

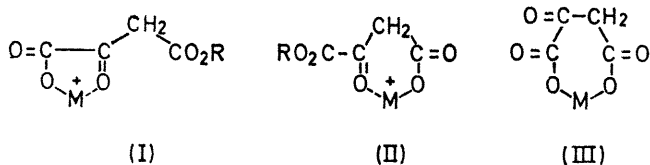
## Nuclear Magnetic Resonance Isotropic Shifts of Europium Oxaloacetates

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**Summary** N.m.r. isotropic shifts of the CH<sub>2</sub> group of europium oxaloacetates provide spectral evidence for the formation of the  $\alpha$ -oxocarboxylate complex between oxaloacetic acid and metal ions in aqueous solution.

THE decarboxylation of oxaloacetic acid is facilitated by transition-metal and lanthanide<sup>1,2</sup> cations which are postulated to form as intermediate the  $\alpha$ -oxocarboxylate complex (I) with oxaloacetic acid.<sup>3,4</sup> In addition to complex (I), the  $\beta$ -oxocarboxylate complex (II) and



R = H or Et

dicarboxylate complex (III) may also form in aqueous solution. Kinetic studies<sup>3</sup> implicate (I) as the active intermediate, but produce neither clear evidence for the formation of large concentrations of (I) during the decarboxylation nor for the presence of other complexes such as (II) and (III).

Making use of the property that Eu<sup>3+</sup> has a very short electron-spin relaxation time, we examined the n.m.r. spectra of complexes of oxaloacetic acid and its monoesters with Eu<sup>3+</sup> in aqueous solutions. Oxaloacetic acid and ethyl oxaloacetate were recrystallized from hexane. Ethoxalylacetic acid was synthesized as described.<sup>5</sup> N.m.r. spectra in H<sub>2</sub>O (Me<sub>3</sub>Si·[CH<sub>2</sub>]<sub>3</sub>·SO<sub>3</sub><sup>-</sup>Na<sup>+</sup> as internal standard) were taken with Varian T-60 and HA-100 instruments. Enough EuCl<sub>3</sub>·6H<sub>2</sub>O was added to give a 1:1 molar ratio to sample solutions (3% w/v).

TABLE

Chemical shifts of CH<sub>2</sub> groups of oxaloacetates and their Eu<sup>3+</sup> complexes (1:1 molar ratio)

	Free chemical shift $\delta$ (in p.p.m.)	Shift on complex formation (in Hz)
HO <sub>2</sub> C·CO·CH <sub>2</sub> ·CO <sub>2</sub> H	.. 3.00	22 (downfield)
EtO·CO·CO·CH <sub>2</sub> ·CO <sub>2</sub> H	.. 3.01	32 (upfield)
HO <sub>2</sub> C·CO·CH <sub>2</sub> ·CO <sub>2</sub> Et	.. 3.03	11 (downfield)

In the study of paramagnetic complexes, two mechanisms, namely, contact and pseudocontact interaction, have been considered responsible for the n.m.r. isotropic shift.<sup>6</sup> With lanthanide ions such as Eu<sup>3+</sup>, the isotropic shift is attributed mainly to the pseudocontact mechanism.<sup>7,8</sup> The isotropic shifts of oxaloacetic acid and its monoesters are given in the Table. Aqueous oxaloacetic acid shows a peak at  $\delta$  3.00 p.p.m. (CH<sub>2</sub>) which shifts downfield by 22 Hz when an 1 mol. equiv. of Eu<sup>3+</sup> is added. The CH<sub>2</sub> peak of ethoxalylacetic acid which forms complex (II) with cations shifts upfield, whereas that of ethyl oxaloacetate forms complex (I) with cations shifts downfield. Molecular models show that the exocyclic CH<sub>2</sub> groups of ethyl oxaloacetate and oxaloacetic acid lying in the plane of the chelate ring show downfield shifts. The cyclic CH<sub>2</sub> group of ethoxalylacetic acid lying out of the plane of the chelate ring produces an upfield shift.

Because both oxaloacetic acid and ethyl oxaloacetate exhibit downfield shifts, it is concluded that oxaloacetic acid preferably forms complex (I) with Eu<sup>3+</sup>. Since Eu<sup>3+</sup> enhances the decarboxylation under the conditions under which the spectra are taken, the  $\alpha$ -oxocarboxylate complex (I) is possible the intermediate in the decarboxylation.

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