Chromium(III) Complexes Containing Bis(salicylaldehyde)ethylenediiminate as a Ligand

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Numerous metal complexes containing bis(salicylaldehyde)ethylenediiminate as a quadridentate ligand (Fig. 1)*1 have been reported in literature.[1-3] However, synthesis of the corresponding chromium(III) complexes has been unsuccessful. In general, synthesis of chromium(III) complexes with *C*,*N*-disubstituted salicylideneiminate ions*2 is known to be very difficult, and the complexes of the type Cr(X-SAL.R)$_3$, for example, have only recently been isolated.[4,5] A recent attempt to produce the bis(salicylaldehyde)ethylenediiminatochromium(III) complex by treating tris(salicylaldehydato)chromium(III) with ethylenediamine was not successful, yielding only bis(*N*-α-aminoethylsalicylideneiminato)chromium(III) series.[4]

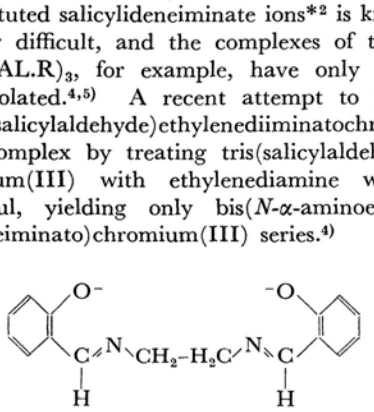

Fig. 1

By employing a method similar to that used for the synthesis of Cr(X-SAL.R)$_3$,[5] we have succeeded in preparing the chromium(III) complexes containing bis(salicylaldehyde)ethylenediiminate as a quadridentate ligand. The new chromium(III) complexes, together with analytical data, are given in Table 1. The compound $[\mathrm{Cr(SAL_2en)(H_2O)_2}]\mathrm{Cl}$ was prepared in the following way. To a solution of chromium(III) chloride hexahydrate (0.1 mol) in ethylene glycol-water-methanol (1:1:3, 300 m*l*) were added salicylaldehyde (0.2 mol) and ethylenediamine (0.1 mol). After the mixture was heated at about 110°C on an oil-bath for about thirty minutes, sodium carbonate (0.06 mol) was gradually added to the solution, followed by reflux of the solution for about three to four hours. Concentrating the solution yielded a reddish brown precipitate, which was recrystallized from 80% methanol to give reddish orange crystals.

The complexes II—V in Table 1 were obtained as orange crystals by reaction of $[\mathrm{Cr(SAL_2en)(H_2O)_2}]\mathrm{Cl}$ with an appropriate amine in methanol, followed by addition of benzene or ethyl ether. The complex VI, $\mathrm{K[Cr(SAL_2en)(CN)_2]\cdot H_2O}$, was obtained as orange crystals by heating at about 60°C a mixture of the complex I and potassium cyanide in 80% methanol for about one hour.

All these chromium(III) complexes are soluble in methanol, ethanol and water, but insoluble in ethyl ether and benzene. The complexes at room temperature show magnetic moments of 3.80 to 3.85 B. M., which correspond to three unpaired electrons for the chromium(III) ion. Infrared spectra of these complexes are similar to those of the corresponding cobalt(III) complexes of the type $[\mathrm{Co(SAL_2en)\text{-}L_2}]\mathrm{X}$, where L denotes various ligands.[6]

TABLE 1. ANALYTICAL DATA OF $[\mathrm{Cr(SAL_2en)L_2}]\mathrm{X}\cdot n\mathrm{H_2O}$

	L	X	n	Calcd, %			Found, %		
				C	H	N	C	H	N
(I)	$\mathrm{H_2O}$	Cl	0	49.30	4.65	7.19	49.04	4.80	7.34
(II)	$\mathrm{NH_3}$	Cl	1.5	46.31	5.59	13.43	46.47	5.53	12.84
(III)	$\mathrm{C_2H_5NH_2}$	Cl	1.5	51.00	6.63	11.90	50.70	6.37	11.98
(IV)	n-$\mathrm{C_3H_7NH_2}$	Cl	1	53.92	6.99	11.43	53.57	7.15	11.25
(V)	n-$\mathrm{C_4H_9NH_2}$	Cl	2	53.77	7.52	10.45	54.02	7.42	10.29
(VI)	$\mathrm{CN^-}$	K	1	50.57	3.77	13.11	49.77	3.75	12.60

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*1 Abbreviated as SAL$_2$en in the present paper.

*2 Abbreviated as X-SAL.R, where R denotes various substituents on the nitrogen atom.

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