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Complexes of Nickel(II) with Schiff Bases Formed from Salicylaldehydes and N-Substituted Trimethylenediamines

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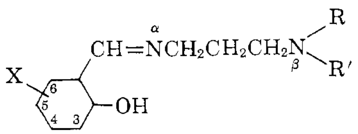
Schiff bases formed from ring-substituted salicylaldehydes and N,N-substituted derivatives of 1,3-diaminopropane (trimethylenediamine, tn) form complexes with nickel (II) of the general formula [X–SALtn–N(R)R′]$_2$Ni. The nature of the substituents R, R′, and X determines whether the ligand is bi- or tridentate. When R = H, R′ = *n*-alkyl or when R, R′ = $(CH_3)_2$, $(CH_2)_4$ the resulting complexes are octahedral. Dipole moment measurements and an X-ray crystallographic analysis show that these complexes have a *trans*-octahedral configuration. When R = CH_3, R′ = C_6H_5 all the complexes have the square-planar configuration, and are diamagnetic. When R = H, R′ = C_6H_5 or R, R′ = $(C_2H_5)_2$, $(CH_2)_5$ the configuration of the complex is determined by the ring substituent X. Some compounds were obtained as both paramagnetic and diamagnetic isomers. In inert solvents the planar and octahedral forms coexist in an equilibrium mixture.

Introduction

We have, in this laboratory, previously studied the complexes of nickel(II)[1,2] and cobalt(II)[3] obtained with Schiff bases formed from ring-substituted salicylaldehydes and N,N-substituted ethylenediamines. The ligand in these complexes (given the general formula [X–SALen–N(R)R′]$_2$M) is either bi- or tridentate depending on the electronic and steric effects of the substituents R, R′, and X. Thus some of the complexes were *cis*-octahedral and some were tetracoordinated (the nickel ones being planar, the cobalt ones tetrahedral), but in other instances five-coordinated complexes were obtained[2] in which one ligand is bidentate and the other is tridentate. In solution an equilibrium mixture of the various species was formed.

We wished to study the effect of an increase in the chain length of the diamines upon the stereochemistry of the complexes. We have therefore chosen as ligands the trimethylenediamine derivatives of the general formula



Schiff bases of this type form complexes with nickel(II) which will be given the abbreviated formula [X–SALtn–N(R)R′]$_2$Ni. The stereochemistry of the complexes was investigated by means of molecular weight, spectroscopic, magnetic, and dielectric polarization measurements.

In this series of complexes, the compound [H–SALtn–N$(CH_3)_2$]$_2$Ni had been prepared and investigated by Holm, *et al.* These authors suggested for this complex a *cis*-octahedral structure.[4]

Experimental Section

Preparation of the Compounds.—The complexes were prepared by heating together the substituted bis(salicylaldehyde)nickel(II) dihydrate complexes (10 mmoles) with the appropriate N-substituted trimethylenediamines (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 trimethylenediamines not commercially available were prepared by the addition of the appropriate amine to acrylonitrile and subsequent catalytic reduction of the resulting nitriles to amines.[5,6] The N-phenyltrimethylenediamine was prepared by reducing 1-phenylpyrazole with sodium in alcohol.[7]

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.[8] The sample tube was calibrated with Hg[Co(NCS)$_4$] and freshly boiled distilled water.[9]

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.

Dielectric Polarization Measurements.—The apparatus and the procedures used have been previously described.[10] The molar refractions for the sodium D line, R_D, of the complexes were calculated by adding the proper values of bond refractions[11] to the measured molar refraction of the bis(N-cyclohexylsalicylaldiminato)cobalt(II) complex.[12] Values of the orientation polarization, P_o, were calculated by assuming a value of 20% R_D for the atom polarization.

