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A Novel and Efficient Nuclear Magnetic Resonance Shift Reagent: Tetrakis-(1,1,1-trifluoro-4-phenylbutane-2,4-dionato)uranium

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Summary The title uranium chelate [U(tfba)$_4$] can be used as an n.m.r. chemical shift reagent.

There has been much recent interest in the use of rare-earth chelates such as Ln(dpm)$_3$[1] (dpm = dipivaloylmethanato; Ln = Eu, Pr, or sometimes Yb) to increase the resolution of the n.m.r. spectra of added substrates (see ref. 2 for applications to ^{1}H resonances, ref. 3 for ^{13}C, and ref. 4 for ^{14}N). Their interest is due to their ability to form an adduct with the substrate, the magnitude of the isotropic shift induced by the electronic magnetic moment of the rare-earth ion, and the very moderate broadening of the lines of the substrate induced by this moment, a feature uncommon for many paramagnetic complexes.[5] The origin and calculation[6] of the isotropic shift, and its temperature dependence[7] have been the subject of controversy.

We report here that U(tfba)$_4$ forms adducts with a variety of Lewis bases and can serve as a chemical shift reagent replacing the usual rare-earth chelates. It was prepared by extraction of U^{IV} from aqueous HCl at pH *ca.* 1, by a solution of 1,1,1-trifluoro-4-phenylbutane-2,4-dione (tfbaH) in CCl$_4$.

The spectra, measured on an NV-14 Varian 60 MHz spectrometer at room temperature, of a solution of pyridine in carbon tetrachloride before and after addition of U(tfba)$_4$ is shown in the Figure, with the resonances of the U(tfba)$_4$ protons removed. The corresponding shifts together with data for n-butyl alcohol, and values of the shifts for pyridine in the presence of Eu(dpm)$_3$ are in the Table.

The pyridine resonances are appreciably shifted by U(tfba)$_4$, as they are with Eu(dpm)$_3$. A single line is observed for the *ortho*-, *meta*-, and *para*-protons in the presence of U(tfba)$_4$, the position of which depends on the relative considerations of pyridine and U(tfba)$_4$, thus indicating rapid exchange of pyridine between a free and a complexed state. The spectra in the Figure are therefore the first evidence of an adduct formed with a uranium diketone. The chemical shifts of the pyridine protons each depend linearly on the molar ratio (ξ) of U(tfba)$_4$ to C$_5$H$_5$N, up to ξ 0·7; measurements at higher values of ξ indicate a 1:1 stocheiometry for the adduct. The rare-earth adduct behaves similarly, although the chemical

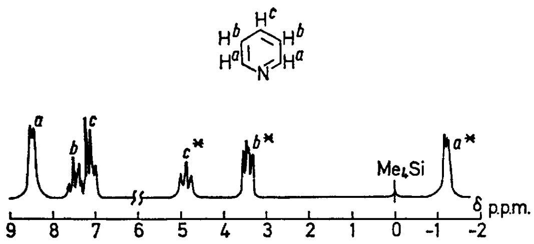

FIGURE. ^{1}H N.m.r. spectrum of pyridine in CCl$_4$ with and without U(tfba)$_4$ (ξ = 0·5). Multiplets *a*, *b*, *c* are for U(tfba)$_4$-free solution; *a**, *b**, *c** are for solutions containing (Utfba)$_4$. The spectrum of U(tfba)$_4$ has been removed. [C$_5$H$_5$N] = 0·08M; [U(tfba)$_4$] = 0·04M.

shift *vs.* molar ratio plot is linear up to a lower value of ξ (*ca.* 0·5). Similar adducts have been observed with U(tfba)$_4$ and a variety of Lewis bases including alcohols, sulphoxides, amides, phosphates, phosphine oxides, and phosphites; an adduct has also been observed with tributylphosphine.

Table. Chemical shifts in p.p.m. from Me$_4$Si for pyridine and n-butyl alcohol in CCl$_4$; accuracy ± 0·1 p.p.m.

Proton		*a*	*b*	*c*
Pyridine	with U(tfba)$_4$	−9·8	−3·6	−2·8
	with Eu(dpm)$_3$	8·2	2·3	2·3

Proton	OH	α	β	γ	δ
Bu^{n}OH with U(tfba)$_4$	−25·0	7·9	−3·7	−2·1	−1·2

Since it is capable of forming adducts with many Lewis bases and inducing proton shifts of a magnitude similar to those obtained with Eu (dpm)$_3$, U(tfba)$_4$ may be useful as a chemical shift reagent.[8] The shifts obtained with each reagent, however, appear to have no simple relationship to one another; in the case of pyridine, they are of opposite signs, and protons *b* and *c* are better resolved by the use of the uranium chelate. The solubilities of the U(tfba)$_4$ adducts are in most cases approximately equal to those of the relevant substrates, so that spectra may be recorded using a reasonable amount of reagent, and appreciable induced shifts observed. In contrast to Ln(dpm)$_3$, U(tfba)$_4$ is not moisture-sensitive.

We have obtained adducts with other uranium(IV) diketones such as U(fod)$_4$ and U(tfea)$_4$ (fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione and tfea = 1,1,1-trifluorohexane-2,4-dione).

Dr. Caro drew our attention to the special feature of rare-earth chelates Ln(dpm)$_3$ and one of us (E.S.) acknowledges financial support from the C.N.R.S.

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[1] C. C. Hinckley, *J. Amer. Chem. Soc.*, 1969, **91**, 5160; J. K. M. Sanders and D. H. Williams, *Chem. Comm.*, 1970, 422.

[2] A. Ahmadi, *Rapport C.E.A.*, 1971, R. 4235; F. Lefevre and M. L. Martin, *Org. Magnetic Resonance*, 1972, **4**, 422; R. von Ammon and R. D. Fischer, *Angew. Chem. Internat. Edn.*, 1972, **11**, 675.

[3] W. B. Smith and D. L. Deavenport, *J. Magnetic Resonance*, 1972, **6**, 256.

[4] M. Witanowski, L. Stefaniak, H. Januszewski, and Z. W. Wolkowski, *Chem. Comm.*, 1971, 1573.

[5] E. de Boer and H. Van Willingen, *Progr. N.M.R. Spectroscopy*, 1967, **2**, 117.

[6] H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, 1958, **29**, 1361; A. J. Vega and D. Fiat, Magnetic Resonance Symposium, Rehovot, Israel, Butterworths, 1972.

[7] R. J. Kurland and B. R. McGarvey, *J. Magnetic Resonance*, 1970, **2**, 286; B. Bleaney, *J. Magnetic Resonance*, 1972, **8**, 91.

[8] Demande de Brevet Francais n$^{\mathrm{o}}$ 73, 18,495, 22 Mai 1973.