ment with the experimental plot.[1] These data have not been refined and are therefore estimated to only 0.1 Å. Parameters of the model are: Be-H(4) = 1.3, Be-H(2) = 1.4, B-H(3) = 1.3, Be-B = 1.8, B-B = 1.8 B-H(2) = 1.3, B-H(1) = 1.2 Å; ∠H(2)-Be-H(2) = 125°, ∠H(3)-B-H(2) = 120°, ∠H(1)-B-H(1) = 92°, ∠B-H(3)-B = 83°, ∠Be-H(2)-B = 83°. Only two Be-H bond distances are known. In the short-lived species BeH, Be-H is 1.343 Å[7] and in [NaOEt₂]·· [Et₄Be₂H₂] the bridging Be-H distance is 1.48 Å.[8] These values are consistent for II but not for I.[9]

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(9) Professor Linus Pauling informs us that his estimation of bond lengths from a consideration of bond numbers agrees to within 0.05 Å of our bond lengths.

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Samarium(II) Dicyclopentadienide 1-Tetrahydrofuranate

Sir:

Although numerous cyclopentadienyl compounds of lanthanides have been reported,[1–7] the only known species of the type $(C_5H_5)_2Ln$ have been possible of synthesis only because of the solubility of Eu and Yb in liquid ammonia.[5,7] We report here the first synthesis of a cyclopentadienyl compound of an ammonia-insoluble lanthanide, *i.e.*, samarium(II) dicyclopentadienide which was isolated as the 1-tetrahydrofuranate. The synthesis procedure employed was a modification of that described previously;[8] the reaction involved is

$$Sm(C_5H_5)_3 + KC_{10}H_8 + C_4H_8O \longrightarrow$$
$$Sm(C_5H_5)_2 \cdot C_4H_8O + KC_5H_5 + C_{10}H_8$$
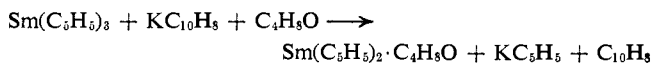
In a typical experiment, 0.499 g of $Sm(C_5H_5)_3$, 0.0527 g of K, 0.128 g of $C_{10}H_8$ (a 25% molar deficiency of naphthalene), and 25 ml of tetrahydrofuran (THF) (freshly distilled under reduced pressure after drying over sodium benzophenone) were mixed in one arm of a U-tube reaction vessel in an anhydrous oxygen-free helium atmosphere and stirred for 48 hr. The purple insoluble product was separated by decantation and washed by a succession of back-distillations of

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THF. Residual solvent was removed at *ca.* 10⁻³ mm for 18 hr at 24°. (This product is very pyrophoric and must be handled only in an anhydrous oxygen-free atmosphere.) *Anal.* Calcd for $Sm(C_5H_5)_2 \cdot C_4H_8O$: C, 47.7; H, 5.12; Sm, 42.7. Found: C, 46.0; H, 5.15; Sm, 42.6.

This tetrahydrofuranate is similar to $Eu(C_5H_5)_3 \cdot C_4H_8O$ in that desolvation at elevated temperatures under reduced pressure is accompanied by decomposition.

Using a modified Curie–Cheneveau balance calibrated with $HgCo(SCN)_4$, $Sm(C_5H_5)_2 \cdot C_4H_8O$ was found to have a molar paramagnetic susceptibility of 5600×10^{-6} cgsu at 298°K ($\mu_{cor} = 3.6 \pm 0.2$). This value compares very favorably with those reported for Sm(II)[9] and Eu(III)[1,9] compounds.

X-Ray diffraction patterns were obtained using $CuK\alpha$ radiation (Ni filter), 35 kV, 15 mA, and exposure times of 6–12 hr; relative intensities were estimated visually. The *d* spacings (Å) corresponding to the most intense lines (I/I_0 in parentheses) were 8.42 (0.5), 4.05 (0.6), 7.34 (1.0), 2.68 (0.5), 5.60 (0.7), 4.78 (0.5), 4.34 (0.5), and 2.99 (0.4).