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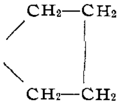
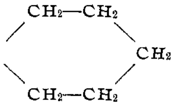
TABLE I

SUMMARY OF PHYSICAL AND ANALYTICAL DATA FOR SUBSTITUTED $[X\text{–}SALtn\text{–}N(R)R']_2Ni$ COMPLEXES

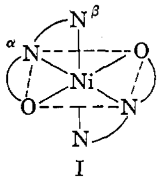
X	R	R′	Crystallization	Formula	Mp, °C	Calcd, % N	Calcd, % Ni	Found, % N	Found, % Ni
H	H	CH_3	$CHCl_3$ + petr ether	$C_{22}H_{30}N_4O_2Ni$	234–236	12.70	13.37	12.63	13.19
5-CH_3			$CHCl_3$ + C_2H_5OH	$C_{24}H_{34}N_4O_2Ni$	221–223	11.93		12.15	
5-Cl			$CHCl_3$ + petr ether	$C_{22}H_{28}N_4O_2Cl_2Ni$	239–240	10.98		10.97	
3,4-Benzo			$CHCl_3$ + petr ether	$C_{30}H_{34}N_4O_2Ni$	262–265	10.35		10.38	
5,6-Benzo			$CHCl_3$ + C_2H_5OH	$C_{30}H_{34}N_4O_2Ni$	265–268	10.35		10.41	
H	H	C_3H_7	$CHCl_3$ + petr ether	$C_{26}H_{38}N_4O_2Ni$	216–218	11.27	11.84	11.28	12.04
5-CH_3			C_2H_5OH	$C_{28}H_{44}N_4O_2Ni$	175–176	10.67		10.62	
5-Cl			$CHCl_3$ + petr ether	$C_{26}H_{36}N_4O_2Cl_2Ni$	204–205	9.89		9.93	
H	CH_3	CH_3	$CHCl_3$ + petr ether	$C_{24}H_{34}N_4O_2Ni$	176–177	11.94	11.72	12.16	11.61
5-CH_3			Toluene	$C_{26}H_{38}N_4O_2Ni$	169–170	11.26		11.32	
5-Cl			$CHCl_3$ + petr ether	$C_{24}H_{32}N_4O_2Cl_2Ni$	197–199	10.41		10.35	
5-NO_2			Toluene	$C_{24}H_{32}N_6O_6Ni$	232–234	15.03		15.02	
3,4-Benzo			*m*-Xylene	$C_{32}H_{38}N_4O_2Ni$	260–263	9.84		9.77	
5,6-Benzo			Toluene	$C_{32}H_{38}N_4O_2Ni$	231–232	9.84		9.81	
H			$CHCl_3$ + C_2H_5OH	$C_{28}H_{38}N_4O_2Ni$	199–200	10.74	11.29	10.68	11.35
5-CH_3			$CHCl_3$ + C_2H_5OH	$C_{30}H_{42}N_4O_2Ni$	207–208	10.20		10.30	
5-Cl			$CHCl_3$ + C_2H_5OH	$C_{28}H_{36}N_4O_2Cl_2Ni$	232–234	9.49		9.53	
3,4-Benzo			Dimethylformamide	$C_{36}H_{42}N_4O_2Ni$	270–272	9.02		9.05	
5,6-Benzo			Dimethylformamide	$C_{36}H_{42}N_4O_2Ni$	242–243	9.02		9.03	
H	C_2H_5	C_2H_5	Petr ether	$C_{28}H_{42}N_4O_2Ni$	48–50	10.66	11.07	10.82	11.09
5-CH_3			Petr ether	$C_{30}H_{46}N_4O_2Ni$	71–72	10.12		10.38	
