Inorganica Chimica Acta, 35 (1979) L313–L315
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Sandwich Macrocycle–Lanthanide Adducts with 12-Crown-4: Synthesis and NMR Study

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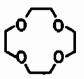
Received March 14, 1979

The complexation of alkali ions by macrocycles has been under active consideration ever since the first report on the synthesis of cyclic polyethers [1]. On the other hand, the coordination of lanthanides by polyoxa and polyaza macrocycles has been little studied until recently [2–7]. The formation of these new macrocycle complexes is not surprising in view of the similarities between the coordination bonds or the ionic radius of the rare earths and those of alkali ions such as sodium [3]. In fact, one can expect that most if not all macrocycles that coordinate sodium should also form adducts with the anhydrous salts of the lighter (*i.e.* larger) lanthanides. This assumption is supported by the present work which deals with the lanthanide complexes with a small twelve membered cycle: 1,4,7,10-tetraoxacyclododecane or 12-crown-4.



The crystal structure of 1:2 adducts between NaCl or NaOH and 12-crown-4 has been reported [8]. The sodium ion forms a symmetrical eight-coordinate sandwich complex.

Experimental

All solutions and reagents were handled and stored in an inert atmosphere dry box. Anhydrous solutions of lanthanide nitrates and perchlorates were obtained as described elsewhere [3]. The cycle 12-crown-4 was synthesized according to Liotta *et al.* [9]. The purity of the compound was checked by elemental analysis. The lanthanide complexes were prepared by dropwise addition with vigorous stirring of a 5 ml acetonitrile solution containing 1 nmol of anhydrous lanthanide salt to a twofold excess of 12-crown-4 dissolved in 1 ml acetonitrile. The precipitate formed nearly immediately and the suspension was refluxed for 1 hr. After cooling, the crystals were filtered, washed with cold acetonitrile and held overnight in vacuum at 80 °C.

The lanthanide perchlorate adducts hydratise exceedingly fast and eventually dissolved in their own water of hydration. Lanthanide elemental analyses were found to be in good agreement with calculated values (*e.g.*: 1:2 complexes, found: La, 17.6; Pr, 17.9; Eu, 19.0; Ho, 20.4; Er, 20.4; Tm, 20.5; Yb, 21.1; calcd.: La, 17.59; Pr, 17.80; Eu, 18.93; Ho, 20.22; Er, 20.45; Tm, 20.61; Yb, 21.00. 1:1 complexes, found: Nd, 28.6; calcd/Nd, 28.50).

Proton NMR spectra were recorded using a Brücker HFX-90 spectrometer at probe temperature. All calculations were carried out with the program CONF described elsewhere [11].

Results and Discussion

The addition of an anhydrous solution of $Nd(NO_3)_3$ in acetonitrile leads to the synthesis of a 1:1 complex. On the other hand, an adduct of 1:2 stoichiometry is obtained with all the rare earth perchlorates in the same operative conditions. This difference is easily understood if one takes into account both the size of the macrocycle and the complexing power of the nitrate ions towards the rare earths. The cycle 12-crown-4 is too small to accommodate a lanthanide ion in its internal cavity, it is thus expected to be a relatively weak complexing agent. The nitrate ion apparently competes favourably with the polyether for the complexation of the rare earths and simple 1:1 adducts are then obtained. On the contrary, the perchlorate ion exhibits very weak complexing properties and the coordination sphere of the lanthanide ions now consists of two tetraoxa macrocycles. It is evident from these data that the complexation of the lanthanides by macrocycles depends not only on the size and the rigidity of the internal cavity as shown earlier [2–7] but also on the complexing properties of the anion involved in the coordination.

The NMR spectra afford further information on the structure of the lanthanide perchlorate complexes. Paramagnetic lanthanide ions are known to induce large proton shifts which are essentially dipolar in origin [10–11]. The paramagnetic shifts are usually interpreted by assuming that the complex under investigation is axially symmetric. The shifts are then a simple function of a geometric factor.

$$\frac{\Delta\nu}{\nu} = -D < \frac{3\cos^2\theta - 1}{r^3} >$$

where θ and r are the polar coordinates of the nucleus under consideration relative to the main magnetic susceptibility axis. D is a magnetic susceptibility term identical for all nuclei of a molecule. The ratio of two

