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Red and Green Forms of Nickel(II) Complexes of Schiff Bases Obtained from 3-Methoxysalicylaldehyde and 4-Halogenoanilines

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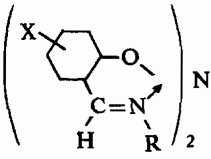
Received August 23, 1968

Crystals of two forms were prepared for complexes of the type $Ni(3{-}CH_3O{-}SAL.4{-}Y{-}Ph)_2$, where Y—Ph denotes a chlorophenyl or bromophenyl. Bis(N-aryl-3-methoxysalicylideneiminato)nickel(II) is abbreviated as $Ni(3{-}CH_3O{-}SAL.aryl)_2$. The two forms of the chloro-series take a structure similar to that of the corresponding forms of the bromo-series. Since both the forms are paramagnetic with a magnetic moment corresponding to two unpaired electrons, the squareplanar configuration is excluded. The electronic spectrum, together with the magnetic moment, indicates that the green crystals (Form II) consist of associated, polymeric species, in which the nickel(II) ions are six-coordinated. In a similar way, it is concluded that the nickel(II) ions in the red crystals (Form I) are five-coordinated. Possible structures for the two forms are discussed.

Introduction

Previous studies[1,2,3] have shown that nickel(II) complexes of the type $Ni(X{-}SAL.R)_2$ (Formula (I)), R being an aryl group, can be isolated as either a paramagnetic, octahedral (polymeric) or a diamagnetic, planar form, depending upon the nature of X and R. In general, one of them is greatly favoured over the other, and no case has ever been reported where both the paramagnetic and the diamagnetic form have been isolated as crystals for any pair of X and R, R being an aryl group. Only for $Ni(H{-}SAL.CH_3)_2$, a diamagnetic, brown-red and a paramagnetic, «yellow-violet» form were obtained as crystals and microcrystalline powder, respectively.[4]



(I)

In the course of the studies about Schiff base metal complexes, the present authors obtained two forms of $Ni(3{-}CH_3O{-}SAL.aryl)_2$ for two pairs of X and the aryl group. The present paper is concerned with the preparation and properties of these complexes.

Experimental Section

Materials. Bis(N-4-chlorophenyl-3-methoxysalicylideneiminato)nickel(II). To a suspension of bis(3-methoxysalicylaldehydato)nickel(II) (0.01 mole) in methanol (200 ml) was added 4-chloroaniline (0.025 mole), and the solution was heated at about 65°. In six hours, red crystals started to appear in the green solution, and the reaction was complete after about ten hours. The crystals were filtered off and washed with ether. Red, rectangular crystals (Form I) were obtained. Under the microscope, the crystals contained no impurity; m.p. 243-5°.

Recrystallization of the red crystals from ether yielded green crystals (Form II), m.p. 151-3° (sintering point 148-9°).

The crystals of both Form (I) and Form (II) are highly soluble in chloroform, dichloromethane and benzene, and slightly soluble in methanol, ethanol and ether, giving a green or greenish-brown solution. They are insoluble in water.

Bis(N-4-bromophenyl-3-methoxysalicylideneiminato)-nickel(II). To a suspension of bis(3-methoxysalicylaldehydato)nickel(II) (0.01 mole) in methanol (200 ml) was added 4-bromoaniline (0.025 mole) and the resulting solution was heated on a water-bath at about 65°. The reaction was complete after about thirty hours. Crystals, which separated in the green solution, were filtered off and washed with ether. Red, rectangular crystals (Form I) were obtained; m.p. 258-9°.

Recrystallization of the red crystals from ether yielded pure green crystals (Form II), m.p. 174-6° (sintering point 161-2°).

The solubility of the crystals is similar to that of the chloro-series.

Elemental analyses of the crystals described above are shown in Table I. Infrared spectra indicate that neither water nor methanol molecule is present in any of these crystals.

Besides the two forms, green crystals of another form were obtained by recrystallization of the red crystals (Form (I)) from methanol or methanol-

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(1) L. Sacconi, *Coord. Chem. Revs.*, *1*, 415 (1966); *Exper. Suppl.*, 9, 148 (1964).

(2) R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, «Progress in Inorganic Chemistry», F. A. Cotton, Ed., Interscience, New York, 7, 83 (1966).

(3) S. Yamada, *Coord. Chem. Revs.*, *1*, 415 (1966).

(4) L. Sacconi, P. Paoletti, and R. Cini, *J. Am. Chem. Soc.*, *80*, 3583 (1958).