5-Cl (green)			Petr ether	$C_{28}H_{40}N_4O_2Ni$	112–115	9.43		9.46	
5-Cl (ochre)			Petr ether	$C_{28}H_{40}N_4O_2Cl_2Ni$	112–114	9.43		9.46	
3,4-Benzo			Cyclohexane	$C_{36}H_{46}N_4O_2Ni$	108–110	8.96		8.92	
5,6-Benzo			Petr ether	$C_{36}H_{46}N_4O_2Ni$	110–112	8.96		9.07	
H			$CHCl_3$ + petr ether	$C_{30}H_{42}N_4O_2Ni$	151–152	10.20	10.80	10.37	11.07
3-CH_3			$CHCl_3$ + petr ether	$C_{32}H_{46}N_4O_2Ni$	176–177	9.70		9.68	
5-CH_3			$CHCl_3$ + petr ether	$C_{32}H_{46}N_4O_2Ni$	140–142	9.70		9.72	
3-Cl			$CHCl_3$ + petr ether	$C_{30}H_{40}N_4O_2Cl_2Ni$	186–187	9.06		9.03	
5-Cl			$CHCl_3$ + petr ether	$C_{30}H_{40}N_4O_2Cl_2Ni$	173–175	9.06		9.10	
5-NO_2			$CHCl_3$ + C_2H_5OH	$C_{30}H_{40}N_6O_6Ni$	208–210	13.15		13.20	
3,4-Benzo			C_2H_5OH	$C_{38}H_{46}N_4O_2Ni$	172–174	8.62		8.78	
5,6-Benzo			$CHCl_3$ + petr ether	$C_{38}H_{46}N_4O_2Ni$	203–205	8.62		8.51	
H (green)	H	C_6H_5	$CHCl_3$ + petr ether	$C_{32}H_{34}N_4O_2Ni$	152–153	9.91	10.36	10.07	10.04
H (ochre)			$CHCl_3$ + petr ether	$C_{32}H_{34}N_4O_2Ni$	151–153	9.91		10.01	
5-CH_3 (green)			$CHCl_3$ + petr ether	$C_{34}H_{38}N_4O_2Ni$	164–165	9.44		9.58	
5-CH_3 (ochre)			$CHCl_3$ + petr ether	$C_{34}H_{38}N_4O_2Ni$	163–164	9.44		9.40	
5-C_2H_5			$CHCl_3$ + petr ether	$C_{36}H_{42}N_4O_2Ni$	165–166	9.02		9.26	
5-Cl			$CHCl_3$ + petr ether	$C_{32}H_{32}N_4O_2Cl_2Ni$	197–199	8.83		8.95	
3,4-Benzo			$CHCl_3$ + petr ether	$C_{40}H_{38}N_4O_2Ni$	194–196	8.42		8.38	
5,6-Benzo			$CHCl_3$ + petr ether	$C_{40}H_{38}N_4O_2Ni$	188–189	8.42		8.41	
H	CH_3	C_6H_5	$CHCl_3$ + C_2H_5OH	$C_{34}H_{38}N_4O_2Ni$	141–142	9.44	9.89	9.71	9.83
5-CH_3			$CHCl_3$ + petr ether	$C_{36}H_{42}N_4O_2Ni$	201–202	9.02		8.95	
3-Cl			$CHCl_3$ + petr ether	$C_{34}H_{36}N_4O_2Cl_2Ni$	155–156	8.46		8.20	
5-Cl			$CHCl_3$	$C_{34}H_{36}N_4O_2Cl_2Ni$	212–213	8.46		8.86	
3,4-Benzo			$CHCl_3$ + petr ether	$C_{42}H_{42}N_4O_2Ni$	201–202	8.08		8.19	
5,6-Benzo			$CHCl_3$ + petr ether	$C_{42}H_{42}N_4O_2Ni$	168–169	8.08		8.04	

