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ISOLATION OF TETRAAMMINE(SALICYLIDENEIMINATO)COBALT(III) CHLORIDE HYDRATE

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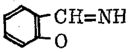
Tetraammine(salicylideneiminato)cobalt(III) chloride hydrate has been isolated and characterized by analytical and spectroscopic methods.

KEYWORDS —— cobalt complex; ammine complex; salicylideneiminato; salicylideneiminato complex; schiff base

Although the preparation of tris(N-substituted salicylideneiminato)-metal(III) complexes, M(sal-R)$_3$, and bis(N-substituted salicylideneiminato)-metal(II) complexes, M(sal-R)$_2$, has already been reported by many researchers,[1-5] the preparation of mono(N-substituted salicylideneiminato)-metal complexes, [M(sal-R)L], has not been described yet. In addition, the preparation of the N-substituted salicylideneiminato complex with other ligands has been the subject of little research except for halogen ligands.[6] We have now isolated tetraammine(salicylideneiminato)cobalt(III) chloride hydrate, [Co( $[Co(C_6H_4(CH{=}NH)O)(NH_3)_4]Cl_2\cdot H_2O$)(NH$_3$)$_4$]Cl$_2$·H$_2$O (**1**). The complex was prepared as follows: a 25% ammonia solution (40 ml) was added to an aqueous solution (20 ml) of CoCl$_2$·6H$_2$O (10.0 g, 42.0 mmol), and about 5 ml of a 30% H$_2$O$_2$ solution was added slowly to the solution at 0 °C. The color of the solution changed to red from brown. A methanol solution (50 ml) of salicylaldehyde (5.13 g, 42.0 mmol) was added dropwise to the solution for 2 h at 50 °C. The solution was stirred for 1 day at 50 °C and was concentrated with a rotary evaporator at 50 °C and dried. Complex **1** was extracted with 200 ml of methanol from the dried reaction mixture. The methanol solution was concentrated to about 50 ml with the rotary evaporator at 50 °C; then the crystallized complex **1** was filtered and recrystallized from water-ethanol. Yield: 3.6 g (25.5%), russet crystal. Anal. Calcd for CoC$_7$H$_{20}$N$_5$O$_2$Cl$_2$ (MW 336.11) C, 25.01; H, 6.00; N, 20.84; Cl, 21.10. Found: C, 25.26; H, 6.34; N, 20.66; Cl, 21.57. dec. 161-163 °C. Complex **1** is very soluble in water and DMSO, and soluble in methanol. The complex is insoluble in most other common organic solvents. Electric conductivity of **1** in an aqueous solution was 220 S cm^2 eq^{-1}.

The ^{1}H NMR spectrum of **1** was measured in DMSO-d_6 solution as shown in Fig. 1. The protons of the coordinated NH_3 ligands of **1** showed three singlet signals in the intensity ratio of 2:1:1. The signal (3.26 ppm, 6H) at the highest field is assigned to the protons of the two ammine ligands of $N(1)H_3$ and $N(4)H_3$ in a position cis to the coordinated salicylideneiminato ligand, because the two ammine ligands are considered to be equivalent. The two singlets at 3.46 (3H) and at 4.07 ppm (3H) are assigned to the protons of the two ammine ligands of $N(3)H_3$ and $N(2)H_3$ in a position trans[7,8] to the oxygen and the nitrogen of chelate ligand, respectively. The multiplet signals at 6.33-7.39 ppm (4H) are assigned to the ring protons[9] of chelate ligand. The signal at 7.99 ppm (1H) is assigned to the =CH proton[9] of chelate ligand. The doublet signal ($^3J_{HNCH}$: 10.0 Hz, 1H) at 11.08 ppm has been assigned to the =NH proton of the coordinated salicylideneiminato ligand of **1**. From the IR spectrum of **1**, the signal of CH=N group[10] was observed at 1625 cm^{-1}.

