Contribution from the Institute of General and Inorganic Chemistry,
University of Florence, Florence, Italy

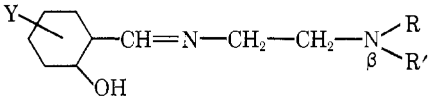
Action of Hydrochloric and Hydrobromic Acids on Nickel(II) Complexes with N-Substituted Salicylideneethylenediamines

By P. NANNELLI and L. SACCONI

Nickel(II) complexes of the type [SALen–N(R)R′]$_2$Ni react, under suitable conditions, with hydrochloric and hydrobromic acids to form complexes of the general formula [SALen–N(R)R′]$_2$Ni·2HX. When R = H the halogen ion coordinates to the central nickel atom, and paramagnetic octahedral complexes are formed with the halogen ions in *cis* positions. When the (β) nitrogen is a tertiary nitrogen, the halogens do not bond to the nickel and diamagnetic planar complexes are obtained.

Introduction

Nickel(II) complexes with Schiff bases, derived from salicylaldehydes and N-substituted ethylenediamines, have been described in previous papers.[1,2] The Schiff bases have the general formula



and, depending on the substituents Y, R, R′, their nickel(II) complexes show various types of stereochemistry in the solid state with the terminal (β) nitrogen either coordinated or not coordinated to the metal atom. Planar, octahedral, and pentacoordinated compounds are obtained. Equilibria between the various species may occur in solution.

The presence in the molecule of the amine group –N(R)R′, either free or coordinated to the central nickel atom, in compounds of this type has prompted us to examine the possibility of protonation of this group by treatment of the complex with hydrohalogen acids under suitable conditions. When such a treatment is too rough, it leads to a complete decomposition of the initial complex. However, an indirect treatment, or a direct treatment performed with great care, leads to the formation of complexes in which the nitrogen atom of the –N(R)R′ group is protonated while the anion is either coordinated to the metal atom or uncoordinated. The stereochemistry of the resulting complexes depends on the substituents R and R′ (Y = H in all cases so far examined). These compounds have been characterized and studied by magnetic measurements, optical and infrared spectra, measurements of molecular weight, and conductivity. In order to obtain conclusive information on the stereochemistry of these compounds, some analogous complexes with catechol have also been prepared and characterized.

Experimental Section

Preparation of Compounds.—Only typical syntheses are described. Parallel reactions were used for the preparation of related substances.

[SALen–N(H)CH$_3$]$_2$Ni·2HBr. Method A.—[SALen–N(H)CH$_3$]$_2$Ni, 2.06 g. (0.005 mole), and finely ground triethylamine hydrobromide, 1.9 g. (0.0103 mole), were placed, together with *ca.* 250 ml. of dry benzene, in a 500-ml. three-necked flask equipped with a mechanical stirrer and a reflux condenser. The suspension was stirred and refluxed for about 4 hr. After cooling the precipitate was recrystallized by dissolving it in the minimum amount of chloroform and precipitating with ligroin. The pure product weighed 1.6 g. (55%). Either N-methylaniline or diphenylamine hydrobromide can be used in place of triethylamine hydrobromide.

Method B.—[SALen–N(H)CH$_3$]$_2$Ni, 1.5 g. (0.0036 mole), dissolved in *ca.* 500 ml. of dry benzene, was placed in a 1-l. three-necked flask equipped with a mechanical stirrer, a reflux condenser, and a dropping funnel with side arm. A benzene solution of hydrogen bromide, obtained by bubbling dry hydrogen bromide in the solvent for few minutes, was added dropwise to the chilled solution of the complex, with vigorous stirring, until the reaction mixture turned colorless or light green. The precipitate was then recrystallized as in method A. The yield of the pure product was 1.5 g. (72%). This method was not applicable to the HCl series. Extensive decomposition of the original complexes occurred.