Results

The compounds listed in Table I were shown by molecular weight measurements not to be appreciably polymerized in benzene solution. Magnetic susceptibility values are given in Tables II and III and details concerning the visible absorption spectra are given in Table IV. Since the ligands absorb strongly above *ca.* 20,000 cm^{-1}, discussion of the spectra is limited to bands having less than this frequency.

Series 1. R, R′ = $(CH_3)_2$, $(CH_2)_4$.—All these compounds have an effective magnetic moment of 3.13–3.24 BM. The dipole moment values were found to be less than 1 D. in benzene at 20°. This points to a nonpolar structure for the complexes and therefore rules out a *cis* structure. The reflectance spectra (Figure 1) show a weak, broad band with more than one maximum in the region 6500–13,000 cm^{-1} and a shoulder at *ca.* 17,000 cm^{-1}. This type of spectrum is indicative of a distorted octahedral structure and is to be compared with the spectra reported for some *trans*-octahedral (D_{4h} symmetry) nickel(II) complexes.[13] In the latter there are two weak, broad bands in the near-infrared region which are attributed to the $^3B_{2g}$ and ^3E_g levels derived from the $^3T_{2g}(F)$ level in octahedral symmetry.

A complete three-dimensional X-ray structural analysis, performed in this Laboratory,[14] has shown that the complex $[H\text{–}SALtn\text{–}N(CH_3)_2]_2Ni$ has a distorted *trans*-octahedral configuration shown schematically as



I

The coordination polyhedron consists of six donor atoms around the nickel; the four nitrogen atoms lie in a plane of symmetry, normal to the twofold axis which passes through the oxygen atoms. The βN–Ni distance is 0.25 A greater than the αN–Ni distance of 2.05 A. This effect is likely due to steric repulsion between the βN methyl groups and the opposite salicylaldimine ring. The angle αN–Ni–βN is *ca.* 83°; hence the point group of the complex is C_{2h}.

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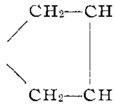
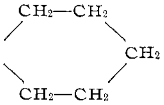
[13] S. M. Nelson and T. M. Shepherd, *J. Chem. Soc.*, 3276 (1965).

[14] M. Di Vaira and P. L. Orioli, to be published.

TABLE II

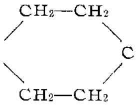
MAGNETIC SUSCEPTIBILITIES DATA FOR SUBSTITUTED $[X\text{-SALtn-N(R)R}']_2Ni$ COMPLEXES IN THE SOLID STATE

X	R	R′	Temp, °C	$10^6\chi_g$	$10^6\chi_{Ni}$[a]	μ_{eff} BM
H	H	CH_3	19	8.79	4150	3.13
5-CH_3			19	8.59	4314	3.18
5-Cl			20	7.58	4162	3.14
3,4-Benzo			20	6.97	4094	3.13
5,6-Benzo			20	6.87	4042	3.10
H	H	C_3H_7	18	7.86	4220	3.15
5-CH_3			19	7.40	4219	3.15
5-Cl			19	6.75	4163	3.14
H	CH_3	CH_3	19	8.73	4394	3.23
5-CH_3			19	8.23	4401	3.22
5-Cl			20	7.26	4226	3.16
5-NO_2			20	7.37	4430	3.22
3,4-Benzo			18	6.68	4160	3.13
5,6-Benzo			19	6.90	4275	3.18
H			19	7.82	4397	3.22
5-CH_3			20	7.14	4265	3.18
5-Cl			19	6.72	4319	3.20
3,4-Benzo			20	6.49	4435	3.24
5,6-Benzo			20	6.28	4280	3.22
H	C_2H_5	C_2H_5	20		Diamagnetic	
5-CH_3			20		Diamagnetic	
5-Cl (green)			22		Diamagnetic	
5-Cl (ochre)			20	6.25	4282	3.19
3,4-Benzo			21	6.21	4286	3.18
5,6-Benzo			20		Diamagnetic	
H			19		Diamagnetic	
3-CH_3			19		Diamagnetic	
5-CH_3			20		Diamagnetic	
3-Cl			18		Diamagnetic	
5-Cl			18		Diamagnetic	
5-NO_2			19	6.20	4670	3.32
3,4-Benzo			19		Diamagnetic	
5,6-Benzo			19		Diamagnetic	
H (green)	H	C_6H_5	18		Diamagnetic	
H (ochre)			21	6.92	4237	3.18
5-CH_3 (green)			19		Diamagnetic	
5-CH_3 (ochre)			18	7.03	4518	3.26
5-C_2H_5			20	6.54	4454	3.25
5-Cl			19	6.09	4240	3.16
3,4-Benzo			20	5.30	3923	3.05
5,6-Benzo			21		Diamagnetic	
H	CH_3	C_6H_5	20		Diamagnetic	
5-CH_3			20		Diamagnetic	
3-Cl			21		Diamagnetic	
5-Cl			20		Diamagnetic	
3,4-Benzo			21		Diamagnetic	
5,6-Benzo			20		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).

