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Chromium(III) Complexes Containing N,N'-Ethylene-bis(salicylideneiminate) as a Ligand

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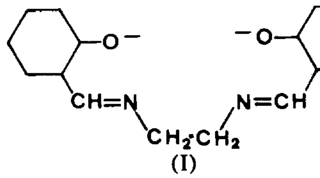
Numerous six-coordinate chromium(III) complexes with N,N'-ethylene-bis(salicylideneiminate) (abbreviated as Salen) have been synthesized. The complexes obtained are $[Cr(Salen)L_2]X \,.\, nH_2O$ *(*$X = Cl$ *or NCS;* $L = H_2O$, NH_3, CH_3NH_2, $C_2H_5NH_2$, $n{-}C_3H_7NH_2$, $n{-}C_4H_9NH_2$, *and pyridine),* $K[Cr(CN)_2Salen]$, $[Cr(ONO)Salen(H_2O)]$, $[CrCl(Salen)py]$, *and* $[Cr(Salen)(H_2O)py]Cl$. *The complexes of the type* $[Cr(Salen)(H_2O)_2]X$ *have been obtained by a reaction of chromium(III) chloride hexahydrate with N,N'-ethylene-bis(salicylideneimine) in ethylene glycol-water-methanol at about 120°, by a reaction of* $NH_4[Cr(NCS)_4(NH_3)_2] \,.\, H_2O$ *with N,N'-ethylene-bis(salicylidenimine) in methanol, and by Collman's modified method using anhydrous chromium(III) chloride in tetrahydrofuran. The other complexes have been derived from* $[Cr(Salen)(H_2O)_2]X$. *The nitrite ion in* $[Cr(ONO)Salen(H_2O)]$ *is bound with the chromium(III) ion through the oxygen atom.*

Introduction

Complexes containing N,N'-ethylene-bis(salicylideneiminate) as a quadridentate ligand have been synthesized with various transition elements.[1] Six-coordinate cobalt(III) complexes containing this ligand and two additional unidentate ligands have also been known for some years.[2-4] The corresponding chromium(III) complexes, however, have never been reported in the literature, and a recent attempt to produce such a complex by treating tris(salicylaldehydato)-chromium(III) with N,N'-ethylene-bis(salicylideneimine) yielded bis(N-α-aminoethylsalicylideneiminato)-chromium(III) salts, in which the ligand was concluded to function as a terdentate ligand.[5] The synthesis of chromium(III) complexes with N-alkyl- of N-aryl-salicylideneiminates has generally been believed to be comparatively difficult, and tris(N-substituted salicylideneiminato)chromium(III) complexes, for example, have only recently been performed.[5-6] The present paper deals with the synthesis and properties of six-coordinate chromium(III) complexes containing N,N'-ethylene-bis(salicylideneiminate) as a quadridentate ligand.



(I)

Experimental Section

Materials. Chromium(III) complexes prepared in the present work are shown in Table I, together with analytical data.

$[Cr(Salen)(H_2O)_2]Cl$. To a solution of chromium(III) chloride hexahydrate (0.1 mole) in ethylene glycol-water-methanol (1:1:3, 300 ml) were added salicylaldehyde (0.2 mole) and ethylenediamine (0.1 mole). After the mixture was heated at about 110° for about 30 min, sodium carbonate (0.06 mole) was added in small portions to the solution, followed by reflux of the solution for about 3 to 4 hr. On concentrating the solution, a reddish brown precipitate was obtained. The precipitate was recrystallized from 80% methanol to give reddish orange crystals of the desirable complex. The crystals are highly soluble in methanol and ethanol, fairly soluble in water, and almost insoluble in benzene and ethyl ether.

This complex was also prepared according to Collman's modified method[7] by refluxing a suspension of

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Table I. Analytical data of [Cr(Salen)XY]Z.nH_2O

X	Y	Z		found, %			calcd., %		
				C	H	N	C	H	N
H_2O	H_2O	Cl	0	49.04	4.80	7.34	49.30	4.65	7.19
H_2O	H_2O	NCS	0	50.12	4.27	10.22	49.51	4.40	10.19
NH_3	NH_3	Cl	2	46.01	5.75	12.61	45.34	5.71	13.22
CH_3NH_2	CH_3NH_2	NCS	1	50.23	5.56	14.87	49.99	5.74	15.34
$C_2H_5NH_2$	$C_2H_5NH_2$	Cl	2	50.70	6.37	11.98	50.05	6.72	11.67
$C_2H_5NH_2$	$C_2H_5NH_2$	NCS	0	53.11	4.97	14.52	53.27	5.11	14.80
n–$C_3H_7NH_2$	n–$C_3H_7NH_2$	Cl	1	53.57	7.15	11.25	53.92	6.99	11.43
n–$C_3H_7NH_2$	n–$C_3H_7NH_2$	NCS	0	55.68	6.32	14.11	55.85	6.52	14.16
n–$C_4H_9NH_2$	n–$C_4H_9NH_2$	Cl	2	54.02	7.42	10.29	53.77	7.52	10.45
py	py	NCS	0	59.65	4.42	13.19	60.67	4.49	13.11
py	H_2O	Cl	0	55.87	4.46	9.55	55.94	4.69	9.32
py	Cl	—	0	58.62	4.26	9.96	58.27	4.42	9.71
H_2O	ONO	—	0	49.71	4.56	10.32	50.25	4.20	10.97
CN	CN	K	1	49.77	3.75	12.60	50.57	3.77	13.11

anhydrous chromium(III) chloride and N,N′-ethylenebis(salicylideneimine) in commercially available tetrahydrofuran.

