

Solid State and Solution Structures of the Lanthanide Complexes with Cryptand (2.2.1): Crystallographic and NMR Studies of a Dimeric Praseodymium (2.2.1) Cryptate Containing Two μ -Hydroxo Bridges

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Abstract. A dimeric lanthanide cryptate was obtained by the addition of an excess of cryptand (2.2.1) to a slightly hydrated solution of the monomeric praseodymium (2.2.1) perchlorate complex in acetonitrile. This new lanthanide compound is centrosymmetric and displays the space group $P2_1/n$. The encrypted metal ions are nine-coordinated, they are bonded to all the heteroatoms of a (2.2.1) ligand and they are linked to each other by two μ -hydroxo bridges. The hydroxyl groups are relegating the cryptands to both end of the dimer and the praseodymium ions are less effectively accommodated in the macrocyclic internal cavities than in the case of the monomeric Pr(2.2.1) complex. The formation of both the monomeric and the dimeric lanthanide complexes is readily observed by proton NMR.

Key words: Crystal structure, lanthanides, praseodymium, dimer, macrocycle, (2.2.1), cryptand, NMR, paramagnetic ion.

Supplementary data relevant to this article are deposited with the British Library Lending Division as Supplementary Publication No. 82050 (24 pages).

1. Introduction

Among the lanthanide macrocyclic complexes [1], the (2.2.1) cryptates (where (2.2.1) stands for pentaoxa-4,7,13,16,21-diaza-1,10-bicyclo[8.8.5]tricosane) are of special interest because they display several unusual properties such as high thermodynamic stability [2–3], kinetic inertness in water [4] and stabilization of the +2 oxidation state [4]. Up to the present, studies of the lanthanide (2.2.1) cryptates have been restricted to solution studies and no crystallographic investigation has yet been reported. The present paper is part of our efforts directed at elucidating the solid-state and solution conformation of these complexes. We report herein the

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structure and the proton NMR spectrum of a new dimeric praseodymium complex $[\text{Pr}_2(2.2.1)_2(\text{OH})_2]4[\text{ClO}_4] \cdot 2[\text{CH}_3\text{CN}]$ whose structure is quite unusual because of the two μ -hydroxo bridges that link the two metal ions. The formation of this dimeric species could account for the unexpected affinity of the lanthanide (2.2.1) cryptates for the hydroxyl ion [4].

2. Experimental

An anhydrous acetonitrile solution of praseodymium perchlorate was obtained by dissolving the dehydrated lanthanide salt [5] in dried acetonitrile. All solutions and reagents were stored and handled in a glove box filled with an inert atmosphere. Mixing equimolar amounts of cryptand (2.2.1) and of the anhydrous praseodymium salt enabled us to obtain crystals of a monomeric complex $[\text{Pr}(2.2.1)(\text{CH}_3\text{CN})_2] \cdot 3[\text{ClO}_4]$ whose structure will be reported in detail elsewhere [6]. Adding a 100% excess or more of cryptand (2.2.1) to an acetonitrile solution of the monomeric praseodymium complex brings about drastic modifications of the NMR spectra as well as crystallization of a new compound. Pale green prismatic crystals suitable for X-ray analysis were selected in a glove box and mounted in capillaries. In our experimental conditions, the direct addition of a large excess of cryptand to praseodymium perchlorate leads to the partial precipitation of praseodymium hydroxide.

The proton NMR spectra were recorded on a Bruker AM spectrometer at 300 MHz.

3. Crystal Data

$[\text{Pr}_2(\text{C}_{16}\text{H}_{32}\text{N}_2\text{O}_5)_2(\text{OH})_2] \cdot 4[\text{ClO}_4] \cdot 2[\text{CH}_3\text{CN}]$, Formula weight = 1460.61. Monoclinic, $a = 10.706(3)$, $b = 20.048(5)$, $c = 13.297(2)$ Å, $\beta = 94.12(1)^\circ$, $V = 2847(2)$ Å³, $Z = 2$, $d(\text{calcd}) = 1.702 \text{ g cm}^{-3}$, $\mu(\text{MoK}\alpha) = 19.731 \text{ cm}^{-1}$.