TABLE III

MAGNETIC SUSCEPTIBILITIES DATA FOR SOME SUBSTITUTED $[X\text{-SALtn-N(R)R}']_2Ni$ COMPLEXES IN CHLOROFORM

X	R	R′	Temp, °C	$10^6\chi_g$	$10^6\chi_{Ni}$	μ_{eff}, BM
H	H	CH_3	20	8.96	4227	3.16
5,6-Benzo			20	6.98	4.97	3.13
H	H	C_3H_7	19	8.04	4302	3.18
5-CH_3			19	7.52	4285	3.17
H	CH_3	CH_3	19	8.57	4319	3.18
5-CH_3			19	7.94	4257	3.17
H	C_2H_5	C_2H_5	19	1.91	1348	1.79
5-CH_3			20	0.47	618	1.26
5-Cl (green)			20	4.16	2569	2.50
5-Cl (ochre)			20	3.92	2721	2.51
3,4-Benzo			20	3.65	2686	2.52
5,6-Benzo			20		Diamagnetic	
H			18	1.47	1170	1.66
3-CH_3			20	0.40	557	1.15
5-CH_3			19	0.49	609	1.20
3-Cl			20	4.39	3116	2.72
5-Cl			18	3.57	2610	2.48
3,4-Benzo			20	3.19	2430	2.40
5,6-Benzo			20		Diamagnetic	
H (green)	H	C_6H_5	20	1.07	938	1.52
H (ochre)			21	1.27	1055	1.53
5-CH_3 (green)			18	0.44	620	1.16
5-CH_3 (ochre)			18	0.30	361	1.15
5-C_2H_5			17	0.86	927	1.47
3,4-Benzo			18	4.34	3285	2.78
5,6-Benzo			18	1.02	1076	1.50
H	CH_3	C_6H_5	18		Diamagnetic	
3-Cl			18		Diamagnetic	
5,6-Benzo			20		Diamagnetic	

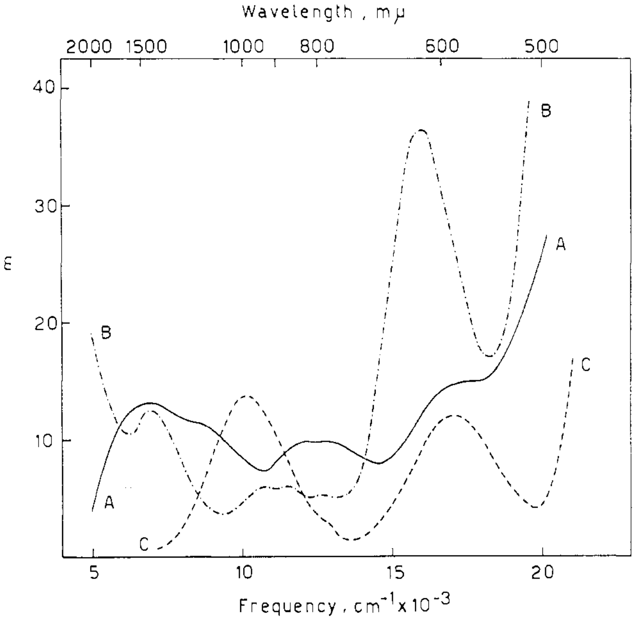


Figure 1.—Reflectance and absorption spectra of the $[H\text{-SALtn-N}(CH_2)_4]_2Ni$ complex at room temperature: A, by reflectance absorption, arbitrary scale; B, in chloroform; C, in pyridine.

The levels $^3T_{2g}$ and $^3T_{1g}$ of the nickel(II) ion in an octahedral crystal field are split into six nondegenerate levels in a field of C_{2h} symmetry. As the center of symmetry is retained, electronic transitions are expected to give rise to weak absorption bands, and the low-frequency bands found can be rationalized on this basis.