[SALen–N(H)CH$_3$]$_2$Ni·C$_6$H$_4$(OH)$_2$.—A mixture of 2.06 g. (0.005 mole) of [SALen–N(H)CH$_3$]$_2$Ni and 0.6 g. (0.0054 mole) of catechol in *ca.* 100 ml. of benzene was refluxed on a steam bath for about 1 hr. After cooling the precipitate was filtered and recrystallized from an alcohol–water mixture; yield 0.7 g. (26%).

Spectra.—Absorption spectra were recorded in the range 5000–25,000 cm.$^{-1}$ at room temperature with a Beckman DK-2 spectrophotometer and 1-cm. silica cells. Solvents were of reagent grade quality. Nitroethane was washed with 5% aqueous sodium bicarbonate, dried with Drierite, and fractionally distilled (b.p. 113°). Chloroform was washed six times with water, dried for 24 hr. over phosphorus pentoxide, and distilled from potassium carbonate under nitrogen. The diffuse reflectance spectra were measured using the standard Beckman reflectance attachment and magnesium oxide as the reference. The infrared spectra were recorded on hexachlorobutadiene mulls using a Perkin-Elmer Model 337 spectrophotometer.

Conductivity Measurements.—The conductivity values were measured with a WTW Model LBR/B conductance bridge. Concentrations of the solutions were approximately 10^{-3} *M*.

Molecular Weight Measurements.—Molecular weights were determined in chloroform at 37° with a Mechrolab Model 301A vapor pressure osmometer calibrated with benzil. Scale readings were made 2 min. after the drop of the solution was placed on the thermistor. Concentrations of the solutions were in the range 10^{-2}–10^{-3} *M*.

Magnetic Measurements.—The magnetic measurements were performed by the Gouy method with the apparatus and experimental technique described previously.[3] The sample tube was calibrated with Hg[Co(NCS)$_4$] and freshly distilled water.[4]

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

(2) L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, *ibid.*, **4**, 943 (1965).

(3) L. Sacconi, R. Cini, M. Ciampolini, and F. Maggio, *J. Am. Chem. Soc.*, **82**, 3487 (1960).

(4) 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 $[SALen{-}N(R)R']_2Ni\cdot 2HX$ AND $[SALen{-}N(R)R']_2Ni\cdot C_6H_4(OH)_2$ COMPLEXES

	$-N(R)R'$	Acid	Crystallization	M.p., °C.	Analysis, %[b] C	H	N	Ni
I	$-N<^{H}_{CH_3}$	HCl	$CHCl_3$ + ligroin	>340	49.41	5.80	11.52	12.07
					49.10	5.71	11.67	12.34
II[a]		HBr	$CHCl_3$ + petr. ether	264	41.77	4.90	9.74	10.20
					42.30	5.20	9.71	9.78
III		$C_6H_4(OH)_2$	$C_2H_5OH + H_2O$	183–184	59.67	6.16	10.70	11.21
					59.95	6.36	10.91	11.51
IV[a]	$-N<^{H}_{C_6H_5}$	HCl	$CHCl_3$	142–144	59.04	5.28	9.18	9.61
					58.60	5.35	8.91	9.21
V		HBr	$CHCl_3$	152	51.53	4.61	8.01	8.39
					51.60	4.85	7.93	8.18
VI		$C_6H_4(OH)_2$	C_2H_5OH	187–189	66.78	5.60	8.65	9.06
					66.97	5.87	8.77	9.21
VII	$-N<^{C_2H_5}_{C_2H_5}$	HBr	CH_3OH + ether	225	47.37	6.11	8.50	8.90
					47.50	6.10	8.78	9.14
VIII	$-N<^{CH_2-CH_2}_{CH_2-CH_2}>CH_2$	HBr	CH_3OH + ether	237–239	49.22	5.90	8.20	8.59
					49.17	6.15	8.21	8.49

[a] Compounds II and IV show molar conductance values of 3 and 10 cm.²/ohm *M*, respectively. The conductivity measurements were made on 1×10^{-3} *M* solutions in nitroethane. Typical molar conductances for 1:1 and 1:2 electrolytes in 10^{-3} *M* solutions are in the ranges 70–85 and 145–160 cm.²/ohm *M*, respectively. For example $[(n\text{-}C_4H_9)_4N]I = 83$ and $[(CH_3)_4N]_2[Co(NCS)_4] = 160$. [b] First line for each substance is the calculated value; the second is the found.

