

The value of the second-order specific rate for formation of the N_2O complex may be compared with the formation rates of other $(NH_3)_5Ru^{II}L^{2+}$ complexes at 25°. For $L = N_2$, $(NH_3)_5RuN_2^{2+}$, N_2O , CO, pyridine, and isonicotinamide, $k = 7.1 \times 10^{-2}$,⁶ 4.2×10^{-2} ,⁶ 7.21×10^{-2} ,¹² 12×10^{-2} ,⁹ 11.8×10^{-2} ,¹⁰ and 6×10^{-2} $M^{-1} sec^{-1}$.¹¹

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(9) D. F. Harrison, Ph.D. Thesis, Stanford University, Stanford, Calif., Jan 1969.

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(11) J. N. Armor, unpublished result.

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Synthesis of Cyclooctatetraenyleuropium and Cyclooctatetraenylytterbium

Sir:

The preparation of bis(cyclooctatetraenyl)uranium-(IV),¹ which has received the trivial name "uranocene," has renewed interest in new types of compounds containing cyclooctatetraene. Aside from uranocene, compounds of formula $M(Cot)_2$, with $M = V, Ti$, have been known for some time. Several compounds of formula $M(Cot)$ are also known,² as is one mixed cyclopentadienyl-cyclooctatetraenyl compound, $Co(cp)(Cot)$,³ and many Cot-carbonyl compounds. We report here the preparations and some properties of cyclooctatetraene compounds of Yb and Eu. We believe these to be the first reported cyclooctatetraene complexes of rare earth elements.

It is well known that solutions of ytterbium and europium in liquid ammonia may be used to prepare the respective cyclopentadienides.⁴ The cyclooctatetraene derivatives of these elements were successfully synthesized using similar techniques. Because of the almost explosive air oxidation of both compounds, all studies were carried out under anaerobic conditions. Also, in contrast to $U(Cot)_2$,¹ both compounds undergo immediate hydrolysis in the presence of water.

One would expect to obtain compounds of the type $M(Cot)$ from Yb and Eu, since these elements both have stable +2 oxidation states. This expectation is fulfilled. Analysis of the Yb compound substantiates the formulation $Yb(Cot)$. The Yb compound is, furthermore, diamagnetic. The Eu compound has an epr spectrum visible at 77°K, which is consistent only with Eu^{2+} . The epr spectrum of the powdered compound consists of a strong resonance 4 kG wide, peak-to-peak, centered on $g = 2.00$.

(1) A. Streitwieser, Jr., and U. Müller-Westerhoff, *J. Am. Chem. Soc.*, **90**, 7364 (1968).

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The compounds appear to have strong interactions with solvents, which affect their appearance markedly. The unsolvated Yb compound is, for example, pink. It is insoluble in ammonia, but becomes orange. Removal of excess ammonia at atmospheric pressure yields a compound which is a very intense blue. Removal of ammonia under vacuum yields the original compounds. $Yb(Cot)$ is insoluble in hydrocarbons and ethers but dissolves in more basic solvents, such as pyridine and dimethylformamide. The solutions are deep red and the solids in contact with them are nearly black. These solvents may be removed under vacuum.

Both compounds are stable to 500° under vacuum. Neither sublimes at 500° and 10 μ .

There is no marked difference between the epr spectra of unsolvated $Eu(Cot)$ and the compound solvated with NH_3 . This means only that there has been no remarkable change in the electrical asymmetry of the environment of the Eu^{2+} in the two cases.

The compounds were prepared by the dropwise addition of cyclooctatetraene to ytterbium or europium metal dissolved in anhydrous ammonia. The reactions were carried out under a purified nitrogen atmosphere. In a typical reaction, 0.01 mole of cyclooctatetraene was added slowly to 0.01 mole of the metal, yielding an orange or light green precipitate for ytterbium or europium, respectively. After stirring for 2 hr, the remaining ammonia was removed and a bright blue or light green product recovered. Upon heating to 200° at 10^{-3} mm, a pink (Yb) or orange (Eu) product was obtained. Carbon and hydrogen analyses were slightly off, but consistent with a 1:1 complex. *Anal.* Calcd: C, 34.7; H, 2.9. Found: C, 30.5; H, 3.0. Metal analysis, carried out in the same manner as that for ytterbium cyclopentadienide,⁵ gave excellent agreement for a 1:1 complex. *Anal.* Calcd for $Yb(Cot)$: Yb, 62.4. Found: Yb, 62.1. Analysis of the pink $Yb(Cot)$ indicated that less than 0.5% nitrogen was present. All solvents used were purified by refluxing over calcium hydride or by contact with potassium mirrors. Electron paramagnetic resonance measurements were performed on a Varian V-4502-15 X-band spectrometer, and magnetic susceptibilities were determined with a simple Gouy balance using $HgCo(NCS)_4$ as a standard.

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Fluxional Behavior of (Trihaptocycloheptatrienyl)-(pentahaptocyclopentadienyl)monocarbonyliron

Sir:

We recently reported the preparation of a substance which was assigned the structure of a 7-monohaptocycloheptatrieneiron complex.¹ Further examination of this substance and a comparison of its nmr spectrum

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