spectra of the 5-Cl derivative are shown in Figure 4. A complete X-ray structural analysis on the 5-Cl derivative, now accomplished in this institute, has shown that the nickel atom in this compound is five-coordinate. One Schiff-base ligand is tridentate while the other has a

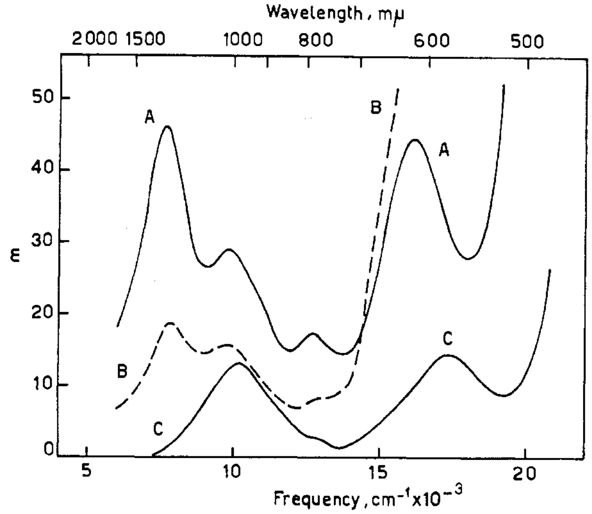
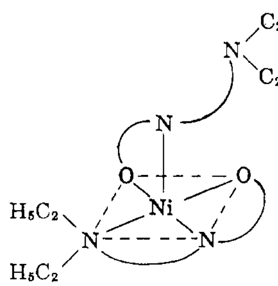


Figure 4.—Absorption spectra of [5-Cl-SALen–N(C_2H_5)$_2$]$_2$Ni complex at room temperature: A, in chloroform; B, in benzene; C, in pyridine.

noncoordinated –N(C_2H_5)$_2$ group. The coordination polyhedron can be regarded as a distorted square-based pyramid, with the nickel atom lying a little above the mean basal plane.[7] A five-coordinate structure of the type III must therefore be attributed to all three compounds in this group. These represent the first example of high-spin nickel(II) complexes with a five-coordinate structure.[8]



III

Series 4. –NR$_2$ = –N(CH$_2$)$_5$.—All the compounds of this series are green and diamagnetic (Table II). The reflectance spectra of the solids (Figure 5) show no absorption bands below 14,000 cm.$^{-1}$, so that one may conclude with confidence that the compounds have the planar structure II, probably *trans* as shown.

Behavior in Solution.—All the complexes studied are monomers in benzene, which precludes the possible presence of polymeric species. The complexes of series 2, 3, and 4 show an effective magnetic moment in benzene, chloroform, and *m*-xylene solutions intermediate between 0 and 3.3 B.M. (Table III). This shows that in solution equilibria exist between planar, diamagnetic forms and species in which the ground state of the nickel atom is a triplet state. The absorption spectra of solutions of compounds in all four series confirm these conclusions: there are often two bands at 10,000–11,000 and 16,000–16,800 cm.$^{-1}$ characteristic of the octahedral species and the four bands at *ca.* 7000, 9800,

(7) L. Sacconi, P. L. Orioli, and M. Di Vaira, *J. Am. Chem. Soc.*, **87**, 2059 (1965).

(8) *Cf.* J. R. Miller, *Advan. Inorg. Chem. Radiochem.*, **4**, 175 (1962).