Table I. Analytical Data of Ni(3–CH$_3$O–SAL.4–Y–Ph)$_2$

Y	Form[b]	Calcd., % C	Calcd., % H	Calcd., % N	Found, % C	Found, % H	Found, % N	μ[a]
Cl	(I) (red)	57.97	3.82	4.83	57.36	3.56	4.80	3.14
	(II) (green)				57.58	3.92	4.70	3.10
Br	(I) (red)	50.26	3.32	4.19	50.24	3.00	3.94	3.18
	(II) (green)				49.35	3.39	3.96	3.06

[a] μ: Magnetic moment in B.M. at 290°K. [b] Although time required for dissolution is longer with the red form than with the green form, the concentration of the solution finally obtained is the same for the two forms.

chloroform. Thecrystals effloresced in the atmosphere so readily that they were not analyzed. When they were heated over phosphoric pentoxide at about 65° for several hours under reduced pressure, they turned into a paramagnetic, yellow-ochre powder, the elemental analysis of which agreed with the formula Ni(3–CH$_3$O–SAL.Y–Ph)$_2$, Y being Cl or Br. It is likely that these crystals may contain water or methanol. They were not further investigated in the present work.

Measurements. Electronic absorption spectra of the complexes in solution and in the solid state were determined with a Shimadzu QR-50 spectrophotometer and a Shimadzu MPS-50L spectrophotometer in the region between 5 and 25 kK.

Infrared spectra were determined in nujol mulls with a Hitachi EPI-S2 infrared spectrophotometer.

Magnetic measurements were carried out by the Gouy method at room temperature using HgCo(NCS)$_4$ as a standard.

Molecular weight measurements were performed using a Mechrolab Model 301-A vapor pressure osmometer.

Results and Discussion

It is to be noted that both the green and the red form of Ni(3–CH$_3$O–SAL.R)$_2$ have been isolated as crystals for R=4–Cl–Ph and 4–Br–Ph. From a remarkable similarity in electronic spectra and magnetic property, as will be discussed below, it is considered that the two forms of the chloro-series take a similar structure to that of the corresponding forms of the bromo-series.

The green crystals of Form (II), obtained in the present work, are paramagnetic with a magnetic moment corresponding to two unpaired electrons (Table I). Inspection of the electronic spectra of Form (II) in the solid state indicates that the nickel(II) ions take an octahedral coordination in this form (Figures 1 and 2, and Table II). The absorption maxima at about 10 kK and 16 kK may be assigned as the transitions $^3T_{2g}(F) \leftarrow {}^3A_{2g}$ and $^3T_{1g}(F) \leftarrow {}^3A_{2g}$, respectively, in the scheme of the O_h ligand field symmetry. It is thus most likely that, for Y=Cl and Br, Form (II) consists of the associated, polymeric species, in which the nickel(II) ions are six-coordinated. This structure for Form (II) corresponds to one of the two kinds which commonly occur for complexes of the type Ni(X–SAL.aryl)$_2$.[1,2,3]

The red crystals of Form (I) are paramagnetic with a magnetic moment corresponding to two unpaired electrons (Table I). This fact shows that Form (I) does not take a planar configuration, for which diamagnetism is predicted. Previous studies indicate that the tetrahedral configuration of a high-spin type for Ni(X–SAL.R)$_2$ seems to be allowed, only if the steric condition is extremely unfavourable for the square-planar configuration.[1,5] The tetrahedral configuration, therefore, is considered to be very unlikely for Form (I), since no or very little steric hindrance may be expected in the present complexes.

Table II. Spectroscopic Data for Ni(3–CH$_3$O–SAL.4–Y–Ph)$_2$

Y	Form	State	Band max. in kK (log ε for soln.[a])
Cl	(I) (red)	solid	5.9, 6.6, 14.3 sh[b]
	(II) (green)	solid	9.9, 15.9
	(I) and (II)	in benzene	9.95 (1.12), 15.6 (1.31)
		in CHCl$_3$	9.9 (1.02), 15.7 (1.60)
		in CH$_2$Cl$_2$	9.9 (1.16), 15.5 (1.43)
		in pyridine	10.2 (1.30), 17.1 (1.24)
Br	(I) (red)	solid	5.85, 6.6, 14.2 sh
	(II) (green)	solid	10.2, 16.2
	(I) and (II)	in benzene	9.73 (1.16), 15.4 (1.30)
		in CHCl$_3$	9.57 (1.02), 16.0 (1.44)
		in CH$_2$Cl$_2$	9.60 (1.14), 15.3 (1.41)
		in pyridine	10.3 (1.28), 17.1 (1.23)

[a] The concentration of the solutions was 5×10^{-3} molar. [b] sh: shoulder.