[Cr(Salen)$(H_2O)_2$]NCS. The compound was synthesized by a method which is different from that for the corresponding chloride. A suspension of NH_4-[Cr$(NCS)_4(NH_3)_2$] . H_2O (0.02 mole) and N,N′-ethylene-bis(salicylideneimine) (0.03 mole) in methanol (70 ml) was refluxed on a water-bath for 3 hr. A reddish product, which separated out, was filtered off and recrystallized from methanol to give yellowish brown crystals.

This compound was also prepared from [Cr(Salen)-$(H_2O)_2$]Cl, as follows. To a solution of [Cr(Salen)-$(H_2O)_2$]Cl (0.01 mole) in 80% methanol (80 ml) was added an aqueous solution (30 ml) of potassium thiocyanate (0.05 mole), and the resulting solution was heated at about 70° for 15 min to give a brown precipitate, which was recrystallized from 80% ethanol to yield yellow-ochre crystals. They are soluble in methanol, but almost insoluble in water, ethanol, and benzene.

[Cr(Salen)$(NH_3)_2$]Cl . $2H_2O$. Into 30 ml of methanol saturated with ammonia, [Cr(Salen)$(H_2O)_2$]Cl (0.01 mole) was added and the resulting solution was stirred for 15 min at about 50°. After the filtered solution was allowed to stand for 1 hr, benzene was added to hte solution, until it began to become turbid. When the resulting solution was allowed to stand overnight, reddish orange needle-like crystals separated out from the solution. They are highly soluble in methanol and ethanol, soluble in water, and almost insoluble in benzene and ethyl ether.

[Cr(Salen)$(C_2H_5NH_2)_2$]Cl . $2H_2O$. This was prepared by a similar method to that for the corresponding diammine-complex described above. An attempt to prepare [Cr(Salen)$(CH_3NH_2)_2$]Cl by a similar method yielded orange crystals, the properties of which seem to agree with those expected for the desirable complex. The values of the elemental analysis, however, deviate from the calculated values, though slightly.

[Cr(Salen)(n–$C_3H_7NH_2)_2$]Cl . H_2O and [Cr(Salen)-(n–$C_4H_9NH_2)_2$]Cl . $2H_2O$. Into a solution of n–propyl or n–butyl amine (about 0.2 to 0.3 mole) in methanol (20 ml), [Cr(Salen)$(H_2O)_2$]Cl (0.01 mole) was added and the solution was stirred for about 15 min at about 50°. To the resulting solution was added ethyl ether, until the solution began to become turbid. After the solution was allowed to stand overnight, orange needle-like crystals were collected. Recrystallization was carried out using methanol as a solvent. These complexes are highly soluble in methanol and ethanol, soluble in water, and almost insoluble in benzene and ethyl ether.

[Cr(Salen)(alkyl amine)$_2$]NCS. These complexes were prepared in the same way as that for the corresponding chlorides, except that [Cr(Salen)$(H_2O)_2$]-NCS was employed instead of [Cr(Salen)$(H_2O)_2$]Cl. They are soluble in methanol, ethanol, water and chloroform, and almost insoluble in benzene and ethyl ether. In general, the solubility of the thiocyanates is lower than that of the corresponding chlorides.

[Cr(Salen)$(py)_2$]NCS. This compound was obtained by a similar method to that for [Cr(Salen)(alkyl amine)$_2$]NCS The notation « py » denotes a molecule of pyridine.

K[Cr$(CN)_2$(Salen)] . H_2O. To a solution of [Cr-(Salen)$(H_2O)_2$] (0.01 mole) in 80% methanol (80 ml) was added a solution of potassium cyanide (0.05 mole) in water (30 ml), and the resulting solution was heated at about 70° for 1 hr. Concentrating the solution yielded the crude product of the desirable complex, which was recrystallized from methanol to give orange crystals. The crystals are highly soluble in methanol and ethanol, soluble in water, and almost insoluble in benzene and ethyl ether.

[CrCl(Salen)py]. A solution of [Cr(Salen)(H_2O)]-Cl (0.01 mole) in pyridine (30 ml) was refluxed at about 110° for about 30 min. Yellow-ochre needle-like crystals were obtained. Recrystallization of the crude product was carried out using methanol as a solvent. The crystals are soluble in pyridine and methanol, but insoluble in ethanol, benzene, water, and ethyl ether.