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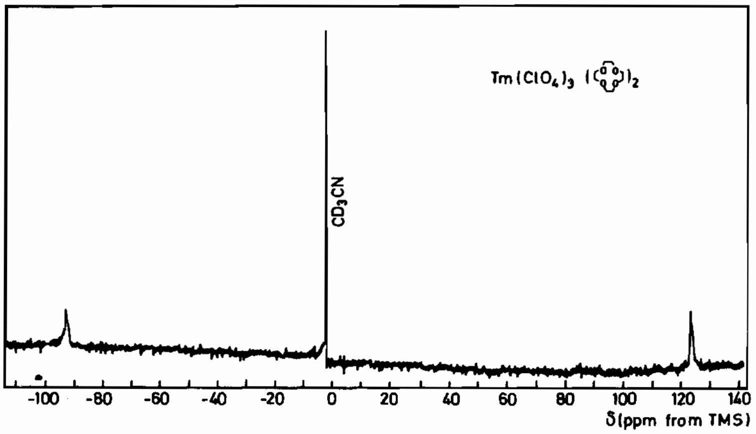
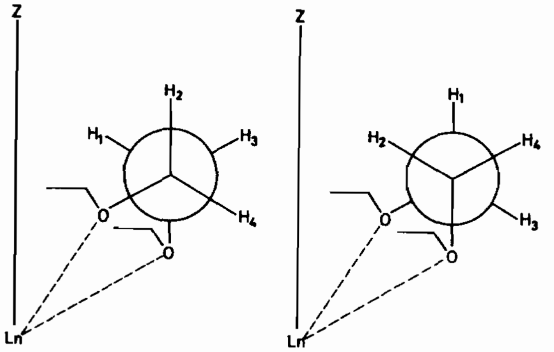


Fig. 1. 90 MHz proton NMR spectrum of an acetonitrile solution of $Tm(ClO_4)_3(12\text{-crown-}4)_2$.

paramagnetic shifts is thus equal to the ratio of their respective geometric factors. This equation is strictly valid only if the complex is axially symmetric, a condition rarely met with lanthanide compounds [10, 11].

If the sodium sandwich complex and the 1:2 lanthanide perchlorate adducts have the same structure, the latter should be axially symmetric with a D_4 axis perpendicular to the mean plane of the macrocycle. The above equation could thus be safely applied.

As illustrated below, two proton peaks are expected in the NMR spectra of symmetric paramagnetic sandwich complexes with 12-crown-4.



Indeed, the interconversion between the two staggered conformations of the ethylene glycol moities brings about the replacement of H_1 by H_2 and *vice versa* and also, the replacement of H_3 by H_4 and *vice versa*. Different geometric factors are thus obtained for the H_1–H_2 and H_3–H_4 pairs. This situation is not to be confused with the steric arrangement in the mono (ethylenediamine) complexes of paramagnetic Ni(II) which exhibit only one single methylene NMR peak because the two conformations are enantiomeric.

The NMR spectrum of the thulium adduct is reproduced in Fig. 1. In keeping with the structural model, the spectrum consists of two proton peaks, respectively at low and high fields. Noteworthy are the very large paramagnetic shifts.

The ratio of the paramagnetic shifts allows one to deduce the distance between the central metal ion and the oxygen donor atoms of the macrocycle. Figure 2 presents the dependence of the ratio R of the geometric factors of the H_1–H_2 and H_3–H_4 pairs upon the metal-oxygen distance. This theoretical curve was computed from the crystallographic structure of the sodium sandwich complex [8]. On this curve are marked the experimental values of the ratio R obtained for the lanthanide adducts for which broadening of the signals did not result in decreased quality of the spectrum.

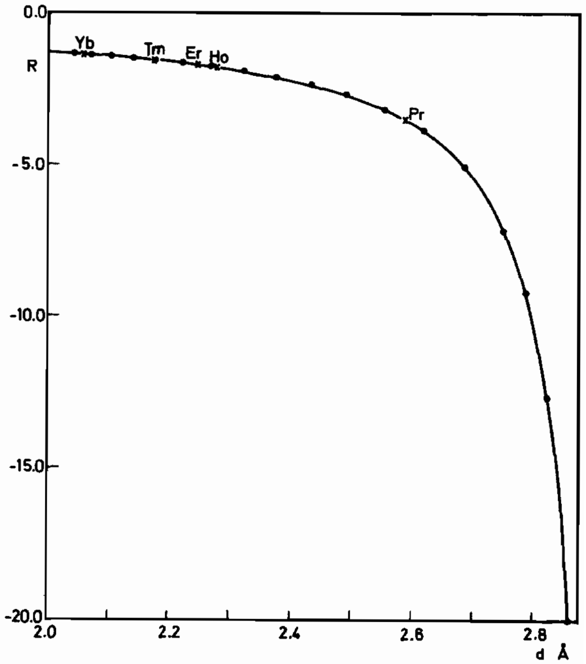


Fig. 2. Influence of the lanthanide contraction of the ratio R of the two paramagnetic proton shifts observed for 12-crown-4 sandwich complexes. d is the metal–oxygen distance.

The metal–oxygen distance is found to decrease from praseodymium to ytterbium obviously because of the lanthanide contraction.

The Yb–oxygen distance appears to be unrealistically short although similar distances were recently reported [12]. It should be borne in mind that in the computation, the assumption was made that all the ethyleneglycol groups are fully staggered which might not be exactly true for the adducts of the smaller lanthanides. Thus, in this particular case, the metal–oxygen distances indicated in Fig. 2 must be accepted with reservation. Also, no data are given for the europium complex as large contact shifts appear to preclude any reliable interpretation of the spectrum [10,11].

The present investigation demonstrates the utility of NMR in the analysis of the solution structure of lanthanide–macrocycle complexes. Of particular pertinence to the analysis reported here is the influence of the lanthanide contraction.

Acknowledgement

We gratefully acknowledge research support from the Fonds National de la Recherche Scientifique of Belgium.

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