Tris(cyclopentadienyl)samarium(III) was prepared by the method of Wilkinson and Birmingham.[3,4] *Anal.* Calcd for $Sm(C_5H_5)_3$: C, 52.5; H, 4.3; Sm, 43.5. Found: C, 51.0; H, 4.7; Sm, 43.5. This yellow-orange solid sublimed at 145° ($\sim$10⁻³ mm), melted at $\sim$330° under helium, $\mu_{corr} = 1.9 \pm 0.3$, and was unstable in air, although much more stable than $Sm(C_5H_5)_2 \cdot C_4H_8O$. X-Ray diffraction data for $Sm(C_5H_5)_3$ were 7.46 (0.3), 7.02 (0.4), 5.88 (1.0), 4.86 (0.5), 2.97 (0.3), 2.84 (0.2), and 2.45 (0.3).

Infrared spectra were recorded on mulls in Nujol and hexachlorobutadiene. The infrared spectrum of $Sm(C_5H_5)_3$ is quite similar to those of $(C_5H_5)_2Fe$,[10] $(C_5H_5)_2Eu$, and $(C_5H_5)_2Yb$,[11] having a C–H stretching frequency at 3100 cm⁻¹ and intense bands at 1014 (C–H bend parallel) and 764 cm⁻¹ (C–H bend perpendicular), with a high-energy shoulder on the latter at 796 cm⁻¹. The antisymmetric metal–ring vibration appears at 390 cm⁻¹. Other weaker bands are found at 1445, 1344, 1309, 1263, 1171, and 1076 cm⁻¹. The ir spectrum of $Sm(C_5H_5)_2 \cdot C_4H_8O$ has bands and intensities very similar to those of $Sm(C_5H_5)_3$ (*i.e.*, 3080 (C–H stretch), 1475, 1347, 1308, 1263, 1163, 1070, 1008 (C–H bend parallel), 775, 740 (C–H bend perpendicular), and 350 cm⁻¹ (antisymmetric metal–ring vibration). Other bands at 2980, 2880, 1375, 725, and 565 cm⁻¹ due to the coordinated tetrahydrofuran are located approximately as expected[12–14] and of intensities similar to the weaker metallocene bands. Interpretation of the spectra as suggested by Fritz[15] indicates that the cyclo-

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pentadienyl rings are pentagonally symmetric and ionically bound in both compounds. Exposure of $Sm(C_5H_5)_2 \cdot C_4H_8O$ to traces of air produces an immediate color change from deep purple to yellow-gray and a drastic reduction in the paramagnetism. Although the resulting material had a relatively sharp X-ray powder pattern, analytical data were not reproducible; consequently, this product was not further characterized.

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A Novel Example of the $[H_5O_2]^+$ Ion. A Neutron Diffraction Study of $HAuCl_4 \cdot 4H_2O^1$

Sir:

The oxonium ion $(H_3O)^+$ has been postulated for many years to be the dominant protonated species in aqueous acid solution. Its existence in the crystalline state has also been predicted and directly confirmed by X-ray diffraction studies of several acid hydrates. Other aquated proton species such as $H_5O_2^+$, $H_7O_3^+$, and $H_9O_4^+$ have also been suggested as possible entities in solution or the crystalline state. The higher species are generally assumed to be aquated oxonium ions, $(H_3O^+ \cdot nH_2O)$. Recently, both neutron and X-ray diffraction studies[2-5] have reported evidence for the first of these, the $H_5O_2^+$ ion, in several crystals. In each case the $H_5O_2^+$ entity has been observed as a nonplanar complex of two H_2O molecules linked by a very short (2.42–2.50 Å) linear hydrogen bond with the bridging proton presumably located at or near the bond center.

We wish to report a novel example of $(H_5O_2)^+$, observed in $HAuCl_4 \cdot 4H_2O$ crystals by neutron diffraction, in which the bridging proton distribution may be described in terms of a double minimum potential. The *bridge* length (O–H–O) in this compound is 2.57 ± 0.01 Å, and the bridge protons are found to be symmetrically disordered about the bond center and, surprisingly, in off-axis locations.