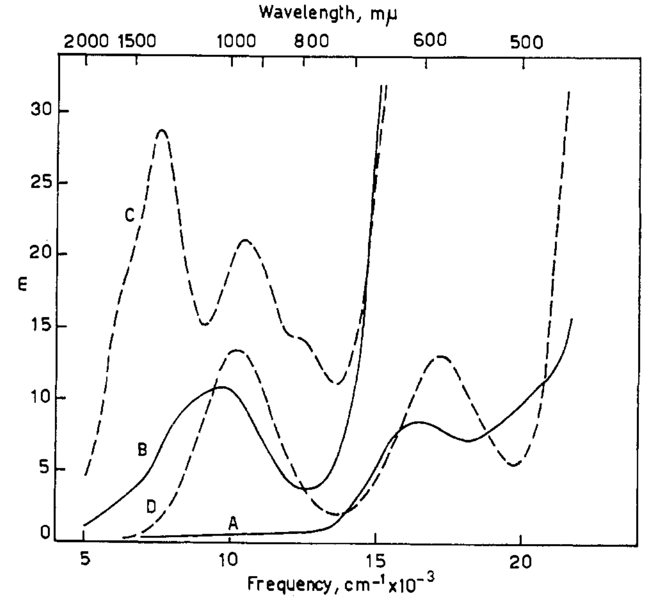


Figure 5.—Reflectance and absorption spectra of [H–SALen–N(CH$_2$)$_5$]$_2$Ni complex at room temperature: A, by reflectance absorption, scale arbitrary; B, in benzene; C, in chloroform; D, in pyridine.

12,700 and 16,200 cm.$^{-1}$ indicative of the five-coordinate species (Figures 1, 2, 4, and 5). Evidently with the process of dissolution and the relaxation of the lattice forces the constraints are removed which force the compound into a given configuration in the solid state, and the different stereochemical forms exist in solution in an equilibrium determined only by the free energies of the dissolved species. One or both of the β-nitrogen atoms bound to the nickel atom in octahedral or five-coordinate complexes may be detached in solution, giving rise to five-coordinate or square-planar complexes and *vice versa*.

The magnetic measurements give the percentage of diamagnetic species in solution, to a reasonable degree of approximation, according to the formula: % diamagnetic species = $100(1 - \mu^2/(3.3)^2)$ (Table III). On the other hand, the absorption spectra give an indication, albeit not a very accurate one, of the relative proportions of the three forms in solution; ϵ_{max} of the band at 16,200 cm.$^{-1}$ approaches a limiting value of *ca.* 90 as the proportion of the planar species increases (the octahedral form has little absorbance in this region). The height of the peak at 9500 cm.$^{-1}$ is roughly proportional to the quantity of octahedral molecules present in equilibrium with only the planar species. The determination of the relative proportion of five- and six-coordinate species in a mixture is more difficult since both types have the same magnetic moment, and also because the extinction coefficients of the five-coordinate species are not known exactly. Nevertheless, the relative heights of the band at 7700 cm.$^{-1}$, which is diagnostic of the five-coordinate species, give an indication of the relative amounts of this species in different solvents. Tables IV and V and Figures 1–5 give spectrophotometric data and absorption spectra.

TABLE III
MAGNETIC SUSCEPTIBILITY DATA FOR SOME SUBSTITUTED $[X-SALen-NR_2]_2Ni$ COMPLEXES IN SOLUTION

Compound	Solvent	Temp., °C.	$10^6\chi_g$	$10^6\chi_{Ni}$	μ_{eff}, B.M.	Param., %
IV	$CHCl_3$	23	8.25	4365	3.23	96
	C_6H_6	23	8.04	4260	3.19	93
VI	$CHCl_3$	22	6.98	4250	3.18	93
VIII	$CHCl_3$	17	6.36	3534	2.88	76
	C_6H_6	22	2.63	1679	2.00	37
	m-$C_6H_4(CH_3)_2$	19	1.55	1142	1.64	25
IX	$CHCl_3$	23	2.65	1787	2.06	39
	C_6H_6	21	0.65	736	1.32	16
X	$CHCl_3$	23	4.05	2525	2.46	56
	C_6H_6	22	0.67	747	1.33	16
XI	$CHCl_3$	20	3.20	2220	2.29	48
	C_6H_6	22	0.91	920	1.47	20
XII	$CHCl_3$	21	6.47	4070	3.15	91
	C_6H_6	20	4.39	2900	2.62	63
XIII	$CHCl_3$	21	4.26	2711	2.53	59
	C_6H_6	22	0.53	647	1.24	14
	m-$C_6H_4(CH_3)_2$	21	−0.06	321	0.87	7
XV	$CHCl_3$	20	6.18	4060	3.10	88
	C_6H_6	22	5.82	3850	3.02	84
XVI	$CHCl_3$	22	1.65	1360	1.80	30
	C_6H_6	20	−0.02	359	0.92	8
XVII	$CHCl_3$	25	5.35	3110	2.74	69
	C_6H_6	23	3.50	2145	2.30	49
	m-$C_6H_4(CH_3)_2$	20	3.17	1940	2.16	43
XVIII	$CHCl_3$	22	3.23	2110	2.22	45
XIX	$CHCl_3$	24	3.83	2450	2.42	54
XX	$CHCl_3$	22	4.07	2755	2.56	60
XXI	$CHCl_3$	23	6.41	4135	3.14	90
XXII	$CHCl_3$	25	3.54	2410	2.41	53