4. Structure Determination

Investigations on a selected single crystal with approximate dimensions $0.15 \times 0.15 \times 0.30$ mm were carried out with an Enraf-Nonius CAD-4 X-ray diffractometer at 293 ± 1 K using MoK α radiation ($\lambda = 0.71073$ Å). The computer programs used were part of the Enraf Nonius SDP Programs [7]. The scattering factors and anomalous dispersion corrections were taken from [8]. Unit cell parameters were determined by least-squares refinement of diffractometer setting angles for 25 diffraction maxima. The space group was unequivocally deduced from the systematic absences. A total of 4843 reflections representing 4603 symmetry-independent reflections were measured in the θ - 2θ scan mode (collection range $3 \leq 2\theta \leq 48^\circ$, h 0/+13, k 0/-23, l +16/-16). During data collection (4 days long), three reflections were monitored at 30 min intervals as a check of the stability of the diffractometer and of the crystal. The maximum anisotropic decay correction applied to the data was 6.3%. Intensities were corrected for Lorentz-polarization effects. Absorption corrections were applied by an empirical method based on a set of scans of reflexions having χ values near $90(1)^\circ$. The transmission factors ranged from 85.2 to 93.5%.

The structure was solved by direct methods. The E-map calculated with the set

of phases presenting the highest combined figure of merit given by the program MULTAN [9] revealed the position of the Pr and of the Cl atoms. Further Fourier and difference Fourier maps in alternance with full-matrix least-squares refinement cycles allowed the location of the remaining non-hydrogen atoms. However, it was not possible to avoid difficulties during the treatment of the data because some parts of the macrocycle underwent high thermal motions. As expected [10], the oxygen atoms belonging to the perchlorate ions also exhibited large temperature factors. Finally, some C—C distances within the macrocycle became abnormally short or long indicating disorder problems. However, when these atoms were omitted in the refinement, they were all recovered at their initial positions in a subsequent difference Fourier calculation. The use of anisotropic thermal parameters resulted in non-positive values for many atoms and only the thermal motions of the Pr, O (hydroxyl) and Cl (perchlorate) atoms were treated anisotropically. The structure was then refined alternatively in two groups of atoms: on the one hand, the atoms belonging to the Pr cryptate, on the other hand, the perchlorate and acetonitrile atoms. Moreover, in order to maintain reasonable interatomic distances, restraints were imposed on some carbon atoms which were forced to ride on one attached neighbour at the distance found in the Fourier map. Finally, the hydrogen atoms were not included in the data treatment. A secondary extinction coefficient applied near the end of the computations refined to $g = 2.71 \times 10^{-7}$ ($F_c = F_o / (1 + g(F_c)^2 L p$ where L is the Lorentz factor and where p is the polarization factor). All parameters were allowed to vary only in the last two cycles of refinement. The final agreement factors $R_1 = \Sigma(|F_0| - |F_c|) / \Sigma|F_0|$ and $R_2 = [\Sigma w(|F_0| - |F_c|)^2 / \Sigma w F_0^2]^{1/2}$ were 0.072 and 0.084 respectively. The largest parameter shift Δ/σ was 0.12. The function minimized was $\Sigma w [|F_c|]^2$ with unit weights for 2936 reflections for which $I > 3\sigma(I)$. The standard deviation of an observation of unit weight $\text{esd} = [\Sigma w(|F_0| - |F_c|)^2 / (m - n)]^{1/2}$ was 3.09. A difference map calculated after the last cycle of refinement showed maximum and minimum excursion densities of +1.8 and -1.5 e Å⁻³, respectively, around the Pr ion.

The coordinates and the isotropic thermal parameters from the final least-square cycle are given in Table I. Anisotropic thermal parameters and calculated structure factors have been deposited with the British Library Lending Division under SUP 82050.