The electronic absorption spectra of Form (I) in the solid state, which are shown in Figures 1 and 2, and Table II, are quite different from the spectra typical of the octahedral and the tetrahedral as well as the planar nickel(II) complexes. The spectra of Form (I) for Y=Cl and Br, however, have the main features characteristic of the spectrum of the five-coordinated, paramagnetic nickel(II) complex.[6,7] In particular, the spectra exhibit the main features similar to those observed for Ni$_2$(H–SAL.CH$_3$)$_4$ doped in Zn$_2$(H–SAL.CH$_3$)$_4$, in which the nickel(II) ions were established to be five-coordinated.[6] It is thus most likely that the nickel(II) ions in the crystals of Form (I) may be five-coordinated. One of the most probable structures for Form (I) may be a binuclear molecule

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(5) S. Yamada and H. Nishikawa, *Bull. Chem. Soc. Japan*, *36*, 755 (1963).

(6) L. Sacconi, M. Ciampolini, and G. P. Speroni, *J. Am. Chem. Soc.*, *87*, 3102 (1965).

(7) M. Ciampolini, N. Nardi, and G. P. Speroni, *Coord. Chem. Revs.*, *1*, 222 (1966).

similar to that of $Co_2(H{-}SAL.CH_3)_4$ or $Zn_2(H{-}SAL.CH_3)_4$, in which the metal ions are five-coordinated.[8]

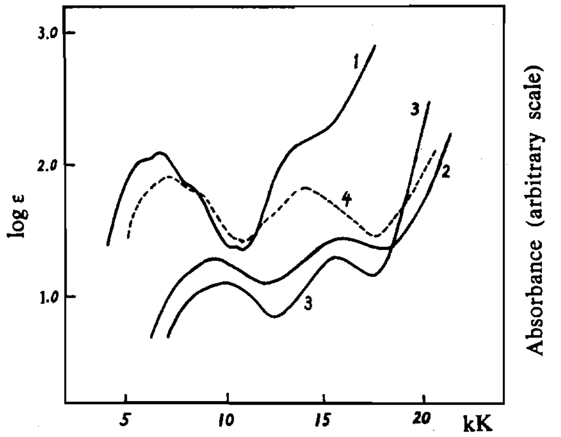

Figure 1. Electronic spectra of nickel(II) complexes. (1), $Ni(3{-}CH_3O{-}SAL.4{-}Cl{-}Ph)_2$, Form (I) (solid); (2), Form (II) (solid); (3), Form (I) or Form (II) in benzene; (4), $Ni_2(H{-}SAL.CH_3)_4$ doped in $Zn_2(H{-}SAL.CH_3)_4$ in the solid state. The curve (4) is taken from ref. 4 in the text. The scale on the left hand side refers to the curve (3), and the scale on the right hand side to the curves (1), (2), and (4).

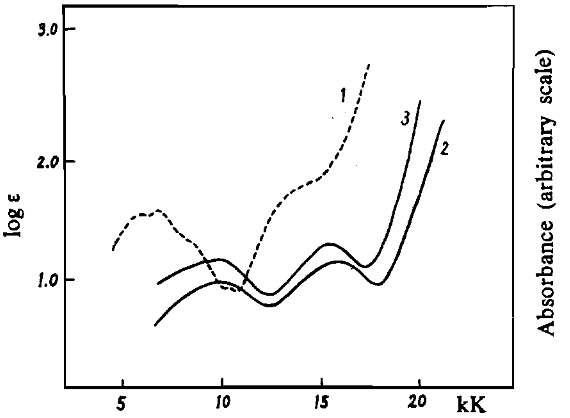

Figure 2. Electronic spectra of $Ni(3{-}CH_3O{-}SAL.4{-}Br{-}Ph)_2$. (1), Form (I) (solid); (2), Form (II) (solid); (3), Form (I) or Form (II) in benzene. The scale on the left hand side refers to the curve (3), and the scale on the right hand side to the curves (1) and (2).

