Schiff Base Cerium(IV) Complexes possibly with Eight-coordination

Shoichiro YAMADA, Akira TAKEUCHI and Hiroki YAMAKITA

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

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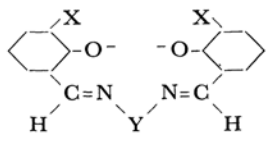
The present communication is concerned with some eight-coordinated complexes of cerium(IV), which are forced to take a dodecahedral or a square-prismatic configuration by the restriction due to the shape of the ligands.

Bis(bis(salicylaldehyde)ethylenediiminato)cerium-(IV) was synthesized by reaction of cerium(III) chloride or acetate (0.01 mol), salicylaldehyde (0.04 mol) and ethylenediamine (0.02 mol) in ethanol. Recrystallization of the crude product from benzene or chloroform yielded dark-brown crystals. Bis(bis(3-methoxysalicylaldehyde) ethylenediiminato)cerium(IV) was obtained in a similar way, except that 3-methoxysalicylaldehyde was used instead of salicylaldehyde. Elemental analyses for carbon, hydrogen and nitrogen are shown in Table 1.[1] Infrared spectra of the complexes also support the presence of these Schiff bases. These oxidation reactions proceeded smoothly without any special oxidizing reagent, and the oxygen from the air possibly acted as an oxidizing agent in these reactions.

TABLE 1. ELEMENTAL ANALYSES OF CERIUM(IV) COMPLEXES OF A $Ce(X\text{-}Sal.Y)_2$ TYPE

X	Y	Found, %			Calcd., %		
		C	H	N	C	H	N
H	CH_2CH_2	57.3	4.07	8.23	57.2	4.17	8.34
	$CH(CH_3)CH_2$	58.3	4.57	8.00	58.3	4.11	7.69
	$CH_2CH_2CH_2$	57.0	4.12	8.27	58.3	4.12	8.27
3-CH_3O	CH_2CH_2	55.3	4.64	6.83	54.6	4.56	7.07

The fact that these complexes are diamagnetic indicates that the cerium is in the quadrivalent state. Since the ligands (Formula I) strongly demand square-planar coordination, the Archimedian antiprism may be definitely excluded for the configuration of these eight-coordinated complexes. The inspection of the steric condition thus indicates that the dodecahedral or the square-prismatic configuration, as shown in Fig. 1, seems to be most likely.



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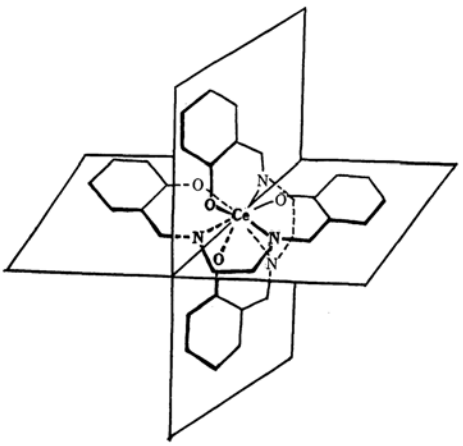

Fig. 1. Proposed structure for bis(bis(salicylaldehyde)ethylenediiminato)cerium(IV).

We have also prepared related complexes, possibly with the same configuration, which are shown in Table 1. The details of the work will be published elsewhere shortly.

1) The ligands of a type of Formula I is abbreviated as X-Sal.Y in the present communication.