5. Results and Discussion

5.1. STRUCTURE OF THE DIMERIC Pr CRYPTATE

The structure of the dimeric complex is depicted in Figure 1 together with the atom-labeling scheme. The complex is centrosymmetric and contains two identical nine-coordinated praseodymium ions linked together by two μ -hydroxo bridges. The idealized symmetry of the dimer is $C_2\hat{h}$ with a C_2 axis passing through the two praseodymium ions and the two O(21) atoms and a mirror plane passing through the two hydroxyl oxygen atoms O(B). The dihedral angle between the mean plane of the N(1), N(10), O(21) and Pr atoms and the plane of the two O(B) and Pr atoms is 36(1)°. The coordination polyhedron around each praseodymium ion is reproduced in Figure 2. As expected, the mean Pr—O(hydroxyl) bond length (2.36 Å) is shorter than the mean Pr—O(cryptand) (2.60 Å) or Pr—N(cryptand) (2.76 Å) bond lengths. The

Table I. Fractional atomic co-ordinates and isotropic thermal parameters with standard deviations in the least significant digits in parentheses.

	x	y	z	$B(\text{\AA}^2)^A$		x	y	z	$B(\text{\AA}^2)$
Pr	0.99833(7)	0.08687(4)	0.93168(6)	2.89(1) ^B	C(19)	0.805(3)	0.233(2)	0.896(3)	10.3(7)
N(1)	0.779(2)	0.154(1)	0.926(2)	9.7(6)	C(20)	0.908(3)	0.245(2)	0.8283(2)	14.5(7)
C(2)	0.690(3)	0.134(2)	0.840(2)	9.3(7)	O(21)	1.008(1)	0.2023(5)	0.8479(8)	4.5(2)
C(3)	0.763(3)	0.116(2)	0.755(3)	10.4(8)	C(22)	1.101(3)	0.223(2)	0.784(2)	12(1)
O(4)	0.851(2)	0.073(1)	0.767(2)	10.7(6)	C(23)	1.193(2)	0.168(2)	0.774(3)	10.3(6)
C(5)	0.889(2)	0.026(1)	0.684(2)	7.5(6)	O(B)	0.8848(9)	-0.0103(5)	0.9634(8)	3.8(2) ^B
C(6)	1.036(3)	0.012(2)	0.690(3)	13.7(7)	Cl(1)	0.9547(5)	0.4345(3)	0.7172(5)	7.5(2) ^B
O(7)	1.074(2)	0.0176(9)	0.788(1)	11.6(6)	O(11')	0.843(1)	0.408(1)	0.746(1)	14.6(5)
C(8)	1.191(3)	0.018(2)	0.760(2)	12(1)	O(12')	0.929(2)	0.467(2)	0.626(1)	15.6(8)
C(9)	1.280(3)	0.055(2)	0.813(3)	14(1)	O(13')	1.001(1)	0.482(1)	0.792(1)	13.3(5)
N(10)	1.230(2)	0.1238(9)	0.862(1)	11.9(8)	O(14')	1.026(2)	0.380(2)	0.700(2)	15.9(6)
C(11)	1.314(3)	0.141(2)	0.966(2)	10.4(8)	Cl(2)	1.0028(6)	0.1668(3)	0.4728(5)	8.7(2) ^B
C(12)	1.240(3)	0.191(2)	1.009(3)	12(1)	O(21')	0.994(2)	0.209(2)	0.397(2)	15.8(9)
O(13)	1.149(2)	0.159(1)	1.055(2)	10.7(6)	O(22')	1.016(2)	0.200(2)	0.557(2)	15.9(9)
C(14)	1.105(2)	0.182(1)	1.144(2)	7.3(6)	O(23')	1.063(2)	0.114(2)	0.468(2)	15.6(8)
C(15)	0.996(2)	0.138(2)	1.187(2)	14.7(5)	O(24')	0.888(3)	0.129(3)	0.461(3)	15.8(9)
O(16)	0.921(2)	0.132(1)	1.100(2)	11.7(6)	N(A)	0.463(2)	0.152(1)	0.607(2)	15.8(7)
C(17)	0.800(3)	0.163(2)	1.105(2)	10.4(9)	C(A1)	0.414(2)	0.109(1)	0.561(2)	11.0(9)
C(18)	0.723(3)	0.144(2)	1.011(3)	11.1(9)	C(A2)	0.345(3)	0.057(2)	0.506(2)	9.5(7)

^A All atoms refined isotropically unless noted otherwise.

^B Atoms refined anisotropically. The isotropic equivalent thermal parameter is defined as $(4/3)[a^2 B(1,1) + b^2 B(2,2) + c^2 B(3,3) + ac \cos \beta B(1,3)]$.

^C Cl(1) and Cl(2) and the oxygen atoms labelled O(m') are atoms belonging to perchlorate ions that are omitted in Figure 1.

