Europium Tricyclopentadienide

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Europium tricyclopentadienide has been prepared by the reaction of dichloroeuropium cyclopentadienide with two equivalents of sodium dicyclopentadienide as well as by the reaction of europium trichloride with three equivalents of sodium cyclopentadienide, both reactions taking place in tetrahydrofuran. It is stable in vacuum at temperatures up to 70 °C.

Birmingham and Wilkinson 1 first reported the preparation of a series of lanthanide tricyclopentadienides by reaction of the metal trilahide with sodium cyclopentadienide. The products were isolated and purified by sublimation, however europium tricyclopentadienide could not be isolated by this method because of decomposition before sublimation 2.

We have prepared europium tricyclopentadienide by crystallization of the reaction mixture of dichloroeuropium cyclopentadienide 3 with two equivalents of sodium cyclopentadienide in tetrahydrofuran. It can also be prepared by direct reaction of three equivalents of sodium cyclopentadienide on europium trichloride using a similar crystallization procedure.

Some of these results were reported previously 4. Later Manastyrskij and Dubec 7 reported the mono-tetrahydrofuranate of europium tricyclopentadienide using essentially the same procedure as employed in these laboratories. They also reported that the tetrahydrofuran free compound could not be prepared.

Our preparation was first carried out using dichloroeuropium cyclopentadienide 5 as a starting material, because it can be easily purified by recrystallization and is soluble in THF, therefore allowing a homogeneous reaction. Thus, the purple monocyclopentadienide was reacted with two equivalents of sodium cyclopentadienide in THF at room temperature and a shiny gold brown crystalline product was obtained by crystallization from the resulting reaction mixture. After recrystallization from THF, it was dried under vacuum for 30 minutes at room temperature and for 10 minutes at 70 °C. From the elemental analysis and the molecular weight it was found to be \((\text{C}_3\text{H}_5)_2\text{Eu}\) which is free from THF. In addition to these data, its infrared spectrum was found to be almost identical with that of samarium tricyclopentadienide which was free from THF, since it was previously purified by sublimation.

Attempted sublimation of the europium tricyclopentadienide was unsuccessful under the sublimation conditions normally employed for the other lanthanide derivatives. It is soluble in THF, benzene and chloroform, but insoluble in pentane. It is more unstable than other lanthanide derivatives in the presence of trace amounts of air and amphotropic solvents, decomposing immediately to form yellow sticky material.

The magnetic susceptibility of europium tricyclopentadienide was measured by the Gou y method and the obtained value of 3.74 B.M. is in agreement with that of europium trivalent ion (3.40 - 3.51 B.M.) and thus indicates that unpaired 4f electrons, as expected, are not effected by the cyclopentadienide ligand. This data thus suggests ionic constitution for this compound like other lanthide tricyclopentadienide, although the extent of outer complex formation, using outer vacant orbitals instead of 4f orbital, is uncertain. Further indication of the ionic character of europium tricyclopentadienide are its solubility behavior, extreme sensitivity to air and moisture and the difficulty in sublimation.

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MANASTYRJSKI and DUBECK reported that they could not remove tetrahydrofuran from the reaction product under vacuum at room temperature. It was also reported that tetrahydrofuran was lost at a temperature in the region of 100 °C., but that no characterizable product was isolated. However, we obtained a THF free compound by pumping the recrystallized product for 30 minutes at room temperature and for 10 minutes at 70 °C. 0.1 mm Hg. This suggests that the compound is stable below 70 °C. and unstable over 100 °C. in vacuum.

Experimental

All the experiments described were carried out under an atmosphere of nitrogen which was obtained from Air Reduction Company, Inc. Elemental analysis was performed by Schwarzkopf Microanalytical Laboratory.

Preparation of Europium Tricyclopentadienide

A) Dichloroeuropium cyclopentadienide tris(tetrahydrofuranate)\(^5\) (2.25 g., 0.004 moles) was dissolved while stirring in 100 ml. of THF. To this purple solution was added 0.008 moles of sodium cyclopentadienide. THF solution (0.79 N) at —78 °C. An immediate color change from purple to brown was observed, but the solution was warmed up to room temperature and kept stirring for 5 hours. A precipitated solid and brown solution were obtained. The brown solution was treated with the same procedure as described in method A. A shiny brown crystalline product (2.1 g., yield 80%) was obtained. The infrared absorption spectrum was identical with that obtained for europium tricyclopentadienide obtained by method A.

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B) Anhydrous europium trichloride (1.9 g., 0.0076 moles) was placed in a Schlenk tube with 100 ml. of THF. To this mixture was added 0.0227 moles of sodium cyclopentadienide in THF solution. (0.79 N) at —78 °C. The color of the solution turned immediately to purple and finally brown, but the solution was warmed up to room temperature and kept stirring for 5 hours. The brown solution was treated with the same procedure as described in method A. A shiny brown crystalline product (2.1 g., yield 80%) was obtained. The infrared absorption spectrum was identical with that obtained for europium tricyclopentadienide obtained by method A.

Molecular weight was determined using the SIGNER method with THF as solvent and ferrocene as a reference. Formula weight for C\(_{15}\)H\(_{15}\)Eu; 347.3. Found: 347.8. Infrared absorption spectrum was obtained in nujol. Major peaks are tabulated and compared with that of known samarium tricyclopentadienide.

\[(C_5H_5)_3Eu: 3020, 1650, 1250, 1090, 1010, 785, 755 \text{ cm}^{-1}\]

\[(C_5H_5)_3Sm: 3020, 1650, 1240, 1110, 1010, 800, 765 \text{ cm}^{-1}\]

The magnetic susceptibility of this compound was measured by the GOUY method. The molar susceptibility was found to be 51,362 × 10\(^{-6}\) C.G.S.U. at 298 °K, which after correction for the diamagnetic contribution gives a magnetic moment of 3.74 B.M.