In solution, Form (I) shows the same absorption spectra as those of Form (II), when the same solvent is employed. However, the configuration of the complexes in solution depends upon the solvent. In aromatic solvents like benzene and toluene, the dependence upon the concentration and temperature is not appreciable, and the configuration of the complexes is nearly the same. The spectra of the complexes in benzene, for example, are typical of the octahedral nickel(II) complex (Figures 1 and 2, and Table II). This is considered to be due to the association of the monomeric species, which leads to the formation of the polymeric species containing six-coordinated nickel(II) ions.

A different result was obtained for the solution in chloroform or dichloromethane. For the solutions in these solvents, the spectra also show the main features typical of the octahedral nickel(II) complexes. The predominant species may be the same octahedral nickel(II) complexes as those existing in the benzene solution. However, the spectra of the solution in chloroform or dichloromethane show some complexity in the lower frequency side of the *d–d* bands in the near-infrared region, suggesting that in these two solvents there may exist an equilibrium possibly involving a few kinds of species. Electronic absorption spectra of the chloroform solutions at different temperatures and concentrations were determined, and some of the typical data for $Ni(3{-}CH_3O{-}SAL.4{-}Br{-}Ph)_2$ are shown in Figure 3. In the absorption curves, three peaks are observed at about 6.8, 9.7, and 16.0 kK for the bromo-series. Comparison of the spectra in Figure 3 with those in Figure 2 shows that the former two peaks correspond to the five- and the six-coordinated nickel(II) complexes respectively.

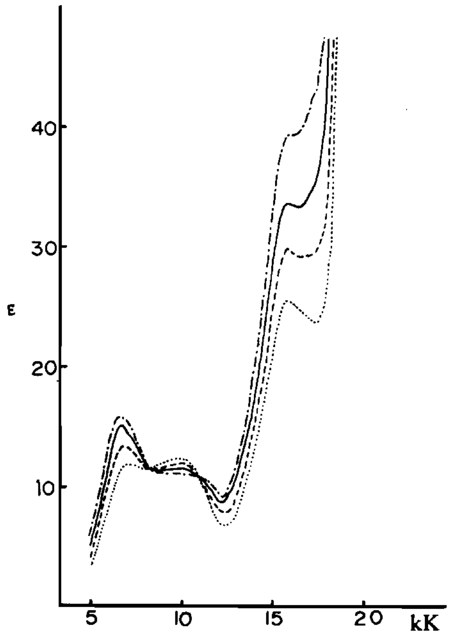

Figure 3. Electronic spectra of $Ni(3{-}CH_3O{-}SAL.4{-}Br{-}Ph)_2$ in chloroform. — · — · —, at 35°, 5 m*M*; ......, at 21°, 20 m*M*; ------, at 35°, 20 m*M*; ———, at 52°, 20 m*M*.

The third peak at 16.0 kK, which does not coincide exactly with the second peak of the six-coordinated, polymeric species (benzene solution), is considered to be due to the square-planar species. Thus in chloroform (or dichloromethane) it is most likely that there exists an equilibrium involving three species with different coordination numbers, that is, four, five and six. Inspection of the absorption spectra also indicates that, as the solution becomes more concentrated, the amount of the four- and the five-coordinated species decreases, while the amount of the six-coordinated species increases. Raising temperature causes a similar effect to that by lowering concentration. A similar result was obtained with the chloro-series. In Table II are listed only the frequencies of the main peaks for the 5×10^{-3} molar solution.

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(8) P. L. Orioli, M. Di Vaira, and L. Sacconi, *Chem. Commun.* (London), 103 (1965).

Table III. Molecular Weights of Ni(3–CH_3O–SAL . 4–X–Ph$)_2$ in Chloroform at 37°C

X	Concentration mole/kg. solv.	Polymerisation number [a]
Cl	9.5×10^{-3}	1.36
	1.96×10^{-2}	1.57
Br	9.5×10^{-3}	1.46
	1.87×10^{-2}	1.55

[a] The ratio of the found to the theoretical molecular weight.

Data for molecular weights of these complexes in chloroform are shown in Table III. It is found that the polymerisation number is not very high, showing the significant contribution of the square-planar, monomeric species to the equilibrium.

In a donor solvent like pyridine, Form (I) and Form (II) show identical absorption spectra typical of the octahedral nickel(II) complexes (Table II), showing the formation of the same species, Ni(3–CH_3O–SAL . R$)_2$(*py*$)_2$, for both Form (I) and Form (II), where *py* denotes a pyridine molecule.

Acknowledgment. Financial support of the Education Ministry of Japan is gratefully acknowledged.