^D N(A)—C(A1)—C(A2) is an acetonitrile molecule omitted in Figure 1.

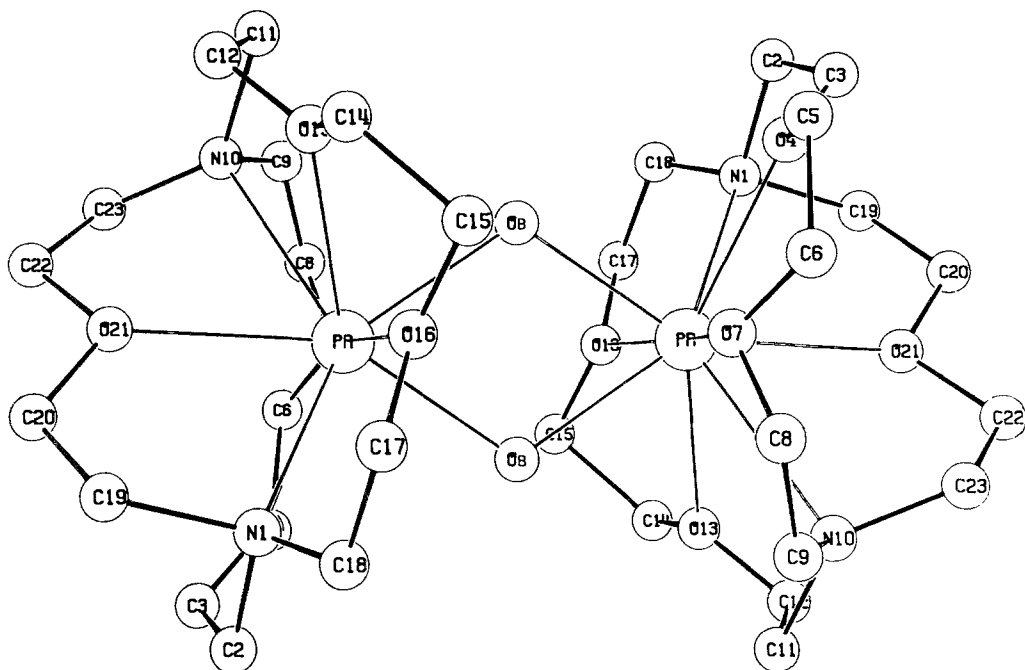


Fig. 1. General view illustrating the molecular structure of the dimeric Pr(2.2.1) cryptate with the two μ -hydroxo bridges.

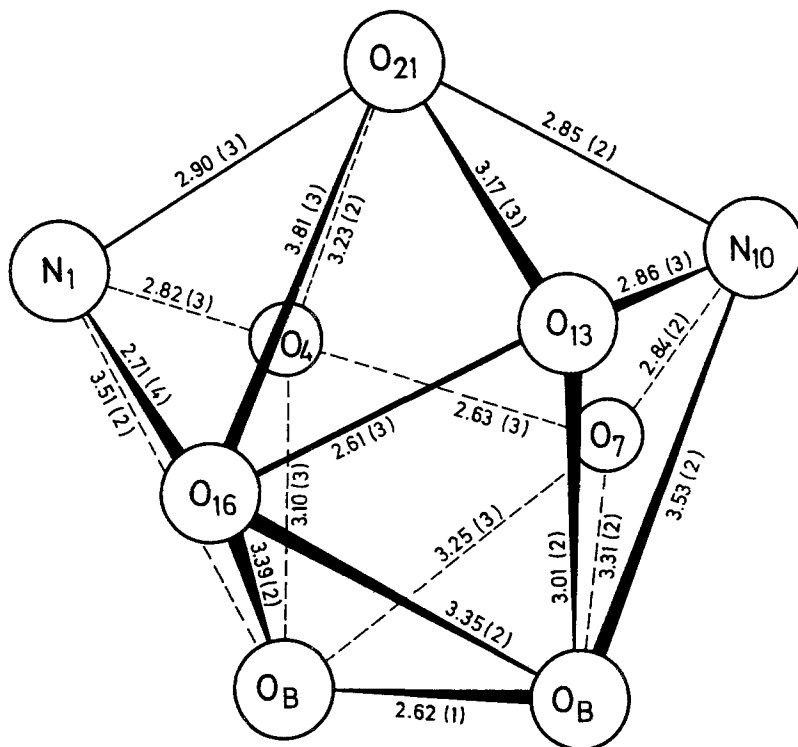


Fig. 2. Coordination polyhedron around each praseodymium ion in the dimeric Pr(2.2.1) complex.

