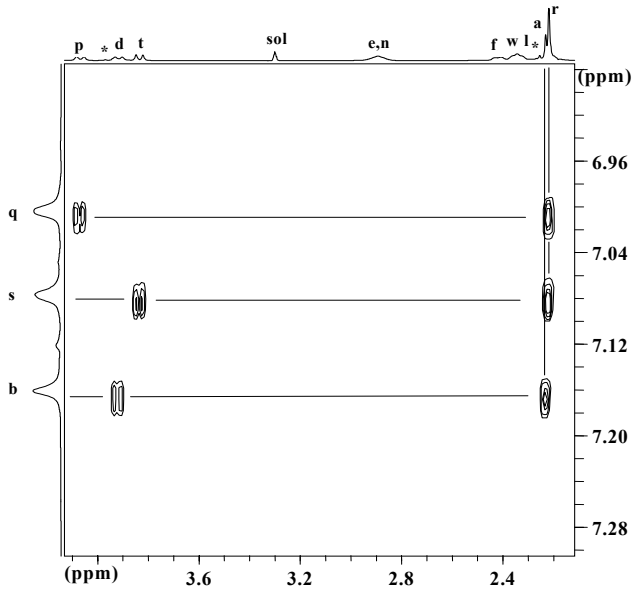
Assignment of NMR lines of the Lu(III) complex.

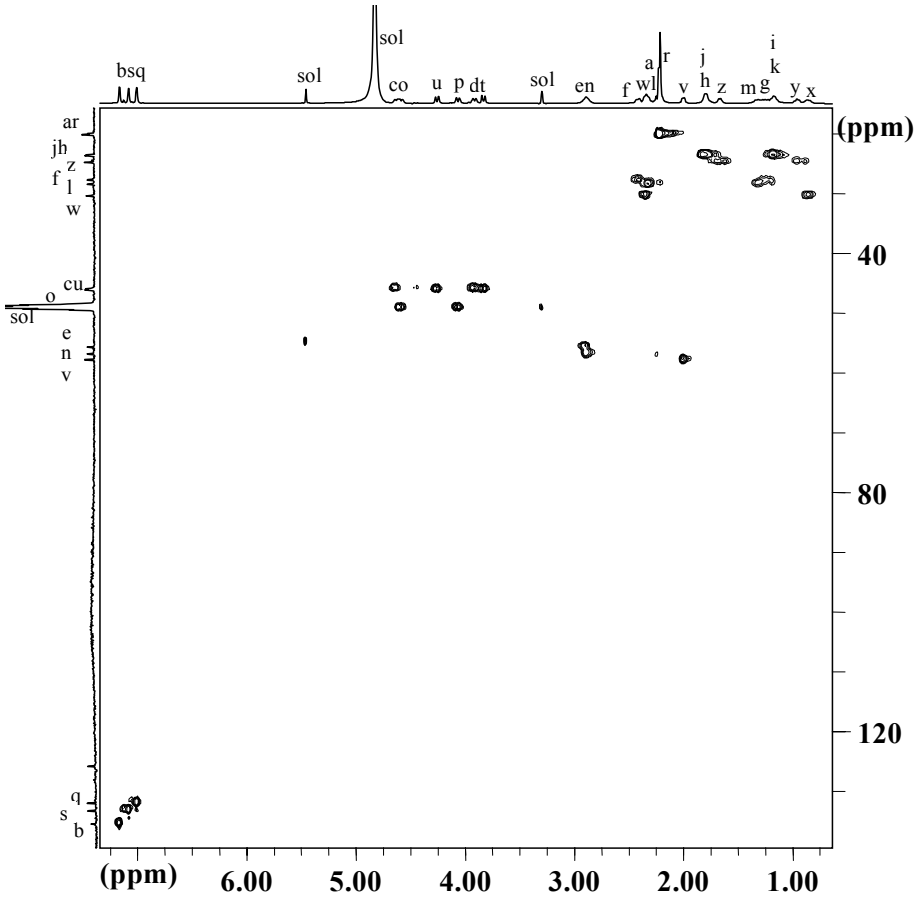
The analysis starts with the easily assigned signals of methyl groups **a** and **r** (Supplementary Fig. 1), that integrate to 3H and 6H, respectively, while all other signals integrate to 2H (see Scheme 1 for the labelling). The TOCSY spectrum (Fig. 3) allows to find the group of 10 correlated signals and group of 5 correlated signals, that have to correspond to two sets of cyclohexane protons: **e**+**f**+**g**+**h**+**i**+**j**+**k**+**l**+**m**+**n** and **v**+**w**+**x**+**y**+**z**, respectively. HMQC spectra (Supplementary Fig. 2) identify the ^{1}H NMR signals of pairs of geminal protons because each signal of given pair is correlated to the same ^{13}C NMR signal. These spectra also allow to find signals of cyclohexane C*H*NH protons that do not have geminal partner, i.e. signal **v** from the group of five TOCSY correlated signals and two signals **e**+**n** from the group of ten TOCSY correlated signals. Signal **a** is NOESY (Supplementary Fig. 1), ROESY (Supplementary Fig. 3) and COSY (Supplementary Fig. 4) correlated to signal of aromatic proton **b**, this in turn is ROESY and NOESY (Supplementary Fig. 1) correlated to both signals of the geminal pair **c**+**d**. Signal **b** exhibit one additional ROESY correlation; inspection of model structure of the complex (as well as X-ray crystal structure of Eu(III) complex, *vide infra*) points to close contact between aromatic proton **b** and equatorial proton **f**. Thus the above ROESY correlations identifies signal of proton **f**, while HMQC spectrum identifies its geminal partner i.e. axial proton **g**. Signal **g** exhibit COSY correlation (Supplementary Fig. 4) to one of the signals from the above assigned group of signals **e**+**n** (that is signal **e**). Signal **n** exhibit COSY correlation to a signal, that on the basis of Karplus relation has to be that of axial proton **m**, and the HMQC-found geminal partner of **m** has to be equatorial proton **l**. In the same way signal **v** is strongly COSY correlated to signal of axial proton **x**, and the HMQC-found geminal partner of **x** is equatorial proton **w**. Similarly, on the basis of Karplus relation that predicts large coupling constants between respective axial protons, signal that is COSY correlated to **x** correspond to axial proton **y**, while the geminal partner of **y** correspond to proton **z**. The remaining COSY crosspeaks corresponding to pairs of axial cyclohexane protons **m**, **k** and and **g**, **i** are more difficult to observe, since they are close to the diagonal and the signals **k** and **i** overlap. Fortunately, the COSY crosspeaks of the corresponding pairs of equatorial signals **f**, **h** and **j**, **l** are resolved. The overlapped signals of

equatorial protons **j** and **h** are, as expected, strongly COSY correlated to the overlapped signals of axial protons **i** and **k**. The overlapping of these signals is confirmed by integration.

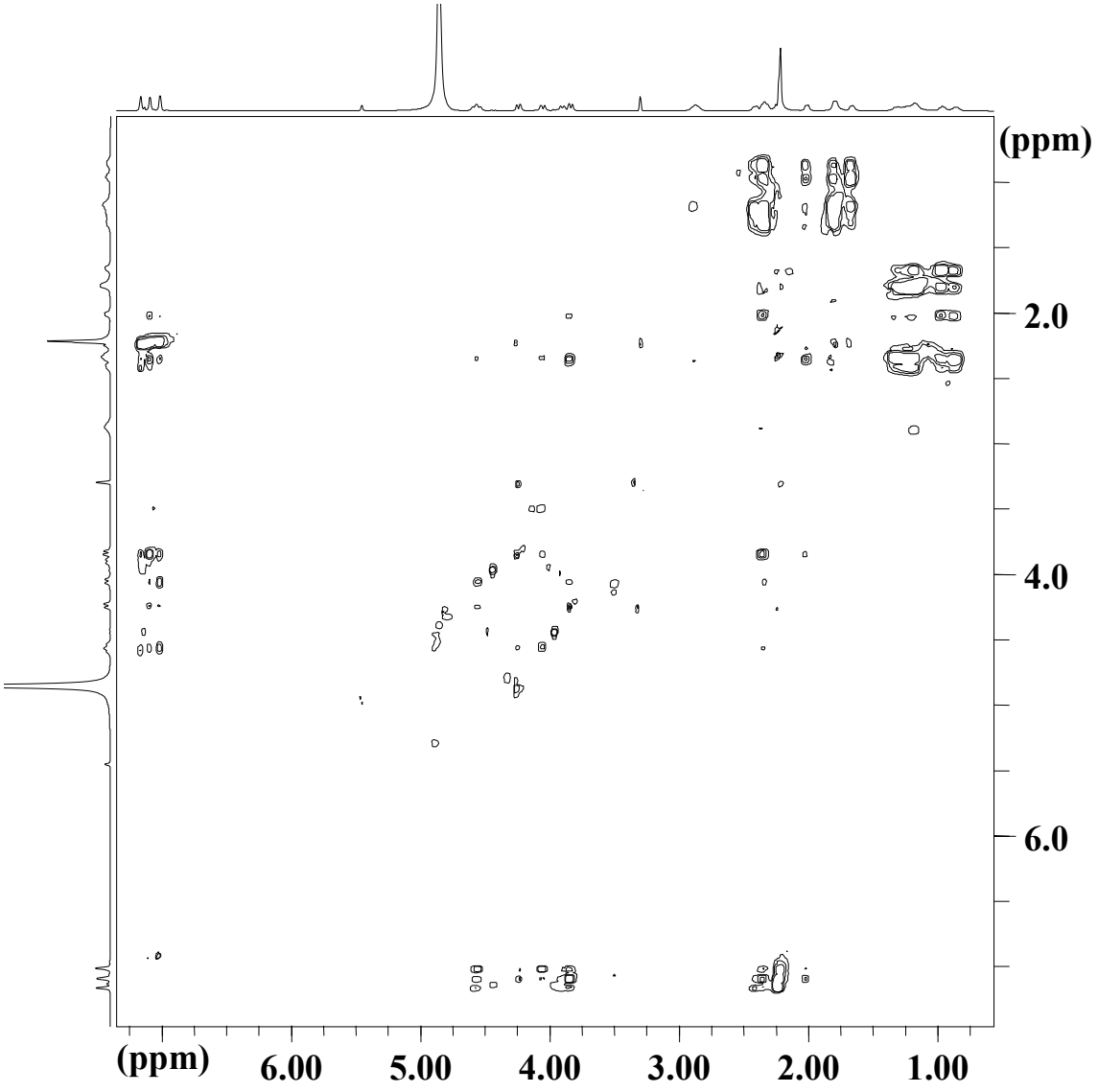
The methyl signal **r** is NOESY (Supplementary Fig. 1) and COSY correlated to the signals of two aromatic protons **q**+**s**. These in turn are ROESY correlated to four signals of methylene bridges, so the group of signals **o**+**p**+**t**+**u** can be identified. The ROESY spectrum also shows crosspeaks