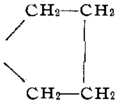
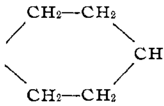
In solution in inert solvents the spectra differ slightly from the reflectance spectra, notably in the appearance of a weak band at *ca.* 5000 cm^{-1}. This signifies that the molecule may be distorted in another way in solution, and the possibility that other species are present in the mixture cannot be excluded. Anyhow, the low value of the dipole moment indicates that the predominant species is still the *trans*-octahedral one. The molar susceptibility values in solution preclude the presence of planar species. In pyridine octahedral adducts are formed, as shown by the absorption spectra.

Series 2. R = H, R′ = CH_3, n-C_3H_6.—All the complexes in this series are paramagnetic and have μ_{eff} values approximately the same as those of compounds in series 1. The reflectance spectra are very similar to those of the analogous $[X\text{-SALen-N(R)R}']_2Ni$ *cis*-octahedral complexes[1] (Figure 2), but the dipole moments are all less than 1 D. compared with 7 D. for the *cis*-octahedral complexes.[1] A *trans*-octahedral structure of the type I must therefore be assigned to the complexes of series 2.

Since in this series one βN substituent is a hydrogen atom the steric hindrance due to R and R′ is less than in the previous series. This allows the β nitrogen

TABLE IV

ELECTRONIC SPECTRA OF THE SOME REPRESENTATIVE COMPLEXES

X	R	R′	State	Absorption max, cm^{-1} (ϵ_{molar} for soln)
H	H	CH_3	Solid	9100 sh, 11,400, 20,000 sh
			$CHCl_3$	9100 sh, 11,200 (6.7), 17,500 sh
			py	10,900 (8.0)
H	H	C_3H_7	Solid	8700 sh, 11,300, 20,000 sh
			$CHCl_3$	8700 sh, 11,100 (6.7), 17,400 sh
			py	10,300 (5.2), 17,200 (4.8)
H	CH_3	CH_3	Solid	7500, 9100, 11,900, 13,300, 17,400 sh
			$CHCl_3$	<5000, 7400 (14.5), 11,000 sh, 16,300 (38.5)
			py	10,300 (14.0), 17,300 (13.7)
H			Solid	7000, 8700 sh, 12,000, 13,000, 17,400 sh
			$CHCl_3$	<5000, 7000 (12.4), 10,800 (5.8), 11,700 (5.9), 12,500 (5.3), 16,000 (36.3)
			py	10,200 (13.6), 17,200 (12.0)
H	C_2H_5	C_2H_5	Solid	8500 sh, 9500, 15,900
			$CHCl_3$	<5000, 7000 (3.7), 10,500 (1.8), 16,000 (65.8)
			py	10,200 (14.4), 17,100 (16.6)
5-Cl (green)			Solid	15,900
5-Cl (ochre)			Solid	6500, 83,00, 12,100, 12,900, 16,700 sh
H			Solid	16,400
			$CHCl_3$	<5000, 7100 (3.7), 11,100 sh, 16,200 (73.0)
			py	10,800 (15.1), 17,400 (14.8)
H (green)	H	C_6H_5	Solid	16,200
			$CHCl_3$	16,200 (67.5)
H (ochre)			Solid	9700, 11,500 sh
			$CHCl_3$	16,300 (64.6)
			py	10,200 (13.7), 17,400 (15.3)
5-CH_3 (green)			Solid	15,900
5-CH_3 (ochre)			Solid	9500, 11,400
H	CH_3	C_6H_5	Solid	15,900
			$CHCl_3$	15,900 (69,2)
			py	10,300 (14.1), 17,100 (11.8)