geometry of the coordination sphere of the metal ions is much distorted with respect to the usual nine-coordinate polyhedra [11] but still exhibits an approximate C_2 axis. Distortions were expected because of the steric requirements of the (2.2.1) ligands and because of the constraints that the hydroxyl ions impart on the dimeric complex. Indeed, the (2.2.1) cryptand molecules have to fold in such a way as to accommodate a Pr^{3+} ion in their internal cavity and are relegated to one hemisphere around each metal ion by the strongly coordinating OH^- groups.

Table II. Selected distances (Å) and mean distances and valency angles ($^\circ$), with standard deviations in parentheses

Pr—N(1)	2.70(2)	Pr—O(13)	2.65(2)
Pr—N(10)	2.81(2)	Pr—O(16)	2.60(3)
Pr—O(4)	2.62(3)	Pr—O(21)	2.57(1)
Pr—O(7)	2.54(2)	Pr—O(B)	2.35(1)
		Pr—O(B)	2.37(1) ^a
Mean C—N distance:	1.54(4)	Mean C—C distance:	1.49(5)
Mean C—O distance:	1.38(4)		
Mean N—C—C angle:	113(3)	Mean C—N—C angle:	111(2)
Mean O—C—C angle:	111(2)	Mean C—O—C angle:	110(2)

^a Refers to atom at $-x+2, -y, -z+2$.

Selected distances and mean distances and angles are listed in Table II. The apparent shortenings or lengthenings of some bonds as well as the abnormal values of some bond angles are mainly spurious effects believed to arise from inadequate treatment of curvilinear molecular thermal motions in the crystallographic analysis. Structural investigations of macrocyclic complexes are often thwarted by similar difficulties [12]. Disorder of the perchlorate anions [10] also limits the refinement of the structure reported here. However, the selection of non-coordinating anions is a prerequisite to reliable comparisons between the solid state and the solution conformations of labile lanthanide complexes [6]. Moreover, the formation of hydroxylated derivatives is probably facilitated by the absence of strongly complexing anions such as NO_3^- , an ion that has been widely used with lanthanide macrocyclic complexes [1].

5.2. COMPARISON WITH THE STRUCTURE OF SOME OTHER MACROCYCLIC LANTHANIDE COMPLEXES

Numerous examples of transition metal polymeric complexes involving two μ -hydroxyl bridges are known. However, only one lanthanide complex of this type has been reported so far. Baraniak *et al.* [13] described the structure of a dimeric di- μ -hydroxo ytterbium complex with pyridine-2-carboxaldehyde-2'-pyridylhydrazone. This dimer was obtained by the addition of a solution of the ligand in ethanol to an equimolar aqueous solution of $YbCl_3$. The ligand being a strong base, the formation of a partially hydrolysed metal complex is not surprising. However, polymeric lanthanide complexes have not attracted much interest so far probably because of difficulties in isolating crystals suitable for structure analysis and because hydrolysis most often leads to the precipitation of lanthanide hydroxides instead of the formation of soluble well-defined complexes.

Traces of water in our solutions of monomeric praseodymium cryptate are most probably responsible for the formation of the dimeric complex reported here. Partial hydrolysis of this complex takes place because the excess of (2.2.1) cryptand brings about a pH increase. Incomplete hydrolysis of a lanthanide macrocyclic complex has also been noted by Bünzli *et al.* [14] who prepared a dimeric praseodymium complex with 1,4,7,10,13-pentaoxacyclododecane (15-crown-5) by dehydrating in vacuo a monomeric species. The metal ions in this dimer are bridged by only one hydroxyl group and by three trifluoroacetate anions. The distance between the two praseodymium ions in the (2.2.1) cryptate reported here is 3.927(1) Å; this value compares very well with the values reported for the two other dinuclear lanthanide complexes mentioned above [13–14].