TABLE II

MAGNETIC SUSCEPTIBILITY DATA FOR SUBSTITUTED $[SALen{-}N(R)R']_2Ni\cdot 2HX$ AND $[SALen{-}N(R)R']_2Ni\cdot C_6H_4(OH)_2$ COMPLEXES IN THE SOLID STATE

Compound	Temp., °C.	$10^6\chi_g$	$10^6\chi_{Ni}$[a]	μ_{eff}, B.M.
I	19	7.84	4100	3.11
II	19	6.49	4045	3.10
III	19	7.40	4170	3.14
IV	16	5.74	3875	3.00
V	27	4.83	3860	3.06
VI	20	5.25	3770	2.98
VII	19		*b*	
VIII	17		*b*	

[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). [b] Diamagnetic.

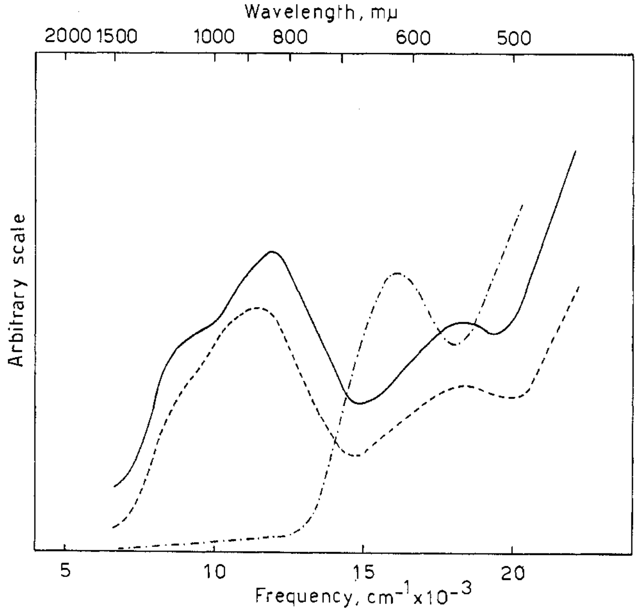

Figure 1.—Reflectance spectra of $[SALen{-}N(H)CH_3]_2Ni\cdot 2HCl$ (– – – –); $[SALen{-}N(H)CH_3]_2Ni\cdot C_6H_4(OH)_2$ (———); $[SALen{-}N(C_2H_5)_2]_2Ni\cdot 2HBr$ (–·–·–·).

Results

Series I: $-N(R)R' = -N(H)CH_3$, $-N(H)C_6H_5$.—The treatment with either HCl or HBr, free or as salts of aliphatic or aromatic amines, leads in every case to bright gray-green compounds which are soluble in alcohol, sparingly soluble in chloroform, and insoluble in nonpolar solvents. When $R' = CH_3$ the complexes are soluble in water. The analytical data (Table I) suggest the general formula $[SALen{-}N(R)R']_2Ni\cdot 2HX$ for these reaction products.

All the compounds of this series are paramagnetic with values of $\mu_{eff} \approx 3.1$ B.M. (Table II). Measurements of conductivity in nitroethane, for the compounds sufficiently soluble in this solvent, give molar conductance values $\leqslant$ 10 cm.²/ohm *M* (Table I), compared with values of *ca.* 80 and 150 cm.²/ohm *M* for uni-univalent and uni-bivalent electrolytes under the same conditions. This indicates that the halogen is bonded to the metal atom. The existence of a definite, although small, conductivity can be attributed to the moderate coordinating ability of nitroethane. This may be represented by an equilibrium of the type

$$NiL_2X_2 + 2S \rightleftharpoons NiL_2S_2^{2+} + 2X^{2-}$$

(X = halogen, L = bidentate ligand, S = solvent molecule)

