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A Novel (3 + 3) Hexaimine Schiff Base Macrocyclic Complex of Lanthanum*

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2,6-Diacetylpyridine and 2-hydroxy-1,3-diaminopropane form macrocyclic compounds when a metal template is used. The form and size of the resultant macrocycle appear to be determined by the metal used. When $Ba(SCN)_2$ is used, a (2 + 2) macrocycle incorporating one barium ion predominates. The OH groups on the macrocycle remain intact and the two thiocyanate ligands balance the positive charge on the barium. A transmetallation reaction with this species using $Cu(ClO_4)_2$ produces a bimetallic copper complex [1, 2]. A proton is lost from one OH group and the alkoxide bridges both copper ions. In the crystal, the intact OH group hydrogen bonds to a molecule stacked below. When $Pb(ClO_4)_2$ is used as a metal template, complete rearrangement of the ligands occurs to form the oxazolidine [1]. It has also been shown that when $Mn(ClO_4)_2$ is used in a transmetallation reaction of the barium (2 + 2) macrocycle, a (4 + 4) macrocycle with four Mn^{2+} ions is formed as a minor product [3]. The authors indicate that this probably is a result of a (4 + 4) macrocycle with two barium ions being present as an impurity in the barium (2 + 2) macrocycle. Further investigations here using FAB mass spectrometry have shown that a (4 + 4) macrocycle with two barium ions is indeed present in a sample of the barium (2 + 2) macrocycle. It is with the versatility of these two ligands in mind that we examined the product of the 2,6-diacetylpyridine and 2-hydroxy-1,3-diaminopropane with lanthanum nitrate as template.

Results and Discussion

With precedence for (2 + 2), (4 + 4) and oxazolidine types of macrocycles, these possibilities were first investigated and discussed on the following grounds. The complexity of the methyl region in the proton NMR spectrum precludes the assignment of the reaction product to a (2 + 2) macrocycle and the integration of the four methyl signals eliminates the possibility of a (4 + 4) macrocycle. Oxazolidine formation can be ruled out on chemical shift arguments. The CH_3 signals in the spectrum are at too high a frequency for protons of an sp^3 carbon which is also attached to O and N substituents.

The product is considered to be a (3 + 3) macrocycle containing three lanthanum ions together with minor species. The NMR spectroscopic results supporting this hypothesis are presented in Fig. 1. The data were obtained with D_2O as solvent since the macrocycle was insoluble in all non-oxidizing organic solvents. Even in D_2O a solution formed very slowly, but heating was avoided as this accelerated the breakdown of the complex. All the experiments were carried out on fresh samples. The ^1H NMR spectrum in D_2O is shown in Fig. 1 and the chemical shifts with the coupling constants of the protons numbered in Fig. 2 are reported in Table I.

Experimental

A methanol solution (3 ml) of $La(NO_3)_3 \cdot 6H_2O$ (1 mmol) was added dropwise to a solution of 2-hydroxy-1,3-diaminopropane (1 mmol) in 3 ml of methanol. The white cloudy precipitate cleared on shaking after each addition. 2,6-Diacetylpyridine (1 mmol), also in 3 ml of methanol, was then added to the resulting clear solution. The solution turned yellow immediately. It was shaken well and heated to boiling then covered and placed in a flask at 50 °C and allowed to stand. Crystallization started to occur after 2 h. The solution was left untouched for 24 h. The supernatant liquid was then decanted and the crystals washed several times in hot methanol and dried under vacuum at 50 °C for 4 h.

Anal. Found: C, 30.61; H, 4.07; N, 13.30. Calc. for (3 + 3) $La_3(NO_3)_6 \cdot 3MeOH$: C, 30.54; H, 3.55; N, 13.70%. FAB Mass spectra: positive ion observed at 1375 with argon gas. Molecular weight for (3 + 3)$\cdot La_3(NO_3)_6 - NO_3$ = 1375.