Series 1. $-NR_2 = -N(CH_3)_2$.—These compounds are not soluble enough to permit the measurements of the magnetic moments in solution. The absorption spectra (Figure 1) indicate that in benzene the complexes are almost exclusively octahedral, while in chloroform there are appreciable quantities of the five-coordinate species.

Series 2. $-NR_2 = -N(CH_2)_4$.—These complexes are predominantly paramagnetic in benzene and chloroform with only a very small percentage of diamagnetic species present in solution. The absorption spectra (Figure 2) are analogous to those of series 1 and lead to the same conclusions.

Series 3. $-NR_2 = -N(C_2H_5)_2$.—Four-, five-, and six-coordinate species of these compounds are present in all solvents (Figure 4). The percentage of the planar, diamagnetic species increases along the series of X substituents in the order 3,4-benzo < 5-Cl < H << 5-CH_3 ≈ 3-CH_3 ≈ 5-C_2H_5 < 5,6-benzo. For example, it increases from 16% for the 3,4-benzo derivative to 92% for the 5,6-benzo derivative in benzene, and correspondingly from 12 to 70% in chloroform. In this behavior the effect of the X substituent is similar to its effect on the equilibrium between the planar and tetrahedral forms of the bis(N-*sec*-alkylsalicylaldimino)-nickel(II) complexes,[9] where the benzo substituent most strongly induces the diamagnetic form when in the 5,6- position, but is more powerful than any other substituent in provoking the tetrahedral configuration when in the 3,4- position. Evidently the electronic and steric effects of the X substituent determine which stereochemical arrangement is adopted.

For the complex $[H-SALen-N(C_2H_5)_2]_2Ni$ the percentage of planar species in solution, estimated from both magnetic and spectroscopic data, appears to decrease with the solvent in the order: benzene ≈ dioxane > chlorobenzene > chloroform ≈ benzonitrile ≈ nitrobenzene > acetonitrile ≈ methanol (Table V). As we have noted, magnetic data alone cannot distinguish between five- and six-coordinate species. In spite of similarities in the spectra, the ratio of the molar absorbances of the band at 7700 cm.$^{-1}$ is indicative of the relative proportion of five-coordinate species in different solvents. This proportion increases along the series from benzene to methanol.

Now, the basicity of the solvents increases in the same order apart from dioxane. There is also a marked increase in polarity of the solvent going from benzene to nitrobenzene.

Series 4. $-NR_2 = -N(CH_2)_5$.—The planar species is always present in solution equilibrium with the octahedral species. The five-coordinate form is not detectable in solutions in aromatic hydrocarbons, but in chlorinated solvent it is present in appreciable amounts which increase along the series of solvents: *p*-chlorotoluene ≈ *m*-chlorotoluene < chlorobenzene < *o*-dichlorobenzene < chloroform. (Table VI).

In all four series the effect of the solvent is to give a maximum proportion of the planar form in benzene

(9) L. Sacconi, M. Ciampolini, and N. Nardi, *J. Am. Chem. Soc.*, **86**, 819 (1964).