The reflectance spectra (Figure 1) show a band at about 18,000 cm.$^{-1}$ and another in the region 10,000–11,000 cm.$^{-1}$ with a shoulder at about 8500 cm.$^{-1}$. These spectra are very similar to those of the hexaco-

TABLE III

SPECTROPHOTOMETRIC ABSORPTION DATA FOR SOME SUBSTITUTED $[SALen–N(R)R']_2Ni·2HX$ AND $[SALen–N(R)R']_2Ni·C_6H_4(OH)_2$ COMPLEXES IN CHLOROFORM AND NITROETHANE SOLUTIONS

Compound	Solvent	ν_{max}, cm.$^{-1}$	ϵ_{max}	ν_{max}, cm.$^{-1}$	ϵ_{max}
I	$CHCl_3$	11,236	25.3	17,857	11.1
	$C_2H_5NO_2$	11,429	25.5		
II	$CHCl_3$	11,299	27.7	17,544	13.0
III	$CHCl_3$	12,048	34.9	18,519	30.0
	$C_2H_5NO_2$	11,765	31.7	18,519	18.9
IV	$CHCl_3$	10,989	29.5	16,807	10.6
	$C_2H_5NO_2$	10,929	29.3	17,241	12.9
V	$CHCl_3$	10,811	37.2	16,949	14.0
	$C_2H_5NO_2$	10,811	33.4	17,094	12.3
VI	$CHCl_3$	11,111	55.4	17,241	51.0
	$C_2H_5NO_2$	11,111	50.7	17,391	47.0

ordinated distorted octahedral compounds of series I, discussed in the previous papers,[1,2] in which the nitrogen atom of the group –N(R)R′ coordinates to the central nickel atom.

Measurements of the molecular weight in chloroform solution give values approximately corresponding to a dimeric formula in the case of *ca.* 10^{-3} *M* solutions. These values increase by about another third with an increase in concentration up to about 10^{-2} *M*.

The infrared spectra, in hexachlorobutadiene mull, in the NaCl region (Figure 2) show a group of bands in the region 3000–3500 cm.$^{-1}$ which can all be assigned to the stretching frequencies of a $>NH_2^+$ group, associated *via* a weak hydrogen bond. In the halogen salts of the amines such a frequency can be found in the region 2400–2900 cm.$^{-1}$ and shows a remarkably fine structure, as it presents itself at times as a quadruplet. The frequency of these bands does not differ with various halogens, although the relative intensities vary.[5] The absorption frequencies due to the stretching of the free NH^+ group, secondary or tertiary, are located at *ca.* 3200 cm.$^{-1}$, as has been seen in the spectra of amine salts with large anions of the type ClO_4^-, PF_6^-, etc. These bands do not show a fine structure, as is to be expected because hydrogen bonds are absent.[6] In our compounds we observe a quadruplet between 3000 and 3500 cm.$^{-1}$ with various relative intensities depending on the halogen and with the highest intensity at *ca.* 3200 cm.$^{-1}$. This appears to represent an intermediate situation between the two extremes quoted above.

In order to obtain further information on the stereochemistry of these complexes, we have also examined the products of the reaction between the same initial complexes and catechol. Bright green compounds are formed for R′ = C_6H_5 and ochre for R′ = CH_3. The analytical data of these derivatives indicate a formula of the type $[SALen–N(H)R']_2NiC_6H_4(OH)_2$ (Table I). These compounds are also paramagnetic (Table II) and their electronic spectra are substantially the same as those of the analogous halogen complexes, in the solid state as well as in solutions of chloroform and nitroethane (Figure 1 and Table III).