Spectroscopic Experimental Details

All the experiments were carried out on a Bruker WH 400 spectrometer equipped with an Aspect 2000 computer. D_2O was used as solvent in all the work and the concentration was 5 mg complex/10.5 ml solvent, at 20 °C. Decoupling difference spectra were recorded with a decoupling power of 16 debye attenuation from 0.5 watt, while the n.O.e. (nuclear Overhauser effect) data was acquired with 40 debye

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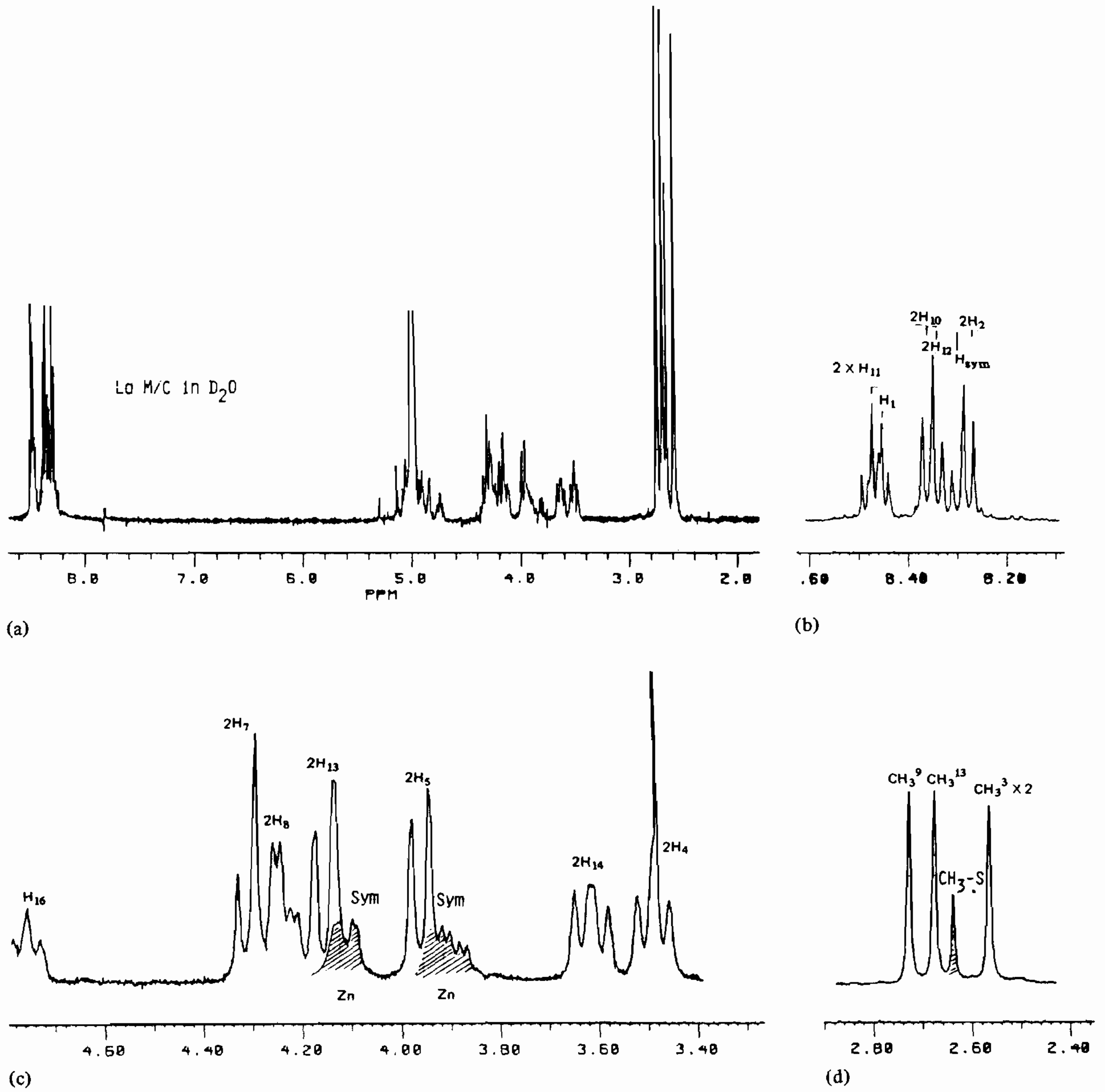

Fig. 1. The ^1H NMR spectrum in D_2O at 20 °C of the product of the template reaction of lanthanum nitrate with 2,6-diacetylpyridine and 2-hydroxy-1,3-diaminopropane: (a) full spectrum; expansions (b), (c) and (d).

attenuation from 0.5 watt. Fresh samples were made up for each series of experiments to avoid further complications from decomposition products.

