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CONFIGURATIONAL ASSIGNMENT OF THIOAMIDES USING PSEUDO CONTACT SHIFTS INDUCED BY $Eu(DPM)_3$

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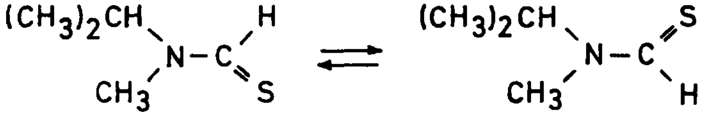
Drago et al. [1] reported on differences of signal shifts in the NMR spectra between the uncomplexed dimethylthioacetamide and the Ni(II)-complex of the thioamide, assuming a coordination between Nickel and the sulfur of the thioamide group.

Recent publications on the influence of tris (dipivalomethanato)europium (III) $[Eu(DPM)_3]$ on the NMR spectra of alcohols [2] and sulfoxides [3] prompted us to investigate the use of this "shift reagent" to correlate signal shifts and configurations of thioamides [4]. When adding $Eu(DPM)_3$ to a solution of N-methyl-N-isopropyl-thioformamide **1** the proton signals of the E- and Z-isomers [5] undergo a considerable however different downfield shift. If the signal shifts are plotted versus concentration of $Eu(DPM)_3$ straight lines are obtained (Tab. 1) the slope of which should be reciprocal proportional to the distance r_i between a certain proton H_i and the europium atom [6].



E **Z**

Z-Isomer		E-Isomer	
signal	slope*	signal	slope*
- C$\underline{H}$S	20.8	- C$\underline{H}$S	20.0
N-C$\underline{H}$	13.4	N-C$\underline{H}$	4.3
C-C$\underline{H}_3$	5.4	C-C$\underline{H}_3$	3.2
N-C$\underline{H}_3$	3.9	N-C$\underline{H}_3$	9.1

Table 1. Pseudo contact shifts induced by Eu(DPM)$_3$ on N-methyl-N-isopropyl thioformamide

$$*: \quad \frac{d(\Delta\tau)}{d\left(\frac{[\mathrm{Eu(DPM)_3}]}{[\mathrm{thioamide}]}\right)}$$

Accordingly it can be assumed that the europium ion is <u>coordinated to the sulfur atom</u>, and thus the largest shifts are induced on protons closest to the sulfur atom. As previously shown in studies on the magnetic anisotropy of the thioamide group [7] the methine proton is located in pseudo-equatorial position to the thioamide group. With respect to this and the inspection of models (Fig. 1) it can be shown that coordination deviates for approximately 40° from the direction of the C-S bond [8].

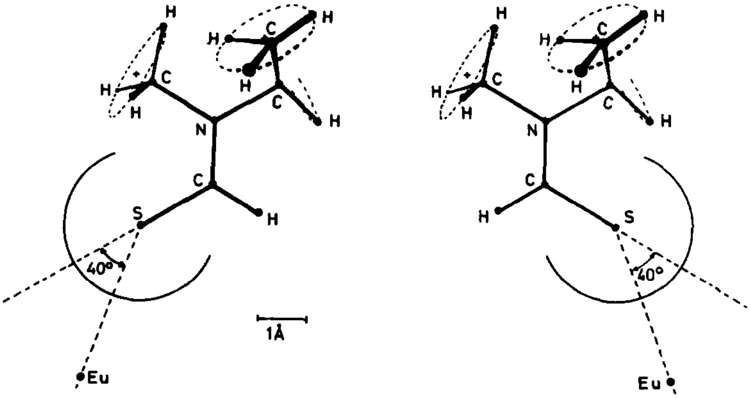


Figure 1: The geometry of the thioamide - Eu(DPM)$_3$ - complex

Assuming the distance between the donor atom and the europium ion to be 3 to 3.5 Å [3a] leads to a calculation of the distances between the europium ion and the different protons of the thioamide molecule, as a result of which the experimental chemical shift differences $\Delta\tau$ show to be reciprocal proportional to the third power of the distances r_i (Fig. 2).

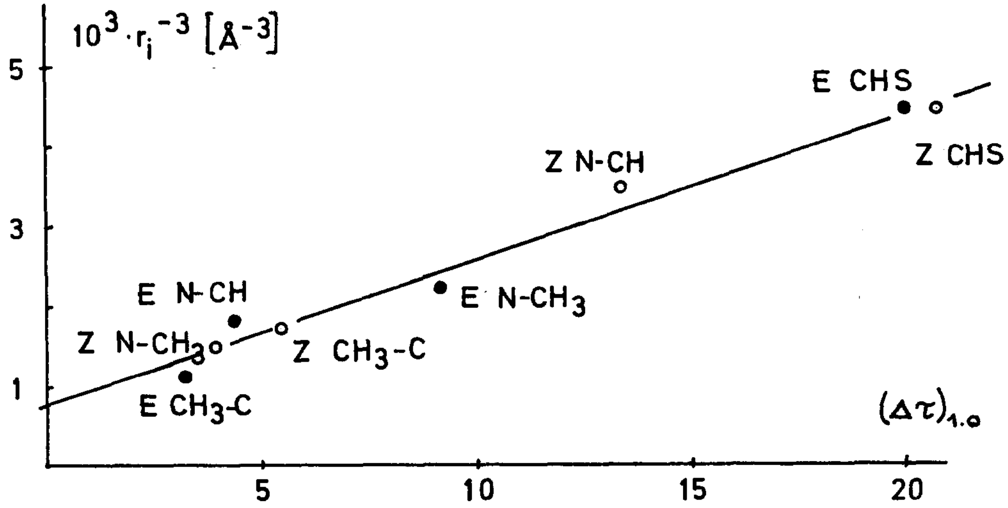


Figure 2

Corresponding results are obtained with thicamides of higher carbonic acids.

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4. Note added in proof: In a recent publication (R. A. Bauman, *Tetrahedron Letters*, **1971**, 419) it was shown, that each proton of the E isomers of thionocarbamate esters show larger shifts than the protons of the Z isomers in the presence of $Eu(DPM)_3$, assuming a coordination between the reagent and the thiocarbonyl sulfur. However no conclusions were made of the geometry of the thionocarbamate ester - $Eu(DPM)_3$ - complex.
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8. Similar results are obtained for the ketone - $Eu(DPM)_3$ - complex [2c].