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Preparation and Properties of Octahedral Nickel(II) Complexes with and Schiff Bases Derived from Substituted Salicylaldehydes and Bis(2-aminoethyl) Sulfide

Kiichi Hori* and Kazuko Takahashi

Department of Chemistry, Faculty of Science, Yamagata University, Yamagata 990

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Synopsis The octahedral complexes listed in the title have been prepared. The magnetic and spectral properties of these complexes indicate that the non- and 5-substituted complexes have a structure bridged by the phenolic oxygen of the Schiff bases and the 3-substituted complexes probably are mononuclear.

The Schiff bases (H_2(X-saldaes), where X is a substituent on the benzene rings) derived from salicylaldehydes and bis(2-aminoethyl) sulfide form nickel(II) complexes which have electronic spectra characteristic of low spin five-coordinate structures and possess magnetic moments ≈1.1 BM in the solid state.[1)] Under certain reaction conditions, three types of nickel(II) complexes with H_2(H-saldaes) were prepared: complexes of planar, octahedral, and polynuclear structures.[2)] It is therefore of interest to investigate the effect of substituents on the benzene ring of the Schiff bases on the stereochemistry of the resulting complexes. In this paper, we report the syntheses and characterization of octahedral nickel(II) complexes with the substituted Schiff bases.

Experimental

Preparation. *Complexes **1** and **3**—**7***: The Schiff base, H_2(X-saldaes), (1 mmol) was dissolved in a minimum quantity of methanol (15—500 cm^3) under reflux. To this hot solution was added a solution of nickel(II) acetate tetrahydrate (1 mmol) in methanol (5 cm^3). The mixture was allowed to stand for 1—2 d at room temperature. For X= 3,5-Cl_2 and 3,5-Br_2, after the mixture had been concentrated to one-third of the volume under reduced pressure, the mixture was allowed to stand. The green crystals which precipitated were collected. The crystals were dissolved in a minimum quantity of methanol and recrystallized by concentrating the solution under reduced pressure.

*Complex **2***: Nickel(II) acetate tetrahydrate (1 mmol) was added to a solution of H_2(5-CH_3-saldaes) (1 mmol) in methanol (10 cm^3). The mixture was stirred, and water (5—10 cm^3) was added in order to facilitate the precipitation. The precipitate, which formed when the solution was cooled, was collected and redissolved in a minimum quantity of methanol. The resulting solution was allowed to stand for a long time (over 30 d) to concentrate very slowly. The green crystals thus precipitated were collected and washed with methanol.

Measurements. The magnetic susceptibilities were measured with a Shimadzu MB-2H magnetic balance over the temperature range of 80—300 K. The effective magnetic moments were calculated from the equation: $\mu_{\mathrm{eff}}=2.83\sqrt{(\chi_A-N\alpha)T}$, where the temperature-independent paramagnetism, $N\alpha$, for nickel(II) ion was assumed to be 193×10^{-6} cgs emu.[3)] The infrared spectra were measured with a JASCO DS-403 infrared spectrophotometer on Nujol mulls and KBr disks. The electronic spectra were measured with a Hitachi EPS-3T spectrophotometer.

Results and Discussion

The complexes obtained are listed in Table 1 with their analytical, spectral, and magnetic data. The Cl- or Br-substituted complexes were easily prepared, whereas the 5-CH_3-substituted complex was prepared with difficulty. Attempts to prepare the complexes with 3-CH_3 or 3-*i*-C_3H_7 substituents were unsuccessful.

The complexes are soluble only with difficulty in most nonpolar and semipolar solvents. They are soluble in solvents of high donor-ability such as pyridine and DMSO, but they decompose in these solvents. The reflectance spectra of the complexes possess two d-d bands (Table 1), indicating that the geometry around nickel(II) ions is octahedral.[4)]

The complexes can be classified into two groups on the basis of the infrared spectral and magnetic data: (A) complexes **1**—**4** and (B) complexes **5**—**7**. The infrared spectra of complexes **1**—**4** show a broad weak band at 3300—3330 cm^{-1}, indicating the presence of a lattice water. The band near 1530 cm^{-1}, which characterizes the coordination mode of the phenolic oxygen in Schiff base complexes, was split into two bands separated by about 15 cm^{-1} (Table 1). This indicates that there are both the terminal and bridged coordination of the phenolic oxygens in complexes **1**—**4**.[5)] For complexes **5**—**7** a relatively sharp weak band was observed at 3560—3570 cm^{-1}, which is assigned to the OH stretchings of a coordinated water from the position and shape of the band.