Supplementary Material

Figures showing (2 + 2) and (4 + 4) macrocycles are available from the authors on request.

References

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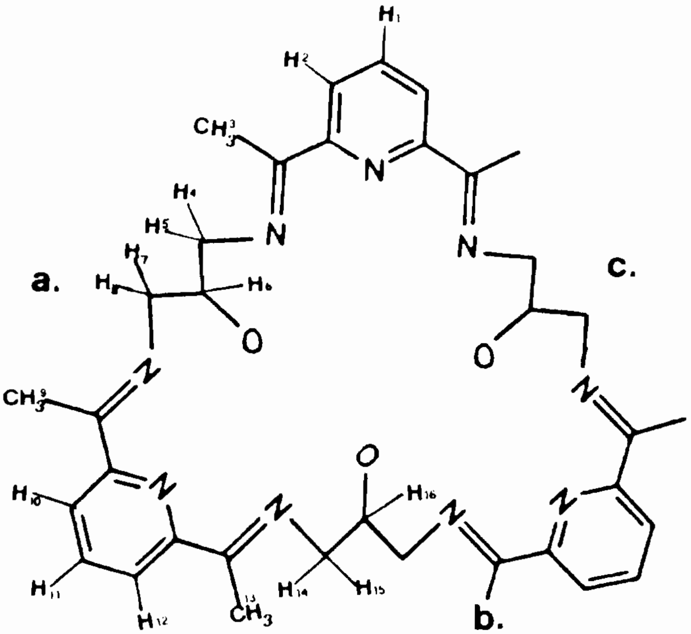

$(La)_3(NO_3)_6 \cdot xCH_3OH$

Fig. 2. A (3 + 3) macrocycle drawn as an isosceles triangle in 2-dimensions with the assignments determined from decouplings and n.O.e. difference spectroscopy.

TABLE I. The Chemical Shifts and Coupling Constants for both the Major and Minor Products from the $La(NO_3)_3$ Template Reaction

Chemical shifts (ppm)	Integrals	Assignments	Coupling constants	(Hz)
Major species				
8.450	2H	2 × H^{11}	JH^1H^2	8
8.445	1H	H^1	$JH^{10}H^{11}$	8
8.348	2H	2 × H^{10}	$JH^{11}H^{12}$	8
8.324	2H	2 × H^{12}		
8.260	2H	2 × H^2		
4.97	2H	2 × H^6	JH^6H^5	2
			JH^6H^4	12
4.75	1H	H^{16}	JH^6H^8	5–6
			JH^4H^5	12
4.32	2H	2 × H^7	JH^7H^8	14
4.25	2H	2 × H^8	$JH^{16}H^{15}$	3
4.16	2H	2 × H^{15} (*cis*)	$JH^{16}H^{14}$	11
3.96	2H	2 × H^5	$JH^{15}H^{14}$	13
3.62	2H	2 × H^{14} (*trans*)		
3.49	2H	2 × H^4		
2.74	6H	2 × CH_3^9		
2.68	6H	2 × CH_3^{13}		
2.57	6H	2 × CH_3^3		
Minor species				
8.435	3 × *n*	H^1	JH^1H^2	8
8.288	3 × 2*n*	2 × *n*H^2	JH^6H^5	3–4
4.75	3 × *n*	H^6	JH^6H^4	7
4.11	3 × 2*n*	H^5	JH^4H^5	16
3.89	3 × 2*n*	H^4		
2.64	3 × 6*n*	CH_3^3		