TABLE IV

SPECTROPHOTOMETRIC ABSORPTION DATA FOR SOME SUBSTITUTED [X-SALen–NR_2]$_2$Ni COMPLEXES IN CHLOROFORM AND IN BENZENE SOLUTIONS

Compound	Solvent	ν_{max}, cm.$^{-1}$ (ϵ_{max})			
I	$CHCl_3$	7630 (23.0);	10,530 (28.6);	... ... ;	16,530 (25.2)
	C_6H_6	... ... ;	10,810 (29.8);	... ... ;	16,670 (26.5)
II	$CHCl_3$	7630 (25.1);	10,930 (32.5);	... ... ;	16,950 (31.6)
IV	$CHCl_3$	7870 (18.8);	10,530 (30.0);	... ... ;	16,450 (24.4)
	C_6H_6	... ... ;	10,580 (30.4);	... ... ;	16,530 (26.4)
V	$CHCl_3$	7810 (21.5);	10,530 (28.2);	... ... ;	16,390 (29.5)
	C_6H_6	... ... ;	10,530 (25.9);	... ... ;	16,310 (34.5)
VI	$CHCl_3$	... ... ;	10,690 (30.2);	... ... ;	16,670 (22.7)
VIII	$CHCl_3$	7690 (36.7);	10,000 (22.9);	12,740 (13.5);	16,180 (46.8)
	C_6H_6	7850 (9.5);	9,600 (8.9):	... ... ;	16,400 (67.0)
IX	$CHCl_3$	7690 (15.9);	10,000 (10.2);	... ... ;	16,000 (77.4)
	C_6H_6	7810 (7.9);	9,600 (5.3);	... ... ;	16,000 (72.4)
X	$CHCl_3$	7690 (30.7);	9,900 (18.6);	... ... ;	16,080 (63.0)
	C_6H_6	7870 (4.8);	9,710 (3.8);	... ... ;	16,080 (86.0)
XI	$CHCl_3$	7690 (16.7);	10,000 (11.5);	12,740 (7.3);	16,130 (59.8)
	C_6H_6	7870 (6.2);	10,000 (4.8);	12,740 (3.3);	16,180 (70.4)
XII	$CHCl_3$	7690 (46.4);	10,000 (38.5);	12,740 (17.5);	16,130 (44.4)
	C_6H_6	7870 (18.5);	9,800 (15.5);	12,740 (7.9);	16,130 (62.2)
XIII	$CHCl_3$	7690 (32.5);	9,900 (19.7);	12,740 (11.8);	16,080 (59.4)
	C_6H_6	7810 (5.2);	9,800 (3.9);	... ... ;	16,130 (84.4)
XV	$CHCl_3$	7690 (56.0);	10,220 (31.8);	12,740 (20.8);	16,180 (49.7)
	C_6H_6	7690 (57.5);	10,000 (31.5);	12,740 (19.5);	16,120 (54.3)
XVI	$CHCl_3$	7810 (23.4);	10,000 (10.7);	12,740 (6.4);	16,950 (127.8)
	C_6H_6	7870 (4.3);	... ... ;	... ... ;	16,950 (142.0)
XVII	$CHCl_3$	7580 (28.7);	10,530 (21.0);	... ... ;	16,260 (46.0)
	C_6H_6	... ... ;	9,800 (10.9);	... .. ;	16,260 (51.8)
XVIII	$CHCl_3$	7460 (14.2);	10,960 (10.7);	... ... ;	16,000 (68.5)
	C_6H_6	7690 (5.4);	10,810 (5.2);	... ... ;	15,870 (73.9)
XIX	$CHCl_3$	7520 (22.9);	10,470 (15.4);	12,500 (10.9);	16,050 (64.6)
	C_6H_6	... ... ;	9,710 (6.0);	... ... ;	16,000 (61.3)
XX	$CHCl_3$	7630 (16.9);	10,635 (15.2);	... ... ;	16,230 (52.8)
	C_6H_6	8000 (7.6);	10,420 (9.7);	... ... ;	16,180 (54.8)
XXI	$CHCl_3$	7580 (37.5);	10,580 (28.2);	12,500 (19.6);	16,340 (41.5)
	C_6H_6	... ... ;	9,610 (20.0);	... ... ;	16,180 (33.1)
XXII	$CHCl_3$	7520 (23.5);	10,470 (15.5);	12,500 (11.2);	16,000 (64.5)
	C_6H_6	... ... ;	9,800 (5.9);	... ... ;	16,000 (80.6)
XXIII	$CHCl_3$	7690 (16.3);	10,750 (8.3);	... ... ;	... ...