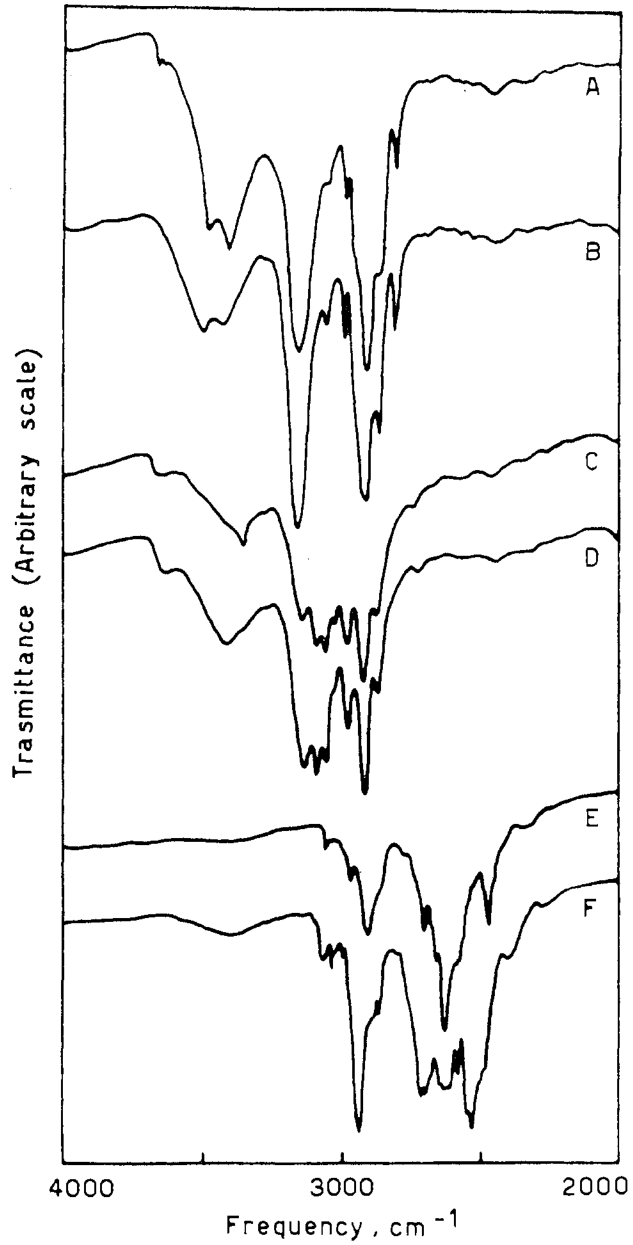

Figure 2.—Infrared spectra of $[SALen–N(H)CH_3]_2Ni·2HCl$ (curve A); $[SALen–N(H)CH_3]_2Ni·2HBr$ (curve B); $[SALen–N(H)C_6H_5]_2Ni·2HCl$ (curve C); $[SALen–N(H)C_6H_5]_2Ni·2HBr$ (curve D); $[SALen–N(C_2H_5)_2]_2Ni·2HBr$ (curve E); $[SALen–N(CH_2)_5]_2Ni·2HBr$ (curve F).

Series II: –N(R)R′ = –N$(C_2H_5)_2$, –N$(CH_2)_5$.—Although it has so far not been possible to isolate or identify the products resulting from the treatment with HCl, action of HBr gives products with a more intense green color which are insoluble in chloroform, nitroethane, and nonpolar solvents, but soluble in both alcohol and water. The analytical data (Table I) are in accordance with a formula of the type $[SALen–N(R)R']_2Ni·2HBr$. These compounds are, however, diamagnetic and the reflectance spectra do not show absorption bands below 14,000 cm.$^{-1}$ (Figure 1).

Infrared spectra, in hexachlorobutadiene mull, show absorption bands in the region 2400–2800 cm.$^{-1}$ (Figure 2), *i.e.*, in the region where the $\geqslant NH^+$ stretching fre-

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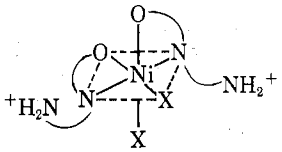
(5) R. C. Lord and R. E. Merrifield, *J. Chem. Phys.*, **21**, 166 (1953).

