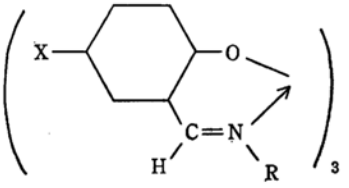
Synthesis of Tris(*N*-isopropyl-*C*-substituted salicylideneiminato)cobalt(III) Complexes

Shoichiro YAMADA, Emiko OHNO and Kuniko YAMANOUCHI

Institute of Chemistry, College of General Education, Osaka University, Toyonaka, Osaka

(Received December 22, 1967)

Numerous cobalt(III) complexes of the Co(X-sal.R)$_3$ type (Formula I)*1 have been reported, but Co(X-sal. *iso*-C_3H_7)$_3$ has never been synthesized up to the present.[1] Thus it has currently been believed that the steric condition arising from the isopropyl groups does not allow the formation of the complexes of this type.[2,3] This statement is no longer correct, as the present authors have succeeded in synthesizing the complexes of the Co(X-sal. *iso*-C_3H_7)$_3$ type, where X denotes 5-NO_2 and 5-Br.



Formula I

A typical method of preparation was as follows. To a solution of Co(X-sal. *iso*-C_3H_7)$_2$ (0.01 mol) and the ligand (0.01 mol) in ethanol (20 m*l*) was added with stirring a 30% solution of H_2O_2 (5 m*l*) drop by drop at about 60°C. The solution was kept at this temperature for about twenty minutes and then allowed to stand overnight at about 5°C. A crystalline precipitate which separated was filtered, and recrystallized from ethanol, chloroform or acetone. Dark-green crystals of Co(X-sal. *iso*-C_3H_7)$_3$ were obtained in good yield. The complexes of the Co(X-sal. *n*-C_3H_7)$_3$ were prepared as dark-green crystals by a method similar to that previously reported.[2]

Analytical data of these complexes, which are given in Table 1, agree with the above formulae. The fact that the complexes prepared are diamagnetic indicates that they are cobalt(III) complexes of a low-spin type. The complexes with R=*iso*-C_3H_7 show clear melting points which are different from those of the corresponding complexes with R=*n*-C_3H_7, as given in Table 1. The infrared spectra of the complexes with R=*iso*-C_3H_7 are different from the spectra of the complexes with R=*n*-C_3H_7, the latter showing bands due to C–C stretching vibrations of the *n*-propyl group at about 1000 to 1100 cm^{-1}, where no absorption band appears for the complexes with R=*iso*-C_3H_7.

Two configurations, a *mer*- and a *fac*-form, are possible for the complexes of the Co(X-sal. R)$_3$ type, but only the *mer*-form has been isolated for all the previously synthesized complexes.[4] It is, therefore, most likely that the complexes prepared in the present work are also of the *mer*-form. The maxima of d-d bands of Co(X-sal. *iso*-C_3H_7)$_3$ are nearly equal to the maxima of Co(X-sal. *n*-C_3H_7)$_3$, for which the *mer*-form is usually found.

It seems to be significant that the complexes which have been claimed to be incapable of existence are isolated as pure crystals. The result of the present work clearly demonstrates that the extent of the steric hindrance is not great enough to forbid the formation of the complexes of the Co(X-sal. *iso*-C_3H_7)$_3$ type, although it is true that there may be more or less remarkable steric hindrance.

TABLE 1. ANALYTICAL DATA OF Co(X-sal·R)$_3$

X	R	mp (°C)		C	H	N (%)
NO_2	*i*-C_3H_7	243.5—245	Found	52.40	4.90	12.22
	n-C_3H_7	216.5—218	Found	52.56	4.74	12.21
			Calcd	52.94	4.89	12.35
Br	*i*-C_3H_7	227.5—229	Found	46.47	4.12	5.20
	n-C_3H_7	232.5—234	Found	46.45	4.31	5.33
			Calcd	46.44	4.25	5.37

---

*1 The complexes represented by Formula 1 are abbreviated as Co(X-sal·R)$_2$ in the present communication.

1) S. Yamada, *Coordin. Chem. Rev.*, **1**, 415 (1966).

2) H. Nishikawa and S. Yamada, This Bulletin, **37**, 1154 (1964).

3) A. Chakravorty and R. H. Holm, *Inorg. Chem.*, **3**, 1521 (1964).

4) M. Ciampolini, F. Maggio and F. P. Cavasino, *ibid.*, **3**, 1188 (1964).