# Interaction of Lanthanide Shift Reagents with Co-ordination Complexes; Direct Observation of Nuclear Magnetic Resonance Signals for Free and Complexed Tris(pentane-2,4-dionato)cobalt(III) at Ambient Temperature, and *X*-Ray Crystal and Molecular Structure of the 1:1 Adduct Formed

By LEONARD F. LINDOY,* HYACINTH C. LIP, and HON WAY LOUIE
(*Department of Chemistry and Biochemistry, James Cook University of North Queensland, Douglas, Queensland 4811, Australia*)

and MICHAEL G. B. DREW* and MICHAEL J. HUDSON
(*Department of Chemistry, University of Reading, Reading* RG6 2AD)

*Summary* The changes in the $^1H$ n.m.r. spectrum of tris(pentane-2,4-dionato)cobalt(III) in $CDCl_3$ on incremental addition of tris(1,1,1,2,2,3,3,-heptafluoro-7,7-[$^2H_6$]dimethyl[$^2H_3$]octane-4,6-dionato)europium {Eu([$^2H_9$]fod)$_3$} have been determined at 32 °C; 1 : 1 adduct formation occurs, chemical exchange with respect to the n.m.r. time-scale being slow, and the 1 : 1 adduct has been shown by *X*-ray diffraction to have an unusual structure containing three bridging oxygen atoms.

---

LANTHANIDE shift reagents (LSR) such as Eu(fod)$_3$ have been used extensively in n.m.r. studies of organic compounds but their use with inorganic metal complexes has been quite limited.[1] In previous studies[2] the chemical exchange between free and complexed substrate has almost invariably been fast on the n.m.r. time-scale when the experiments were performed at ambient n.m.r. probe temperatures. However, Evans and Wyatt[2] showed that the exchange between free and complexed substrate for a number of simple organic substrates such as dimethyl sulphoxide can be slowed by lowering the temperature to −80 °C.

We now report that adduct formation occurs in $CDCl_3$ between the deuteriated LSR, $Eu([^2H_9]fod)_3$, and tris(pentane-2,4-dionato)cobalt(III), $Co(acac)_3$, and that slow chemical exchange occurs at ambient n.m.r. probe temperature (32 °C). The changes in the n.m.r. spectrum when $Eu([^2H_9]fod)_3$ is added incrementally are shown in Figure 1. As the LSR is added the intensity of the original methyl and -CH= signals resulting from the cobalt complex decreases and the signals broaden while four new signals appear. As further $Eu([^2H_9]fod)_3$ is added these latter signals increase in intensity and there is a concomitant decrease in intensity of the original peaks. When greater than a 1 : 1 mole ratio of $Eu([^2H_9]fod)_3$ to cobalt complex is present then only the four new signals together with a -CH= signal from free $Eu([^2H_9]fod)_3$ are present (see Figure 1).

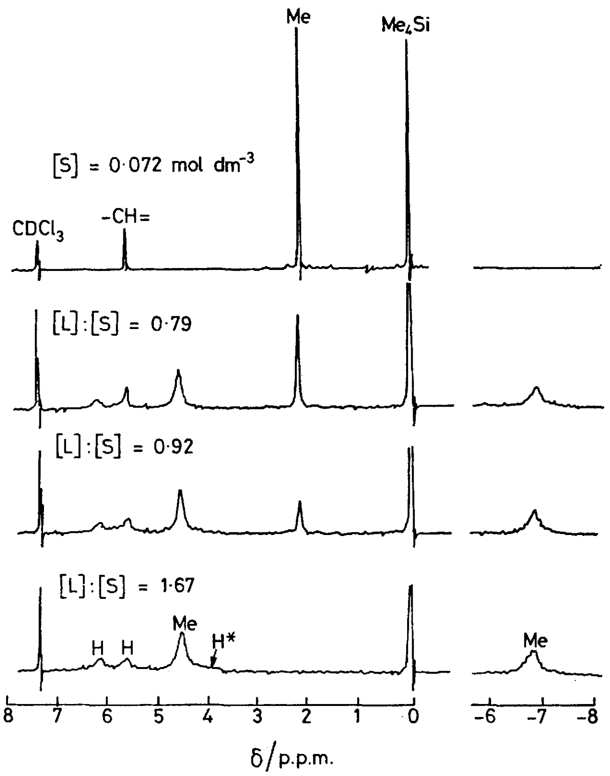

Figure 1. $^1H$ N.m.r. spectra (100 MHz) showing the effect of addition of $Eu([^2H_9]fod)_3$ (L) to $Co(acac)_3$ (S) in $CDCl_3$. *Signal from -CH= group of uncomplexed $Eu([^2H_9]fod)_3$; the position of this peak was confirmed by rerunning the spectrum at higher amplitude and also at higher $Eu([^2H_9]fod)_3$ concentrations.

The occurrence of four signals for the adduct strongly suggests that it has a 1 : 1 stoicheiometry. The signals at δ 4·52 and −6·80 are assigned to the methyl groups and suggest that adduct formation occurs along a $C_3$ axis of tris(pentane-2,4-dionato)cobalt(III) such that three β-diketone oxygen atoms (around one face of the octahedron) bridge to the LSR.

