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Cerium(IV) Complexes of Schiff Bases Obtained from Substituted Salicylaldehydes and Diamines

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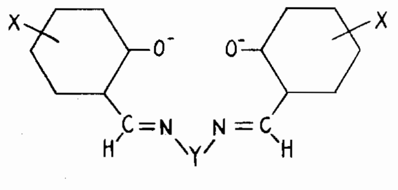
Cerium(IV) complexes of Schiff bases obtained from substituted salicylaldehydes and diamines have been synthesized as dark-red or dark-brown crystals. The substituted salicylaldehydes include salicylaldehyde, 3-methoxysalicylaldehyde, 5-bromosalicylaldehyde, and 2-hydroxy-1-naphthaldehyde, and the diamines employed are ethylenediamine, 1,2-propanediamine, and 1,3-propanediamine. The quadridentate ligands are abbreviated as X–SAL$_2$.Y. These cerium(IV) complexes, represented by the general formula Ce(X–SAL$_2$.Y)$_2$, are diamagnetic, and take an eight-coordinate configuration. The steric requirements of the ligands exclude the square-antiprismatic configuration. A possible structure for these complexes is proposed on the basis of the steric condition.

Introduction

It is known that N-substituted salicylideneimines form complexes with a wide variety of metal ions. No cerium(IV) complexes of these ligands, however, have so far been reported.

The present paper is concerned with the synthesis and characterization of cerium(IV) complexes with N-substituted salicylideneimines and other related ligands (Formula I, abbreviated as X–SAL$_2$.Y). These cerium(IV) complexes provide examples of eight-coordinated complexes, which are constrained by steric requirements to adopt a dodecahedral configuration.



(I)

Experimental Section

Materials. For preparation of the cerium(IV) complexes of the type Ce(X–SAL$_2$.Y)$_2$, where X=H, 3–CH$_3$O, 5–Br, and 5,6-benzo, and Y=CH$_2$CH$_2$, CH(CH$_3$)CH$_2$, and CH$_2$CH$_2$CH$_2$, the following three methods were successfully employed. Any of cerium(III) chloride, acetate and sulphate hydrate was found to be suitable for the starting material.

(a) To a suspension of a cerium(III) salt (0.01 mole) in 85% ethanol (25 ml) were added a substituted salicylaldehyde (0.04 mole) and one of the diamines (0.02 mole) with stirring. The reaction proceeded quickly, and a brown deposit started to appear in the solution in about five minutes. The solution was heated at about 50° for about 30 minutes. The product was filtered off and recrystallized from benzene or chloroform.

(b) The method (b) is similar to the method (a), except that the corresponding Schiff base (0.02 mole) is employed instead of the substituted salicylaldehyde and the diamine. The reaction in this case proceeded more slowly than in the method (a). The reaction proceeded smoothly without an oxidizing agent, but addition of a small amount of 30% hydrogen peroxide to the reaction mixture enormously accelerated the reaction.

(c) This method is similar to the methods (a) and (b), except that cerium(IV) sulphate hydrate is employed instead of the cerium(III) salts.

Typical data of elemental analyses of the complexes prepared are shown in Table I. All these cerium(IV) complexes were obtained as dark-red or dark-brown crystals, which are stable to light and the atmosphere at room temperature. They are highly soluble in benzene, dichloromethane and chloroform, less soluble in methanol and ethanol, and insoluble in water.

Measurements. Electronic absorption spectra were determined with a Shimadzu QR 50 spectrophotometer. In all the measurements it was confirmed that Beer's law was obeyed.

Infrared spectra in Nujol mulls and in potassium bromide discs were determined with a Hitachi EPI-2 spectrophotometer.

Diamagnetism of these complexes was detected by the Gouy method.

Table I. Analytical data of $Ce(X\text{—}SAL_2 . Y)_2$

X	Y	Found, % C	Found, % H	Found, % N	Calcd., % C	Calcd., % H	Calcd., % N
H	CH_2CH_2	57.32	4.07	8.23	57.19	4.17	8.34
	$CH(CH_3)CH_2$	58.28	4.57	8.00	58.32	4.11	7.69
	$CH_2CH_2CH_2$	57.95	4.12	8.27	58.32	4.11	7.69
3—CH_3O	CH_2CH_2	54.80	4.64	6.83	54.54	4.56	7.07
	$CH(CH_3)CH_2$	55.62	4.81	6.88	55.58	4.91	6.83
	$CH_2CH_2CH_2$	55.15	4.76	6.58	55.58	4.91	6.83
5—Br	CH_2CH_2	39.13	2.26	5.52	38.89	2.45	5.67
5,6—benzo	CH_2CH_2	66.31	3.70	6.31	66.04	4.16	6.42