TABLE V

SPECTROPHOTOMETRIC ABSORPTION DATA FOR [H–SALen–N(C_2H_5)$_2$]$_2$Ni COMPLEX IN DIFFERENT SOLVENTS

Solvent	ν_{max}, cm.$^{-1}$ (ϵ_{max})			
Methanol	7690 (39.5);	10,200 (28.7);	12,750 (14.4);	16,250 (32.4)
Acetonitrile	7690 (39.2);	10,000 (26.1);	12,750 (14.7);	16,150 (34.2)
Chloroform	7690 (36.7);	10,000 (22.9);	12,750 (13.5);	16,200 (46.8)
Benzonitrile	7690 (34.5);	10,000 (23.1);	12,750 (13.5);	16,250 (45.3)
Nitrobenzene	7690 (29.4);	10,000 (19.8);	12,750 (12.3);	16,350 (41.3)
Chlorobenzene	7690 (17.7);	9,800 (12.4);	12,750 (7.7);	16,250 (61.4)
Dioxane	7690 (9.6);	9,610 (7.1);	12,500 (4.5);	16,250 (65.5)
Benzene	7870 (9.5);	9,610 (8.9);	12,500 (3.8);	16,200 (67.0)

TABLE VI

SPECTROPHOTOMETRIC ABSORPTION DATA FOR [H-SALen–N(CH_2)$_5$]$_2$Ni COMPLEX IN DIFFERENT SOLVENTS

Solvent	ν_{max}, cm.$^{-1}$ (ϵ_{max})		
Benzene	... ... ;	9,800 (10.9);	16,250 (51.8)
Toluene	... ... ;	9,500 (9.3);	16,150 (54.6)
o-Xylene	... ... ;	9,500 (6.9);	16,150 (61.4)
m-Xylene	... ... ;	9,500 (9.5);	16,250 (77.6)
p-Chlorotoluene	7870 (7.8);	10,250 (8.0);	16,150 (61.5)
m-Chlorotoluene	8000 (8.0);	10,250 (8.6);	16,200 (60.3)
Chlorobenzene	7690 (10.9);	10,500 (10.4);	16,250 (58.6)
o-Dichlorobenzene	7690 (15.0);	10,500 (14.1);	16,250 (54.2)
Chloroform	7580 (28.7);	10,550 (21.0);	16,250 (46.0)

and a greater proportion of the five-coordinate form in chloroform. In pyridine six-coordinate species are formed in all cases.

For a given X substituent and solvent, the percentage of the planar species increases according to the $-NR_2$ group in the order: $-N(CH_3)_2 < -N(CH_2)_4 < -N(C_2H_5)_2 < -N(CH_2)_5$. It will be remembered that the donor power of the corresponding amines toward the complex Ni(DBH) has been measured in aprotic solvents.[10] In that case the donor power was found to decrease in the order $HN(CH_3)_2 \approx HN(CH_2)_4 > HN(CH_2)_5 >$

(10) L. Sacconi, G. Lombardo, and P. Paoletti, *J. Chem. Soc.*, 848 (1958); L. Sacconi and G. Lombardo, *J. Am. Chem. Soc.*, **82**, 6266 (1960).

$HN(C_2H_5)_2$. Stuart models of the $[X\text{–SALen–}NR_2]_2Ni$ complexes have shown that the steric hindrance to coordination of the terminal amino group increases in the order of the former group. It is therefore clear that the greater donor power of an amino group can be offset by its greater bulkiness, and that is why the strongly basic piperidino group gives a weaker complex than the diethylamino group.

The Effect of Temperature on the Conformational Equilibria.—The effect of temperature on the equilibria can be studied in the fused complex $[H\text{–SALen–}N(C_2H_5)_2]_2Ni$ as its melting point is sufficiently low to allow magnetic measurements to be made on the pure liquid complex. In the fused state the effective magnetic moment drops with temperature and the percentage of the diamagnetic species in the equilibrium mixture, calculated by the same methods as before, increases from 44% at 70° to 61% at 120° (Table VII).