between two signals of the latter group and the already assigned signal of proton **v**. The stronger of these two crosspeaks identifies equatorial proton **t**, while the weaker the axial proton **u**, since the distance **v**-**t** is shorter than **v**-**u**. Additionally ROESY crosspeak corresponding to the close equatorial protons **w** and **t** is observed. Both signals **u** and **t** are ROESY correlated to signal of proton **s**, thus the remaining signal of aromatic proton has to correspond to signal **q**. Signal **q** is ROESY correlated to signals of the methylene protons **o** and **p**, that are in turn correlated to the already assigned signal of proton **l**. In this way chemical shifts of all protons can be assigned: δ (ppm) 0.86 **x**, 0.96 **y**, 1.18 **i**, **k**, 1.22 **g**, 1.30 **m**, 1.65 **z**, 1.79 **h**, **j**, 2.00 **v**, 2.21 **r**, 2.22 **a**, 2.33 **w**,**l**, 2.40 **f**, 2.87 **e**, **n**, 3.83 **t**, 3.90 **d**, 4.05 **p**, 4.23 **u**, 4.54 **o**, 4.57 **c**, 7.00 **q**, 7.08 **s**, 7.15 **b**. The above assignment is additionally confirmed by the observation of COSY correlation between aromatic signals **s** and **q**, ROESY correlation between signals **q**, **s** and **w**, as well as COSY and NOESY correlations between the signals of geminal protons and the remaining COSY correlations of the cyclohexane signals. The ^{1}H NMR assignment and HMQC spectra allow to identify the ^{13}C NMR signals of the respective carbon atoms: δ (ppm) 20.06 **a**, 20.25 **r**, 23.62 **h**, 23.76 **j**, 24.88 **y**, 27.81 **f**, 28.52 **l**, 30.45 **w**, 46.01 **c**, 46.15 **t**, 49.18 **o**, 55.72 **e**, 56.87 **n**, 57.84 **v**, 131.91 **q**, 133.22 **s**, 135.43 **b**.