The magnetic moments of complexes **1**—**4** are 2.83—2.88 BM at 295 K and 2.10—2.25 BM at 80 K. The

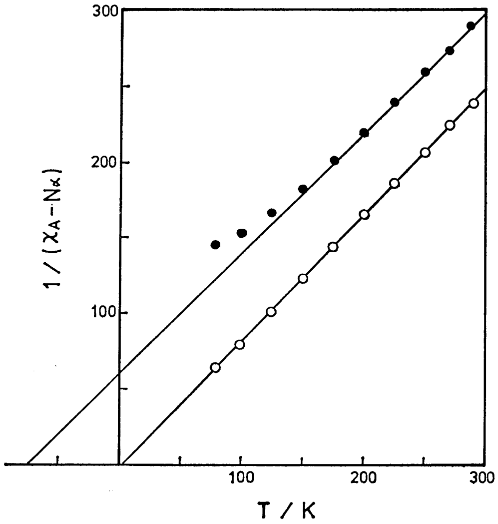

Fig. 1. Temperature dependence of magnetic susceptibility of (●) complex **1** and (○) complex **5**.

TABLE 1. ANALYTICAL, SPECTRAL, AND MAGNETIC DATA OF THE COMPLEXES

	Complex	Found (%)			Calcd (%)			Reflectance spectra[a] d-d Band $\tilde{\nu}/10^3\,\mathrm{cm}^{-1}$		IR spectra $\tilde{\nu}/\mathrm{cm}^{-1}$ Band near $1530\,\mathrm{cm}^{-1}$		Magnetic data μ_{eff}/BM		θ/K
		C	H	N	C	H	N					295 K	80 K	
1	Ni(H-saldaes)H_2O	53.53	5.18	6.80	53.63	5.00	6.95	8.62	16.08	1542	1525	2.87	2.20	−73
2	Ni(5-CH_3-saldaes)H_2O	55.41	5.80	6.42	55.71	5.61	6.50	8.55	15.43	1540	1527	2.83	2.15	−75
3	Ni(5-Cl-saldaes)H_2O	46.02	4.06	5.90	45.80	3.84	5.94	8.64	15.60	1535	1519	2.88	2.10	−98
4	Ni(5-Br-saldaes)H_2O	38.62	3.54	4.77	38.54	3.24	4.99	8.66	15.63	1530	1517	2.87	2.25	−75
5	Ni(3-Cl-saldaes)H_2O	45.60	4.07	5.92	45.80	3.84	5.94	9.01	16.95	1522		3.14	3.14	+3
6	Ni(3,5-Cl_2-saldaes)H_2O	39.94	2.86	5.19	39.97	2.98	5.18	9.09	17.0sh	1510		3.14	3.14	+2
7	Ni(3,5-Br_2-saldaes)H_2O	30.10	2.03	4.03	30.08	2.24	3.90	9.35	17.2sh	1500		3.15	3.15	0

a) sh = Shoulder.

value at 80 K is greatly less than the spin-only value, 2.83 BM. The temperature dependence of magnetic susceptibility of complex **1** is shown in Fig. 1 as a representative. The magnetic susceptibilities of complexes **1**—**4** obey the Curie-Weiss law over the temperature range of 150—300 K, but deviate in the temperature range of 80—100 K. The Weiss constants show negative large values (Table 1). It is likely that there is a strong antiferromagnetic interaction between nickel(II) ions in the complexes. These facts suggest that in the conformation around the bridging phenolic oxygen in the complexes, the phenolic C–O bond is coplanar with the two bridged nickel(II) ions.[6] The Schiff bases in the complexes seem to function as a quinquedentate ligand, because the analogous quadridentate Schiff bases[7] form nickel(II) complexes with a structure different from that of the present complexes. All the results shown above suggest that complexes **1**—**4** have a binuclear structure bridged by the phenolic oxygen.

On the other hand, complexes **5**—**7** show the magnetic moment value of 3.14—3.15 BM, which falls within the range usually found for octahedral mononuclear nickel(II) complexes. Their magnetic susceptibilities obey the Curie-Weiss law with very small values of the Weiss constant (θ=0—3 K) over the temperature range of 80—300 K. These results indicate that complexes **5**—**7** are magnetically diluted. It is thus probable that complexes **5**—**7** have an octahedral mononuclear structure in which the Schiff bases function as a quinquedentate ligand to form a six-coordination of the nickel(II) ion together with a molecule of water.

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