Results and Discussion

A number of new cerium(IV) complexes of Schiff bases have been prepared in the present work.[1] The analytical data, which are shown in Table I, agree with the general formula $Ce(X\text{—}SAL_2 . Y)_2$. The fact that these complexes are diamagnetic indicates that they contain quadrivalent cerium, in agreement with the formula determined from the analytical data. Since the infrared spectra of these cerium(IV) complexes exhibit absorption peaks at about 1540 and 1620 cm^{-1}, which are considered to be characteristic of the Schiff bases bonded to the metal ion,[2,3] it is found that the Schiff bases are present as ligands in these complexes. All these findings combined indicate that the complexes prepared are eight-coordinate cerium(IV) compounds of the Schiff bases. It is interesting to note that the cerium(IV) complexes are formed even from the cerium(III) salts as the starting material without any special oxidizing agent. The oxygen molecules from the air may possibly have acted as an oxidizing agent in these reactions.

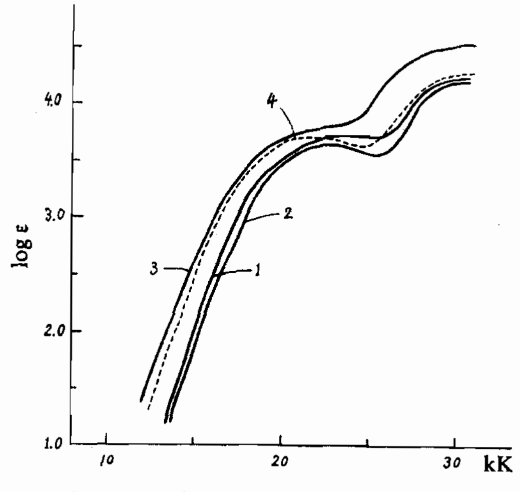


Figure 1. Electronic absorption spectra of $Ce(X\text{—}SAL_2 . Y)_2$ in chloroform. 1, X=H, $Y=(CH_2)_2$; 2, X=H, $Y=(CH_2)_3$; 3, X=5,6-benzo, $Y=(CH_2)_2$; 4, $X=3\text{-}CH_3O$, $Y=(CH_2)_2$.

The cerium(IV) complexes prepared in this work show similar electronic absorption spectra with a band maximum at about 21.5-22.5 kK (log ε about 3.6-4.0). Some of the typical spectra are shown in Figure 1. The broad absorption band in the visible region may be regarded as due to a charge transfer process, possibly from the ligand to the empty 4f orbital of the central metal ion. Using Jørgensen's method and the value of 2.0 for the optical electronegativity of Ce^{IV},[4] the optical electronegativity of $X\text{—}SAL_2 . Y$ is estimated to be approximately 2.7.

For eight-coordinate complexes, three basic types of polyhedra have been found.[5] These include the square-antiprism, the dodecahedron and the hexagonal bipyramid, but examples of the hexagonal bipyramid appear to be confined to uranyl complexes. Structure determination has so far been carried out with some of cerium(IV) complexes, and the dodecahedral and the antiprismatic structure have been reported.[5,6,7] For the cerium(IV) complexes in the present work, the antiprismatic configuration may be definitely excluded, since the quadridentate ligands of the type $X\text{—}SAL_2 . (CH_2)_2$ strongly demand essentially square-planar coordination. For $X\text{—}SAL_2 . (CH_2)_3$, nearly planar coordination is also most likely, although the planar coordination may be slightly less favourable than for $X\text{—}SAL_2 . (CH_2)_2$. The examination of the steric condition thus shows that the structure shown in Figure 2 seems to be one of the most probable for these cerium(IV) complexes.

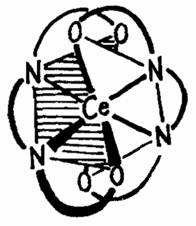


Figure 2. A proposed configuration for $Ce(X\text{—}SAL_2 . Y)_2$.

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(1) A brief account was previously published as a short communication: S. Yamada, A. Takcuchi, and H. Yamakita, *Bull. Chem. Soc. Japan*, *40*, 430 (1967).

(2) L. H. Vogt, Jr., H. M. Faigenbaum, and S. E. Wiberley, *Chem. Rev.*, *63*, 269 (1963).

(3) L. J. Bellamy and R. F. Branch, *J. Chem. Soc.*, 4487 and 4491 (1954).

(4) C. K. Jørgensen, *Mol. Phys.*, *2*, 309 (1959); *ibid.*, *5*, 271 (1962).

(5) J. S. Wood, *Coord. Chem. Rev.*, *2*, 403 (1967).

(6) L. Wolf and H. Barnighausen, *Acta Cryst.*, *13*, 778 (1960).

(7) S. J. Lippard, F. A. Cotton, and P. Legzdins, *J. Am. Chem. Soc.*, *88*, 5930 (1966).