The solid state structure of the monomeric praseodymium (2.2.1) cryptate [6] synthesised in acetonitrile is presented schematically in Figure 3. The metal ion achieves the same coordination number as in the dimeric cryptate, two hydroxyl groups being replaced by two acetonitrile molecules. The macrocyclic ligand again displays an approximate twofold symmetry and its conformational arrangement is similar to the geometry adopted by the (2.2.1) cryptand in the dimeric compound.

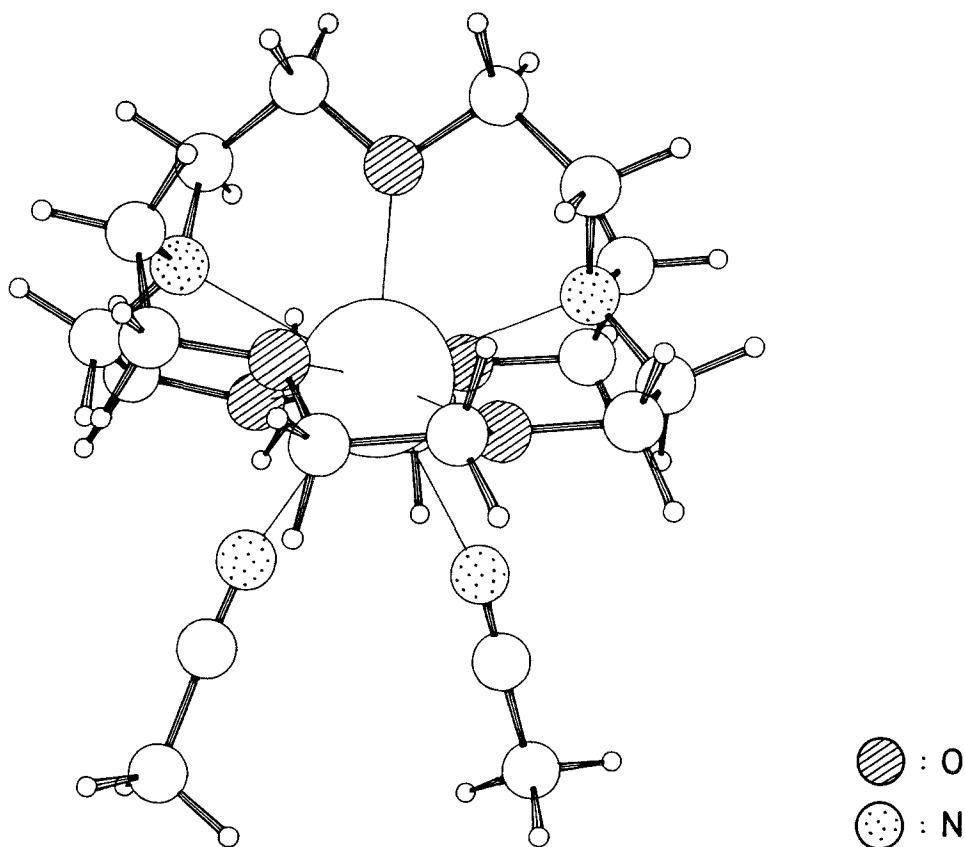


Fig. 3. Schematic presentation of the molecular structure of the monomeric praseodymium (2.2.1) cryptate solvated by two acetonitrile molecules [6]. The approximate C_2 axis is in the plane of the Figure and passes through the praseodymium ion and the oxygen atom of the monoxygen strand.

However, there is a significant difference between the two species: the metal cations are pulled out of the cryptate internal cavity by the two hydroxyl groups. In the monomeric complex, the lanthanide is located 0.13 Å above the mean plane defined by the four oxygen atoms of the 18-membered cycle of the cryptand while it lies 0.18 Å below this plane in the dimeric complex.

Finally, it is worth mentioning here that our structural analysis could account for the unusual affinity of the lanthanide cryptates for the hydroxide ion. According to Yee *et al.* [4], both the $\text{Eu}(2.2.1)^{3+}$ cryptate and the uncomplexed Eu^{3+} ion associate very strongly with the hydroxide ion. The crystallographic structures shown in Figures 1 and 3 clearly indicate that there is ample space available for the coordination of additional ligands around the encapsulated lanthanides and that hydroxylated complexes can be stabilized by the formation of polymers.