[Cr(Salen)(H_2O)py]. To a solution of [Cr(Salen)-$(H_2O)_2$]Cl (0.01 mole) in pyridine (30 ml) was added ethyl ether at room temperature, until the solution began to become turbid. After the solution was allowed to stand overnight, reddish orange crystals were collected and recrystallized from methanol or ethanol. The crystals are highly soluble in methanol and ethanol, moderately soluble in water, and insoluble in benzene and ethyl ether.

Measurements. Electronic absorption spectra of the chromium(III) complexes were determined with a Shimadzu MPS-50L spectrophotometer. Infrared spectra were measured with a Hitachi EPI-2 infrared spectrophotometer using the Nujol mull technique.

Results and Discussion

Since it is well known that N,N'-ethylene-bis(salicylideneiminate) as a quadridentate ligand strongly demands square-planar coordination, it is considered that the chromium(III) complexes prepared in the present work have a six-coordinate *trans*-configuration. The formulation of [Cr(Salen)(H_2O)py]Cl is supported by the finding that these complexes in solution give a precipitate of silver chloride immediately upon addition of an aqueous solution of silver nitrate.

The compound [Cr(Salen)$(H_2O)_2$]NCS shows the CN stretching and CS stretching vibrations at about 2055 cm^{-1} and 750 cm^{-1}, respectively, which may be assigned as the vibrations of the free thiocyanate ion. The electronic spectrum of [Cr(Salen)$(H_2O)_2$]NCS is found to be the same as that of [Cr(Salen)$(H_2O)_2$]Cl .

The complex [Cr(ONO)(Salen)(H_2O)] shows vibrations at about 1395 cm^{-1}, 1035 cm^{-1}, and 840 cm^{-1}, which may be ascribed to the nitrite ion bound through the oxygen atom with the metal ion.[8] It may, therefore, be concluded that the nitrite ion in this complex is bound with the chromium(III) ion through the oxygen atom. Previous studies have shown that generally the nitrite ion in chromium(III) complexes is bound with the metal ion through the oxygen atom, and any chromium(III) complex, in which the nitrite ion is established with reasonable certainty to be bound through the nitrogen atom, has never been reported.[9]

Electronic absorption spectra of some of these chromium(III) complexes are shown in Figure 1. The inflation at the lower frequency side suggests the presence of an absorption band at about 20 kK with log ε of about 2.5. Inspection of the spectra also indicates that all the chromium(III) complexes of this series have absorption bands at about 20, 25, 30, and 37 kK. It is considered that the bands at about 25, 30, and 37 kK are not *d–d* bands, but that they arise from internal transitions within the ligand Salen. The corresponding bands are observed with the free ligand.

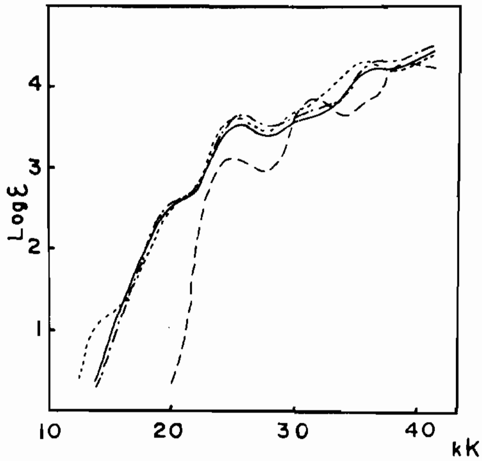

Figure 1. Electronic absorption spectra of [Cr(Salen)X_2]Z.nH_2O in methanol. (1) X=H_2O, Z=Cl, 0.01 *M* CH_3COOH (-----); (2) X=n–$C_3H_7NH_2$, Z=Cl, n=1 (———); (3) X=CN, Z=K, n=1 (—·—); (4) N,N'-ethylene-bis(salicylideneimine) (— — —).

The absorption band at about 20 kK might be considered to arise from *d–d* transitions, judging from its intensity. This assignment, however, seems to be less likely, since the position and intensity of this band are almost equal for all these chromium(III) complexes, irrespectively of the fifth and the sixth ligand. It may be particularly noteworthy that the maximum of this band for $[Cr(CN)_2(Salen)]^-$ is nearly equal to those for $[Cr(Salen)(RNH_2)_2]^+$ and $[Cr(Salen)(H_2O)_2]^+$, in spite of the fact that the cyanide ion is far apart from H_2O in the spectrochemical series. It is most likely that the peak at about 20 kK corresponds to the transition, in which the ligand Salen is mainly involved.

The *d–d* absorption bands are regarded as almost hidden under much more intense bands of other origins, except for $[Cr(Salen)(H_2O)_2]^+$, which shows a shoulder at about 15 kK corersponding to a *d–d* band.

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