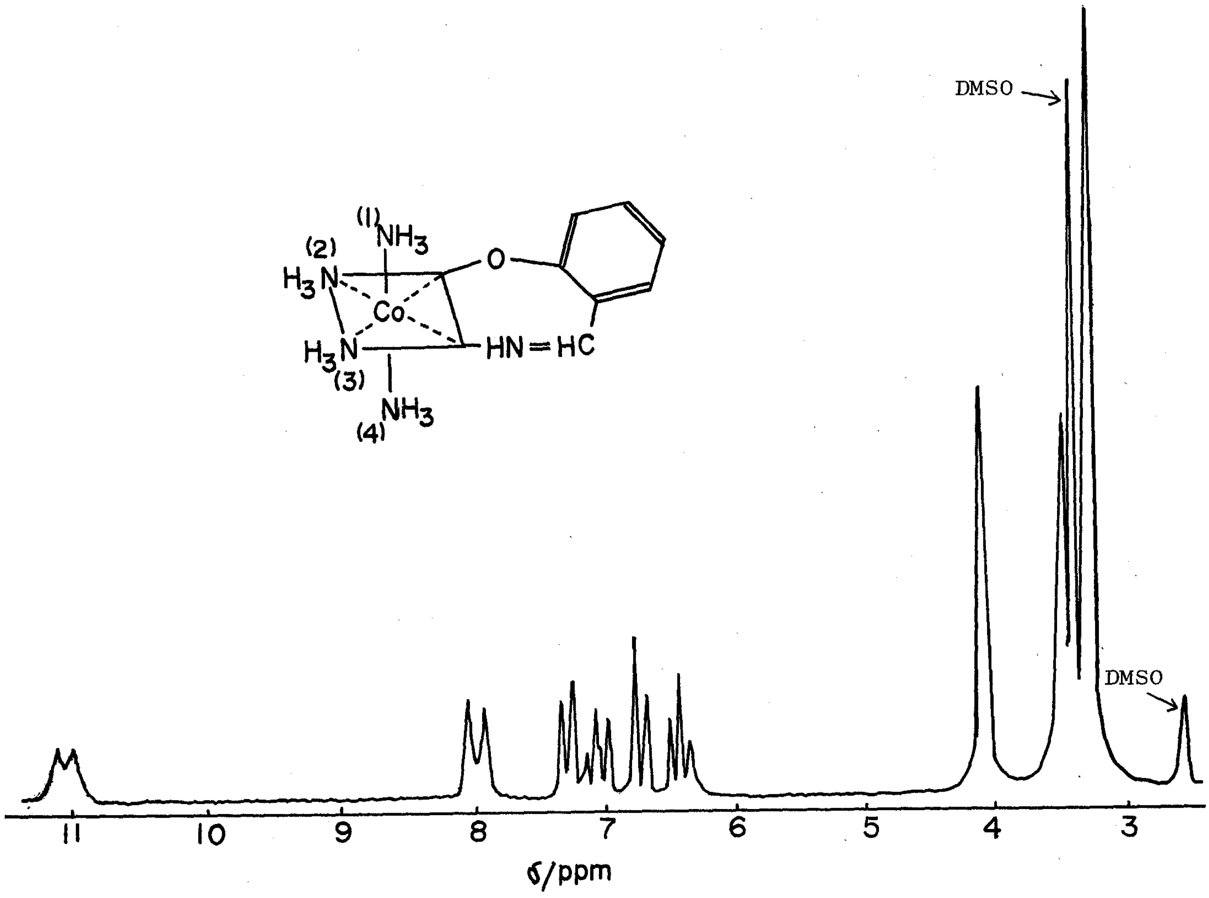


Fig. 1. The ^{1}H NMR Spectrum and the Structure of Complex **1**

The visible absorption spectrum of **1** in methanol has three absorption bands at 378 nm (ε=2744), 475 (183) and 550 (109). Complex **1** is diamagnetic, and should be a cobalt(III) complex of the low spin type.

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