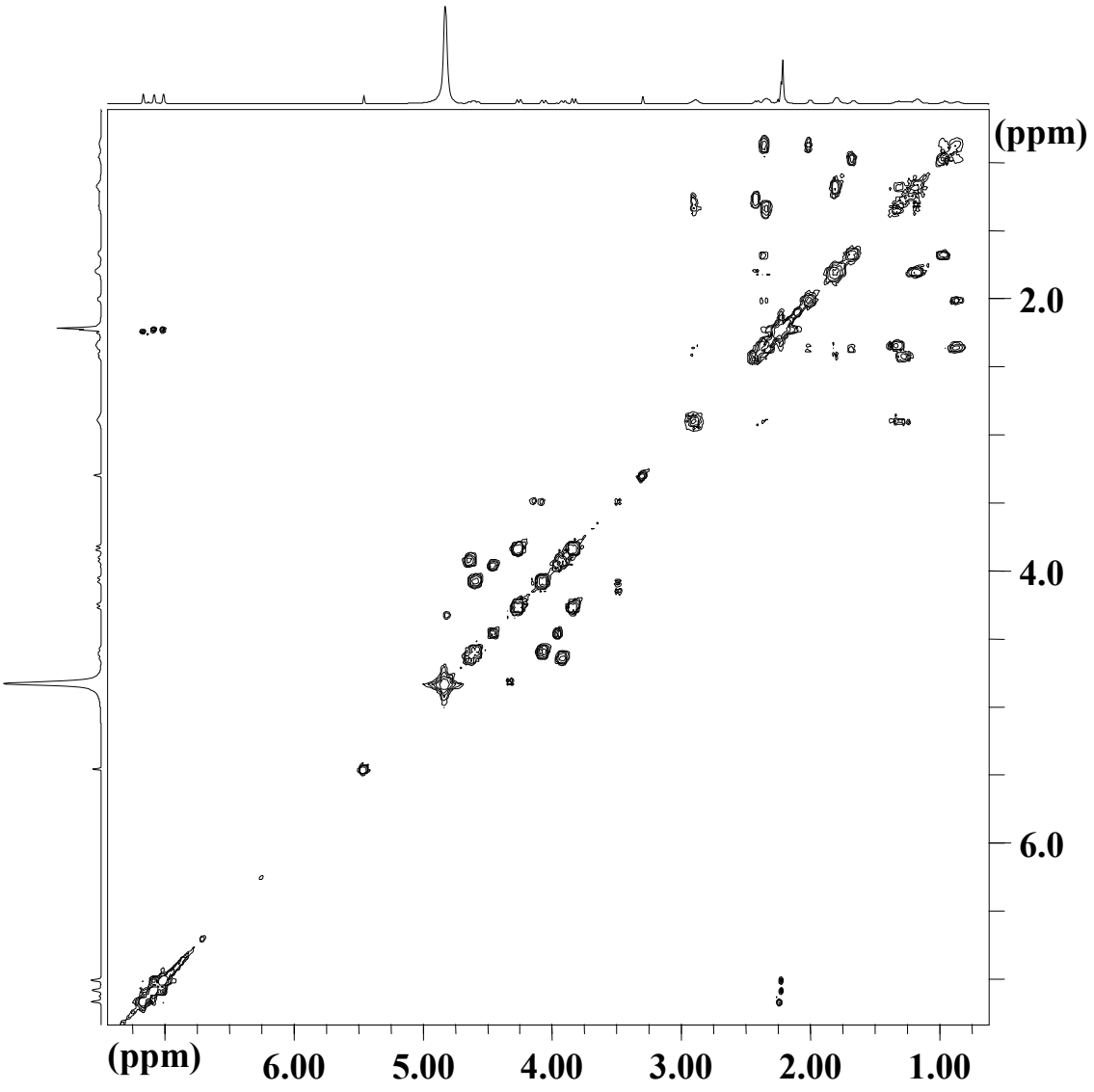
Supplementary Fig. 1 NOESY spectrum (fragment) of solution containing H_3L and 1.9 equivalents of $LuCl_3 \cdot 6H_2O$ (298 K, D_2O/CD_3OD 2:1 v/v), * denotes signals of uncomplexed macrocycle.