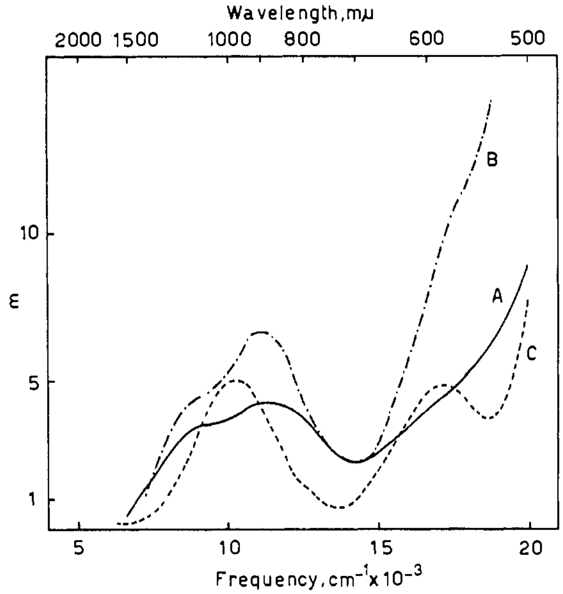


Figure 2.—Reflectance and absorption spectra of the [H-SALtn-N(H)C_3H_7]$_2$Ni complex at room temperature: A, by reflectance absorption, arbitrary scale; B, in chloroform; C, in pyridine.

atom to approach more closely to the central nickel atom and accounts for the similarity to the spectra of the SAL-en-N(R)R′ derivatives and the differences from compounds of series 1.

The spectra in inert solvents are identical with those of the solids, and the values of μ_{eff} in solution range from 3.13 to 3.18 BM. These facts, together with the low molar absorbance at 16,000 cm^{-1}, allow one to conclude that the equilibrium concentration of planar species in solution is negligible. The spectra of the R′ = CH_3 derivatives are unchanged in pyridine, whereas when R′ = *n*-C_3H_7 the spectrum characteristic of the *trans* adduct is obtained.

Series 3. R, R′ = $(C_2H_5)_2$, $(CH_2)_5$.—In the solid state the 3,4-benzo derivative is paramagnetic. For [5-Cl-SALtn-N$(C_2H_5)_2$]$_2$Ni both an ochre-colored, paramagnetic isomer and a green, diamagnetic isomer are isolated. All the other complexes are green and diamagnetic. The reflectance spectra of the paramagnetic complexes are similar to those of series 1 and therefore an analogous distorted *trans*-octahedral configuration is to be attributed to them.

In inert solvents all compounds (except the derivative X = 5,6-benzo) give a spectrum characteristic of an equilibrium mixture of planar and octahedral species of the kind that we have reported previously.[1] The absorption in the near-infrared region is very low, but, in contrast with the absorption spectra of the previous series, the intensity of the band at *ca.* 16,000 cm^{-1} is very high ($\epsilon \approx 50$–70). In fact, besides the weak absorption of the octahedral form, the absorption of the planar diamagnetic form also falls in this region. The presence of this species in solution is confirmed by the value of the magnetic moments, which range from 1.79 to 2.72 BM. The percentage of the planar diamagnetic form increases with the temperature, as shown by the absorption spectra. For instance, in the case of [5-Cl-SALtn-N$(CH_2)_5$]$_2$Ni the molar absorbance at 16,000 cm^{-1} increases from 66.4 at 5° to 88.8 at 110°, whereas the molar absorbances at 10,000 and 7000 cm^{-1}, due presumably to the octahedral species, decrease from 6.6 and 5.3 at

5° to 2.4 and 4.0 at 110°, respectively. The band at 5000 cm^{-1}, which is also present in this case, shows a decrease in intensity by increasing the temperature. Octahedral adducts are formed in pyridine.

Series 4. R = H, R′ = C_6H_5.—The 5-Cl, 5-C_2H_5, and 3,4-benzo derivatives are paramagnetic and ochre in color, and the 5,6-benzo derivative is diamagnetic and green in color. Both a green, diamagnetic and an ochre, paramagnetic isomer were obtained for 5-CH_3 and H. The reflectance spectra (Figure 3) of the paramagnetic compounds are intermediate in type between those of the series 1 and series 2 compounds. This implies that the coordination polyhedron is distorted in an intermediate fashion compared with the compounds of series 1 and 2. Indeed it is reasonable to assume that the βN–Ni distance increases with the substituents in the order N(H)alkyl < N(H)aryl < N(alkyl)$_2$. Although the N(H)C_6H_5 group is a poorer electron donor than the N(CH_3)$_2$ group, it is less subject to the steric hindrance which is responsible for the particularity large βN–Ni distance with the latter group.