Single crystals of $HAuCl_4 \cdot 4H_2O$ protected in sealed-glass capillaries were examined by X-ray and neutron diffraction techniques. The monoclinic cell parameters are $a = 11.78$, $b = 4.62$, $c = 8.89$ Å; $\beta = 101.9°$; and $Z = 2$. The space group, confirmed by statistical tests and successful refinement, is C2/m. A full three-dimensional neutron structure investigation, utilizing 853 independent reflections measured at λ 1.052 Å on the Argonne computer controlled diffractometer,[6]

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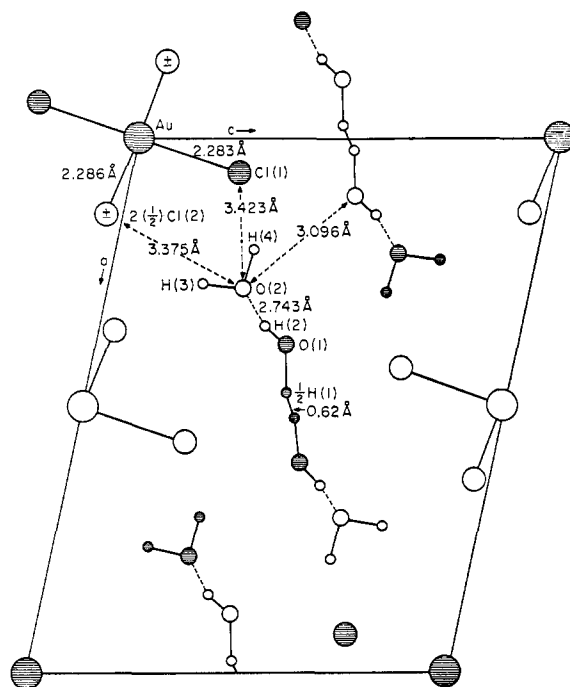

Figure 1. Projection on the *ac* plane of the unit cell contents of $HAuCl_4 \cdot 4H_2O$. Cross-hatched atoms lie in the mirror plane intersecting *y* at 0. Circles are used to represent atoms which are, in order to decreasing size, Au, Cl, O, and H. The Cl atoms designated ± lie above and below the mirror plane in apparent disorder. The $[H_5O_2]^+$ group consists of two O(1) and two $^{1}/_{2}$H(1) atoms in the mirror plane plus two pairs of H(2) atoms which project onto the mirror as two atoms. Dashed lines indicate hydrogen-bonded and other close atom approaches.

was carried out. The structure was solved directly from the neutron Patterson function. A chlorine atom disorder in the structure was recognized at the initial Patterson stage. Structure refinement was carried out by Fourier and least-squares methods; the final R factor was 9.7%.

The crystal structure, shown in *b* axis projection in Figure 1, consists of layers, extending parallel to *a* and *b*, of square-planar $(AuCl_4)^-$ ions stacked along *b* with interleaved layers of $(H_5O_2)^+$ ions interconnected by H_2O molecules. The $(AuCl_4)^-$ groups are tilted with respect to the mirror plane which gives rise to the mirror image tilted configuration and the chlorine atom disorder mentioned above. Packing considerations suggest that the $(AuCl_4)^-$ groups are stacked along *b* in an orderly fashion within one layer; thus the disorder may be attributed to random variations in stacking from layer to layer.

The $(H_5O_2)^+$ groups, distinguished by the short O–H–O bridge distance and the extra proton, are linked by water molecules by means of normal hydrogen bonds (2.74 Å) into infinite chains extended along the *b* axis. The repeating unit in the chain is $(H_9O_4)^+$ which, as can be seen in Figure 2, has a markedly different configuration than the trihydrated oxonium ion (also $H_9O_4^+$), proposed by Wicke, Eigen, and Ackermann[7] as a major component of aqueous solutions of strong acids. Another unit which may be of significance is the $(H_{14}O_6)^{2+}$ ring shown in Figure 2

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