TABLE VII
MAGNETIC DATA FOR $[H\text{–SALen–}N(C_2H_5)_2]_2Ni$ COMPLEX IN THE MOLTEN STATE BETWEEN 70 AND 120°

T, °C.	μ_{eff}, B.M.	% diam. form
70	2.30	44
100	2.06	55
120	1.90	61

The effect of temperature on solutions of the complex $[H\text{–SALen–}N(CH_2)_5]_2Ni$ was also studied, and again it was found that increasing temperature favors the planar species. In *m*-xylene, for example, magnetic measurements show that the proportion of the planar species rises from 57% at 20° to 80% at 80°. The equilibrium was also studied spectrophotometrically in *m*-xylene, where the five-coordinate species is absent. The composition of the equilibrium mixture was ascertained by using the molar absorbance at 9500 $cm.^{-1}$ as a means of calculating the percentage of the octahedral species, known from magnetic data to be 43% at room temperature (Table VIII).

TABLE VIII
MAGNETIC DATA FOR $[H\text{–SALen–}N(CH_2)_5]_2Ni$ COMPLEX IN *m*-XYLENE SOLUTION BETWEEN 20 AND 80°

T, °C.	μ_{eff}, B.M.	% diam. form
20	2.16	57
30	1.67	74
50	1.33	84
80	1.02	90

The equilibrium constant K = [octahedral species]/[planar species] was thus calculated. As log K was found to be inversely proportional, within experimental error, to the absolute temperature (Figure 6), the following values were easily obtained: $\Delta F = 0.17$ kcal./mole^{-1} (20°), $\Delta H = 3.4$ kcal./mole^{-1}, and

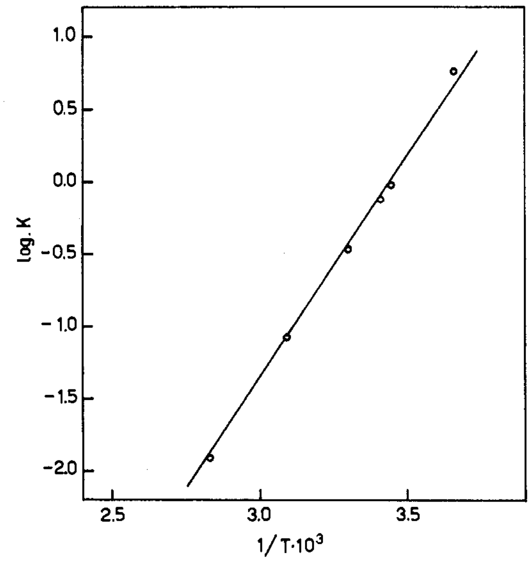


Figure 6.—Plot of log K against $1/T$ for the diamagnetic ⇌ paramagnetic equilibrium in $[H\text{–SALen–}N(CH_2)_5]_2Ni$ complex.

$\Delta S = 12$ e.u. It will be seen that the enthalpy of formation of the planar form is not greatly different from that of the octahedral form. In fact it is small enough for the two forms to exist in comparable amounts in solution at room temperature. At high temperatures, however, the percentage of the planar form increases. The transformation to the planar form is therefore an endothermic process, as it is for the compounds of series 3 in the previous paper.[1] It is reasonable to assume that increasing thermal agitation will favor the rupture of bonds between the sterically hindered amino groups and the nickel atom, with the formation of the four-coordinate species. The solution equilibria can be represented by the following scheme.

octahedral paramagnetic form
I ⇅ ⇌(II) planar diamagnetic form
five-coordinate paramagnetic form

The effect of temperature on equilibrium II has been noted, but nothing can at present be said with regard to equilibrium I.

The difference of 12 e.u. in the entropies of formation of the two species mentioned above must mainly be attributed to the greater freedom of movement that the $-CH_2-CH_2-N(CH_2)_5$ group attains in the planar form. Both the effects of the higher statistical weight of the triplet electronic ground state in the octahedral complex as compared with the planar one and the possibility that the latter is more solvated should contribute factors to the entropy difference which would favor the octahedral form.

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