The relative intensities of the four signals for the adduct (see Figure 1) were found to be 1 : 1 : 3 : 3 and this ratio remained constant throughout the run (except where spectral overlap occurs, each resonance was within ±10% of the required relative intensity) and thus there is no evidence that other than a 1 : 1 interaction occurs.

The adduct has been crystallized from solution and the elemental analysis confirms its 1 : 1 stoicheiometry. There is little change in the visible spectrum of the precursor cobalt complex (in chloroform) on adduct formation and this, together with the n.m.r. evidence discussed above, strongly suggests that the co-ordination shell of the cobalt complex remains intact; indeed, the kinetic inertness of such cobalt(III) complexes makes ligand exchange (within the time of the experiment) extremely unlikely. In order to confirm this an *X*-ray diffraction study has been performed on a single crystal obtained by recrystallization of the adduct from benzene.

*Crystal data:* $Co(C_5H_7O_2)_3–Eu(C_{10}H_{10}O_2F_7)_3 \cdot \frac{1}{2}C_6H_6$, $C_{48}H_{54}CoEuF_{21}O_{12}$ $M = 1438 \cdot 8$, cubic, $a = 22 \cdot 909(8)$ Å, $U = 12023 \cdot 1$ Å$^3$. $Z = 8$, $D_m = 1 \cdot 56(3)$, $D_c = 1 \cdot 50$ g cm$^{-3}$, Mo-$K_\alpha$ radiation, space group $Pa3$. 985 independent reflections above background were measured on a G.E.XRD 5 diffractometer and refined with Eu and Co anisotropic and O, C, and F, isotropic to $R$ 0·10; the $-CMe_3$ and $-C_3F_7$ parts of the fod ligands are disordered as are the solvent benzene molecules.†

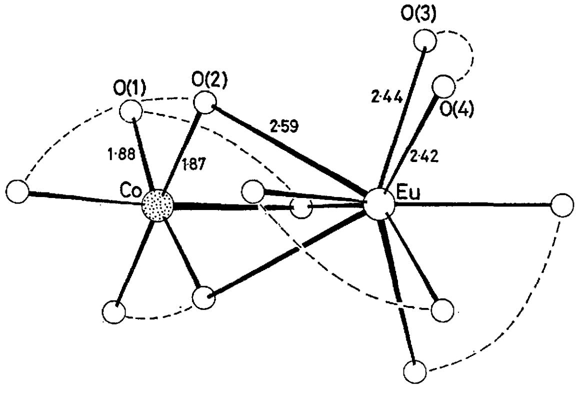

Figure 2. The structure of $Co(acac)_3 \cdot Eu(fod)_3$ showing selected bond lengths (Å).

The molecule $Co(acac)_3 \cdot Eu(fod)_3$ has crystallographically imposed $C_3$ symmetry with both Co and Eu lying on the body diagonal of the cubic unit cell (Figure 2). The geometry of the complex consists of an octahedron around the cobalt atom sharing a triangular face with a tricapped trigonal prism around the europium atom. The geometry

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

of the $Co(acac)_3$ species is relatively unchanged by the sharing of three oxygen atoms with europium; Co–O(1) and Co–O(2) have equivalent lengths to each other and to the value found in $Co(acac)_3$[3] (1·888 Å mean) and the angle O(1)–Co–O(2) is 89·7(11)°. The triangular prism face of the tricapped trigonal prism is however very cramped with O(2)–Eu–O(2) angles of 57·9(7)° compared to values of 75·9(8)° in the other unshared, triangular face. The Eu–O(2) bond lengths are also much longer [2·59(2) Å] than the other Eu–O bonds which are similar at 2·44(2) and 2·42(2) Å. These shorter bonds are comparable to those found in Eu(benzoylacetonato)$_4$ (2·33—2·43 Å)[4] and Eu(hexafluoroacetylacetonato)$_4$ (2·36—2·43 Å).[5]

L. F. L. thanks the Australian Research Grants Committee for support.

(*Received*, 22*nd August* 1977; *Com.* 889.)

[1] L. F. Lindoy and W. E. Moody, *J. Amer. Chem. Soc.*, 1975, **97**, 2275; 1977, **98**, 5863; J. K. Beattie, L. F. Lindoy, and W. E. Moody, *Inorg. Chem.*, 1975, **15**, 3170.

[2] D. F. Evans and W. Wyatt, *J.C.S. Chem. Comm.*, 1972, 312; 1973, 339; *J.C.S. Dalton*, 1974, 765.

[3] G. J. Kruger and E. C. Reynhardt, *Acta. Cryst.*, 1974, **B30**, 822.

[4] A. L. Il'inskii, M. A. Porai Koshits, L. A. Aslanov, and P. I. Lazarev, *J. Struct. Chem.*, 1972, **13**, 254.

[5] J. H. Burns and M. D. Danford, *Inorg. Chem.*, 1969, **8**, 1780.