(6) R. H. Nuttal, D. W. A. Sharp, and T. C. Waddington, *J. Chem. Soc.*, 4965 (1960).

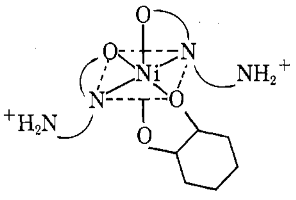
quencies are found for normal hydrobromides of tertiary amines.[7] Because these reaction products are insoluble in "inert" solvents it has not been possible to study their behavior in solution.

Discussion

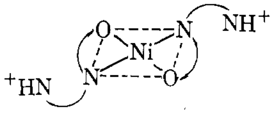
In Ni(II) complexes with Schiff bases derived from salicylaldehydes and N-substituted ethylenediamines, the ligand molecule is bi- or tridentate, according to the substituents Y, R, R′. In general, for a given Y, octahedral forms are favored in the case of both electron-releasing and small R, R′ groups, while planar forms are obtained in the case of large and electron-attracting substituents. In intermediate cases pentacoordinated complexes are also obtained.[2] Different structures, depending on the variations of R and R′, can be assigned to the halogen derivatives of this class of compounds. While conductivity measurement data suggest, for the compounds of series I, that the halogens are coordinated to the central nickel atom, the magnetic and spectral data lead us to assign a distorted octahedral configuration to them. The spectra are in fact those of a distorted octahedral structure. The bands at 8500 and 10,000–11,500 cm.$^{-1}$ can be assigned to the components of the ν_1 transition ($^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$) in a regular octahedral field, which is split due to the distortion of the environment, while the third band can be attributed to the ν_2 transition ($^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$). The magnetic and spectral data do not, however, yield any information regarding the two possible structures, *cis* and *trans*, for the halogen atoms. Nevertheless, a comparison of the spectra of these compounds and those derived from catechol shows that the two types of spectra are substantially the same (Figure 1). Because the derivatives of catechol must of necessity be *cis* forms (II), the *cis* configuration (I) must be assigned to the complexes of series I.



I



II



III

The diamagnetism and the absence of absorption below 14,000 cm.$^{-1}$ in the crystal field spectra of the derivatives of series II leads us to attribute a *trans* planar structure of type III to them. In this structure the bromide ions are not coordinated to the central nickel.

The occurrence of planar and octahedral structures, for the states described here, cannot be easily explained only on the basis of steric effects of the R and R′ substituents or of different donor properties of the (β) nitrogen with various R and R′ groups. This donor grouping is, in each case, outside the coordination sphere because of the protonation of the nitrogen. On the other hand it is noticeable that a distorted octahedral structure is obtained when the terminal amine group is a secondary –N(H)R′ group. Planar complexes are, however, obtained when this amine group is tertiary, of the –N(R)R′ type.

It is known that in amine salts with hydrohalogen acids, hydrogen bonds of the type $\geqslant \mathrm{NH}^+\cdots \mathrm{X}^-$ are stronger in the case of tertiary amines than in secondary ones. This difference may explain the two different stereochemical forms observed in our complexes. When the nitrogen is secondary (series I), it is attached to the halogen atom by relatively weak bonds, thus allowing the halogen to coordinate to the metal atom. It may be observed from the infrared spectra that the hydrogen bonds $>\mathrm{NH}_2^+\cdots \mathrm{X}^-$ are rather weak in this case. The molecular weight measurements in chloroform solution suggest the existence of weak intermolecular hydrogen bonds in this solvent, but it cannot be excluded that the rather high molecular weight values are the result of molecular associations of the dipole–dipole type. In the compounds of series II a tertiary (β) nitrogen is present, and the polarization of the halogen, due to strong hydrogen bonding with the protonated amine group, prevents the coordination of the halogen ion to the central nickel. This interpretation is confirmed by the infrared spectra of these compounds, which show absorptions characteristic of normal salts of tertiary amines.

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(7) B. Chenon and C. Sandorfy, *Can. J. Chem.*, **36**, 1181 (1958).