April, 1984] NOTES Bull. Chem. Soc. Jpn., 57, 1153—1154 (1984) 1153

# Paramagnetic Cobalt(III) Complexes with Organic Ligands. VIII.[1] The NMR Spectra of Paramagnetic Tetraammine(5-nitrosalicylato)cobalt(III) Chloride Nitrate Hydrate and the Related Compounds

Yoshihisa YAMAMOTO,* Shigezo SHIMOKAWA,† and Eiji YAMADA†
*Faculty of Pharmaceutical Sciences, Higashi Nippon Gakuen University, Ishikari-Tobetsu, Hokkaido 061-02*
†*NMR Laboratory, Faculty of Engineering, Hokkaido University, Sapporo 060*

(Received July 13, 1983)

**Synopsis.** The ring proton signals have been assigned for the $^1$H NMR spectra of the green paramagnetic tetraammine(5-nitrosalicylato)cobalt(III) chloride nitrate hydrate and (quadridentate amine)(5-nitrosalicylato)cobalt(III) chloride nitrate hydrate, $[Co(5\text{-}NO_2sal)L]Cl\cdot NO_3\cdot nH_2O$ (L: $(NH_3)_4$, trien, 2,3,2-tet, and 3,2,3-tet). The $^1$H NMR spectra indicate that the unpaired electron on the coordinated 5-nitrosalicylato ligand of the title complexes is located over the $\pi$-orbital of the chelated ligand

Previously, we have been concerned with the XPS[1,2] of the green paramagnetic tetraammine(5-nitro(or nitroso)salicylato)cobalt(III) complexes, *i.e.*, it has been established that an unpaired electron of these complexes is delocalized partly on the cobalt atom and partly on the chelated ligand (coordinated 5-nitrosalicylato ligand). In the NMR spectra of these complexes, the signals of the ammine proton have been assigned,[3] but the ring proton and carbon signals of the chelated ligand have so far remained unsolved. We have now devised appropriate conditions for the measurement of the NMR spectra of the green paramagnetic cobalt(III) complexes. The present paper deals with the measurement of the ring protons of the green paramagnetic tetraammine(5-nitrosalicylato)cobalt(III) chloride nitrate hydrate and the related compounds.

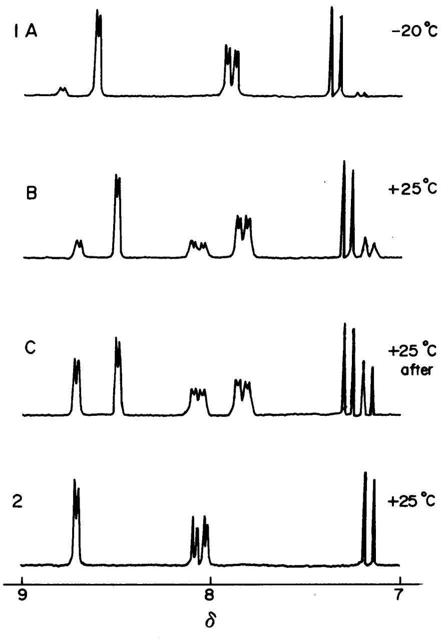


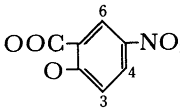
Fig. 1. The $^1$H NMR spectra of the paramagnetic complex **1** and the diamagnetic complex **2** in 1.8 mol dm$^{-3}$ $D_2SO_4$.
1A-C: $[Co(5\text{-}NO_2sal)(NH_3)_4]Cl\cdot NO_3\cdot H_2O$,
**2**: $[Co(5\text{-}NO_2sal)(NH_3)_4]NO_3\cdot H_2O$.

## Results and Discussion

The $^1$H NMR spectra of the chelated ligand of the green paramagnetic tetraammine(5-nitrosalicylato)cobalt(III) chloride nitrate hydrate, $[Co(5\text{-}NO_2sal)(NH_3)_4]Cl\cdot NO_3\cdot H_2O$ (**1**), have not previously been observed, because the measurement is difficult. However, appropriate conditions for the NMR measurement of the green paramagnetic cobalt(III) complexes are now established as follows: The concentration and solvent, temperature and accumulation number are $4.6\pm0.2\times10^{-2}$ mol dm$^{-3}$ in 1.8 mol $D_2SO_4$ solution, −20 °C and two hundred times, respectively. On the other hand, the $^{13}$C NMR spectrum of **1** did not show the expected signals, because of paramagnetism. The $^1$H NMR spectra of **1**, as is shown in Fig. 1(A), have indicated three ring protons at $\delta$ 7.36, 7.91, and 8.61 under the same conditions. This spectrum showed six signals at 25 °C as is shown in Fig. 1(B). In addition, after 10 min, as is shown in Fig. 1(C), these signals decrease with increase of the ring proton signals at $\delta$ 7.16, 8.05, and 8.71; these are chemical shifts of the ring protons of the corresponding orange diamagnetic nitrate hydrate, $[Co(5\text{-}NO_2sal)(NH_3)_4]NO_3\cdot H_2O$ (**2**). Finally, the ring proton signals of **1** are similar to those of **2**. Thus, the signals at $\delta$ 7.36 (d, H), 7.91 (dd, H),and 8.61 (d, H) of **1** have been assigned to the $H_3$, $H_4$, and $H_6$ ring protons, respectively. The chemical shifts and the coupling constants of the ring protons of **1** are closely similar to those of **2** as is shown in Table 1. Thus, the $\sigma$-bonds which are formed from protons and carbons (sp$^2$ configuration) of the chelated ligand of **1** resemble the $\sigma$-bonds of **2**, *i.e.*, the partly unpaired electron can not be delocalized over a hydrogen of the chelated ligand and a substituted methyl group[3] of the corresponding green paramagnetic tetraammine(4-methyl-5-nitrosalicylato)cobalt(III) chloride trihydrate, $[Co(4\text{-}Me\text{-}5\text{-}NO_2sal)(NH_3)_4]Cl_2\cdot 3H_2O$ (**3**), previous reported. It can be concluded that the partly unpaired electron on the chelated ligand is localized over the $\pi$-orbital of the chelated ligand. This is in agreement with the XPS results,[2] *i.e.*, the C 1s binding energy and FWHM of **1** are different from those of **2**. Then, the electronic state of the $\pi$-orbital of the chelated ligand of **1** should be different from that of **2**.