In chloroform planar and octahedral species are in equilibrium and μ_{eff} varies from 1.16 to 2.78 BM (Table III) at room temperature according to the substituent X. Adducts are formed in pyridine as in the previous cases.

Series 5. R = CH_3, R′ = C_6H_5.—All these compounds are green and diamagnetic, both as solids and in solution. The dipole moment values, which range from 0.80 and 1.00 D., are indicative of a *trans*-planar configuration.

Discussion

Since the azomethine nitrogen atom (α) in Schiff base metal complexes is planar sp^2 hydridized, the carbon atom of the methylene group attached to it must lie in the plane defined by this nitrogen atom, the oxygen atom, and the central metal atom. When the SALen behave as tridentate ligands the β nitrogen atom is constrained to lie in approximately the same plane. Thus, SALen derivatives form *cis*-octahedral complexes. In the case of the SALtn complexes, the extra methylene group gives greater flexibility to the side chain and the β nitrogen atom is able to reach the apical positions of the octahedron, and consequently *trans*-octahedral complexes can be, and are, formed. Differences in the bulkiness and inductive effects of the substituents R and R′ gave rise to different degrees of distortion from a regular *trans*-octahedral configuration. With SALen–N(R)R′ complexes, on the other hand, when R and R′ are bulky, five-coordinated species are formed[2] in which one ligand is tridentate and the other is bidentate. When the groups R and R′ are electron withdrawing as well as bulky, planar, diamagnetic complexes, in which both ligands are bidentate, are formed for both SALtn and SALen derivatives.

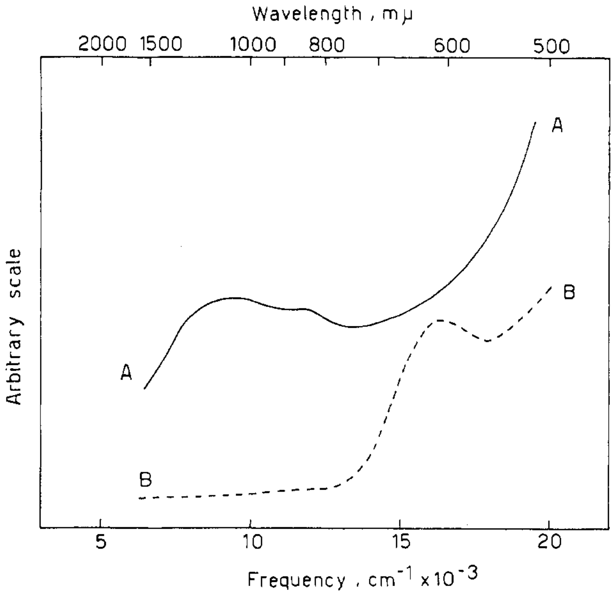


Figure 3.—Reflectance spectra of the [H–SALtn–N(H)C_6H_5]$_2$Ni complex: A, ochre isomer; B, green isomer.

The solution magnetism of the SALtn complexes shows that for any given substituents R and R′ the substituents X favor the formation of octahedral species in the order 5,6-benzo < 5-CH_3 < H ≈ 5-Cl < 3,4-benzo. This series is substantially in agreement with the order for the planar $\rightleftharpoons$ tetrahedral equilibrium in bis(N-*sec*-alkylsalicylaldimino)nickel(II) complexes[15] and the planar $\rightleftharpoons$ octahedral[1] and planar $\rightleftharpoons$ five-coordinated[2] equilibria in the complexes [X–SALen–N(R)R′]$_2$Ni. In all cases the 5,6-benzo substituent most strongly induces the formation of the planar species, and the 3,4-benzo (and sometimes 5-Cl) substituent induces the most strongly the formation of paramagnetic species.

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