5.3. NMR STUDIES

The formation of at least two lanthanide (2.2.1) species in acetonitrile is easily demonstrated by proton NMR spectroscopy. The proton NMR spectrum of monomeric $\text{Pr}(2.2.1)$ cryptate displays eight peaks that are shifted from their diamagnetic position by the paramagnetism of the metal ion. The assignment of these peaks required [6] the synthesis of several partially deuterated derivatives of cryptand

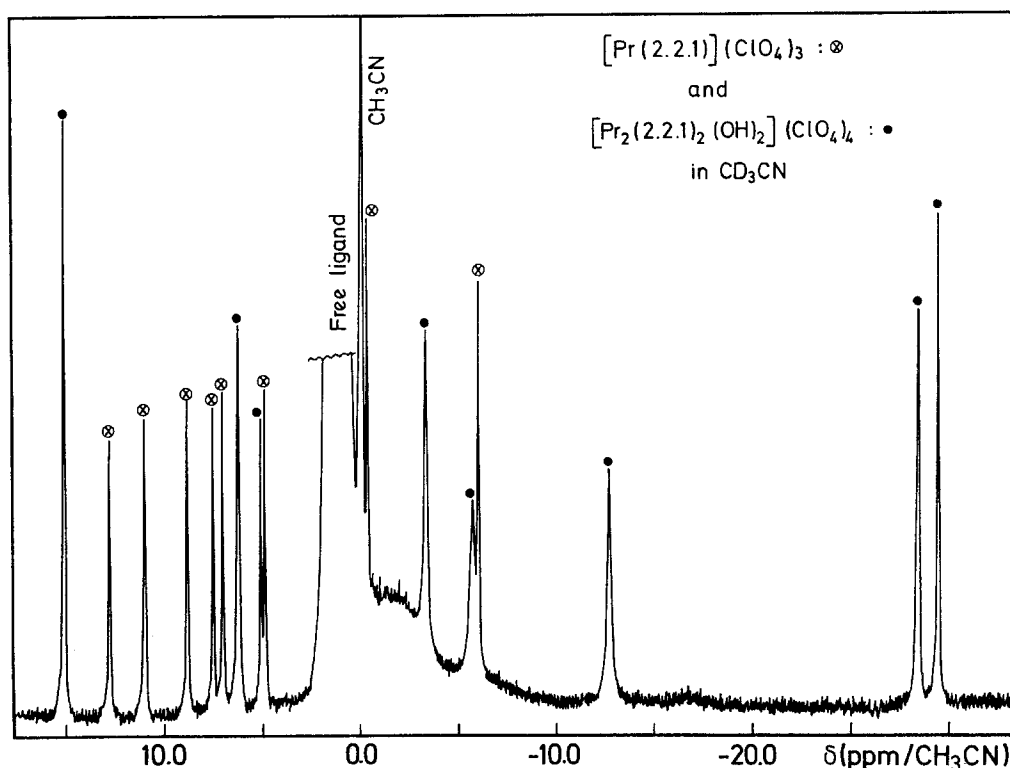


Fig. 4. 300 MHz proton NMR spectrum of an acetonitrile solution of the monomeric $\text{Pr}(2.2.1)$ complex containing an excess of cryptand (2.2.1).

(2.2.1). A quantitative analysis of the induced shifts indicated that the NMR spectrum of monomeric $\text{Pr}(2.2.1)^{3+}$ arises from metal-centered rearrangements that lead to eight distinct proton environments. The conformational changes occur without alteration of the geometrical configuration of the complex. As shown in Figure 4, the NMR spectrum shows 16 resonances if an excess of cryptand (2.2.1) is added to an acetonitrile solution of monomeric $\text{Pr}(2.2.1)$ perchlorate. The new peaks are tentatively attributed to the formation of the dimeric compound because the relative areas of the two sets of peaks depend upon the excess of ligand and because the crystals of the dimer were obtained under the same experimental conditions as used for recording the NMR spectra. However, a more quantitative analysis [15] of the solution conformation of the dimer was hampered by difficulties in interpreting the relative magnitude of the induced shifts. Indeed, the dimeric complex features two paramagnetic centers and the ligands seem to undergo intricate conformational changes.

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