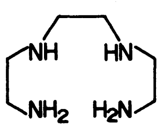
The ring proton signals of the corresponding green paramagnetic (5-nitrosalicylato)cobalt(III) complexes with the quadridentate amine ligands such as trien (**4**, **5**), 2,3,2-tet (**6**), and 3,2,3-tet (**7**) were measured under the same conditions and the results are collected in Table 1. The ring proton signals of the chelated ligand

Table 1. $^1$H NMR spectra of complexes **1**, **2**, and **4**—**7**

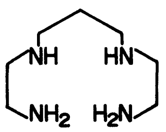


| No. | Complex | $H_3$<br>$\delta$ | $^3J_{HCCH}$<br>Hz | $H_4$<br>$\delta$ | $^3J_{HCCH}$<br>Hz | $^4J_{HCCCH}$<br>Hz | $H_6$<br>$\delta$ | $^4J_{HCCCH}$<br>Hz | Temp<br>°C |
|---|---|---|---|---|---|---|---|---|---|
| **1** | $[Co(5\text{-}NO_2sal)(NH_3)_4]Cl\cdot NO_3\cdot H_2O$ | 7.36 d | 9.6 | 7.91 dd | 9.6 | 4.0 | 8.61 d | 4.0 | −20 |
| | | 7.28 d | 9.6 | 7.85 dd | 9.6 | 4.0 | 8.50 d | 4.0 | +25 |
| **4** | $[Co(5\text{-}NO_2sal)trien]Cl\cdot NO_3\cdot 2H_2O$ | 7.34$^a$ | | 7.92$^a$ | | | 8.64$^a$ | | +25 |
| **5** | $[Co(4\text{-}Me\text{-}5\text{-}NO_2sal)trien]$ $Cl\cdot NO_3\cdot 2H_2O$ | 7.27 s | | — | | | 8.34 s | | +25 |
| **6** | $[Co(5\text{-}NO_2sal)(2,3,2\text{-}tet)]$ $Cl\cdot NO_3\cdot 2H_2O$ | 7.40 d | 9.6 | 7.96 d | 9.6 | | 8.66$^a$ | | +25 |
| **7** | $[Co(5\text{-}NO_2sal)(3,2,3\text{-}tet)]$ $Cl\cdot NO_3\cdot 2H_2O$ | 7.22 d | 9.6 | 7.78 dd | 9.6 | 4.0 | 8.46 d | 4.0 | +25 |
| **2** | $[Co(5\text{-}NO_2sal)(NH_3)_4]NO_3\cdot H_2O$ | 7.16 d | 9.3 | 8.05 dd | 9.3 | 3.5 | 8.71 d | 3.5 | +25 |

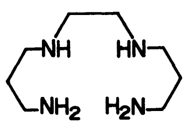
Solvent: 1.8 mol dm$^{-3}$ $D_2SO_4$; Standard: internal DSS ($\delta$=0). a: broad signal.



**trien**



**2,3,2-tet**



**3,2,3-tet**

of complex **7** are very sharp similar to those of **1**, though those of complex **4** are broad. Thus, the ring proton signals of the chelated ligand of complexes **4**—**7** are sharp with the increase of the total number of the center methylene carbons of the quadridentate amine ligands. This property is attributable to the coordinated quadridentate ligands.[4)]

On the other hand, the ammine proton signals at $\delta$ 3.44 (s, 6H) and 3.94 (s, 6H) of **1** are similar to those ($\delta$ 3.44 (s, 6H) and 3.94 (s, 6H)) of **2** under the same conditions. This result agrees with that of XPS of **2**,[2)] *i.e.*, the N ls binding energy of ammine ligands of **1** is similar to that of **2**.

## Experimental

*Measurements.* The NMR spectra were recorded with Varian XL-200 NMR spectrometer.

*Complexes.* Green paramagnetic tetraammine- or (quadridentate amine)(5-nitrosalicylato)cobalt(III) chloride nitrate hydrate[5)] (**1**, **4**—**7**) and orange diamagnetic tetraammine(5-nitrosalicylato)cobalt(III) nitrate hydrate[3)] (**2**) were prepared by the methods of the previous papers.

## References

1) Part VII: Y. Yamamoto, H. Kudo, M. Mori, and H. Konno, *Bull. Chem. Soc. Jpn.*, **55**, 136 (1982).

2) Y. Yamamoto, M. Mori, and H. Konno, *Bull. Chem. Soc. Jpn.*, **54**, 1995 (1981).

3) Y. Yamamoto, *Bull. Chem. Soc. Jpn.*, **51**, 2894 (1978).

4) Y. Yamamoto, H. Kudo, and E. Toyota, *Bull. Chem. Soc. Jpn.*, **56**, 1051 (1983).

5) Y. Yamamoto, K. Ito, H. Yoneda, and M. Mori, *Bull. Chem. Soc. Jpn.*, **40**, 2580 (1967); Y. Yamamoto, E. Toyota, and N. Mitsudera, *ibid.*, **53**, 3517 (1980); Y. Yamamoto and H. Kudo, *ibid.*, **57**, 287 (1984).