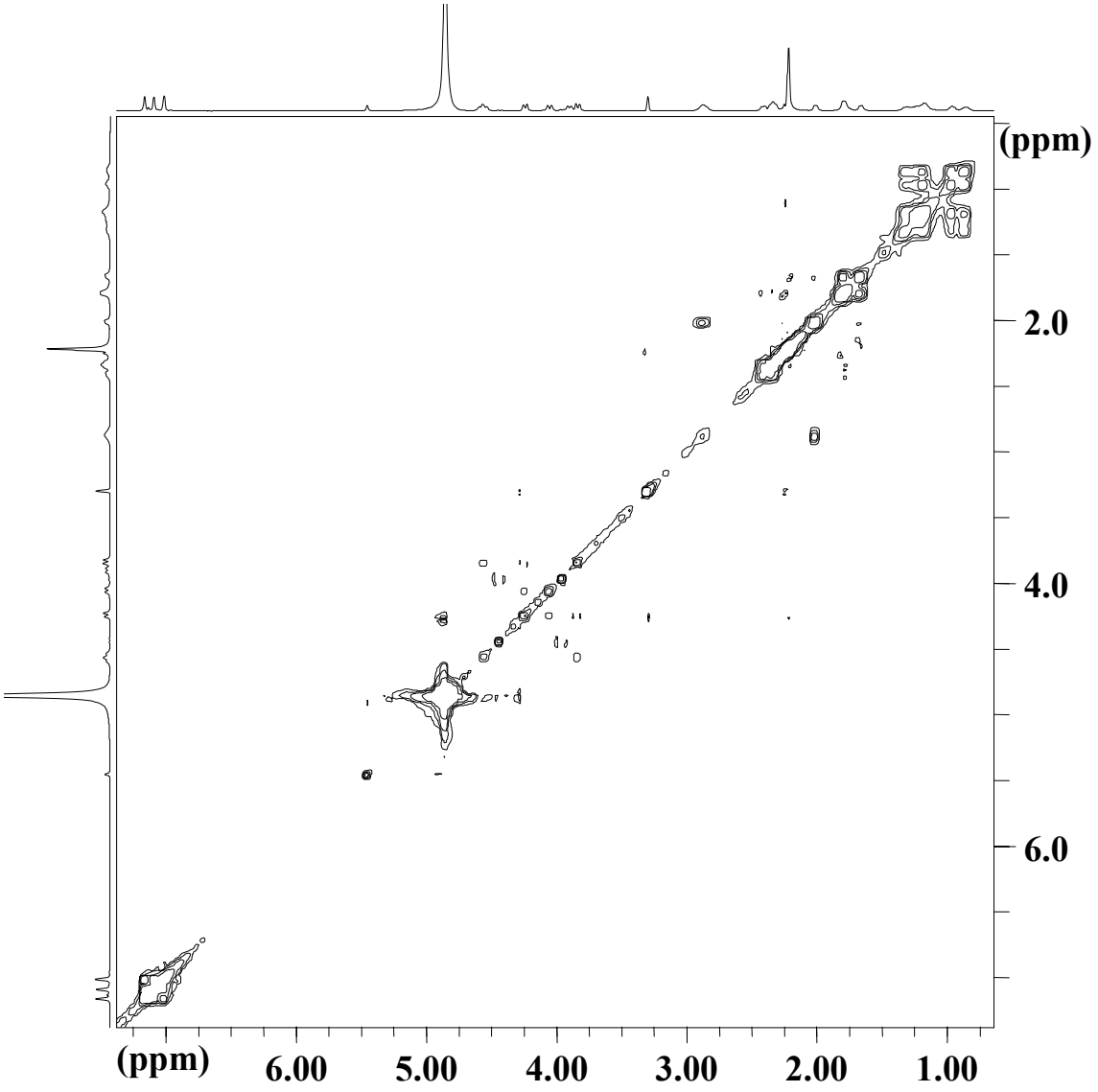
Supplementary Fig. 2 HMQC spectrum of solution containing H_3L and 1.9 equivalents of $LuCl_3 \cdot 6H_2O$ (298 K, D_2O/CD_3OD 2:1 v/v) , sol denotes residual solvent and CH_2Cl_2 signals.



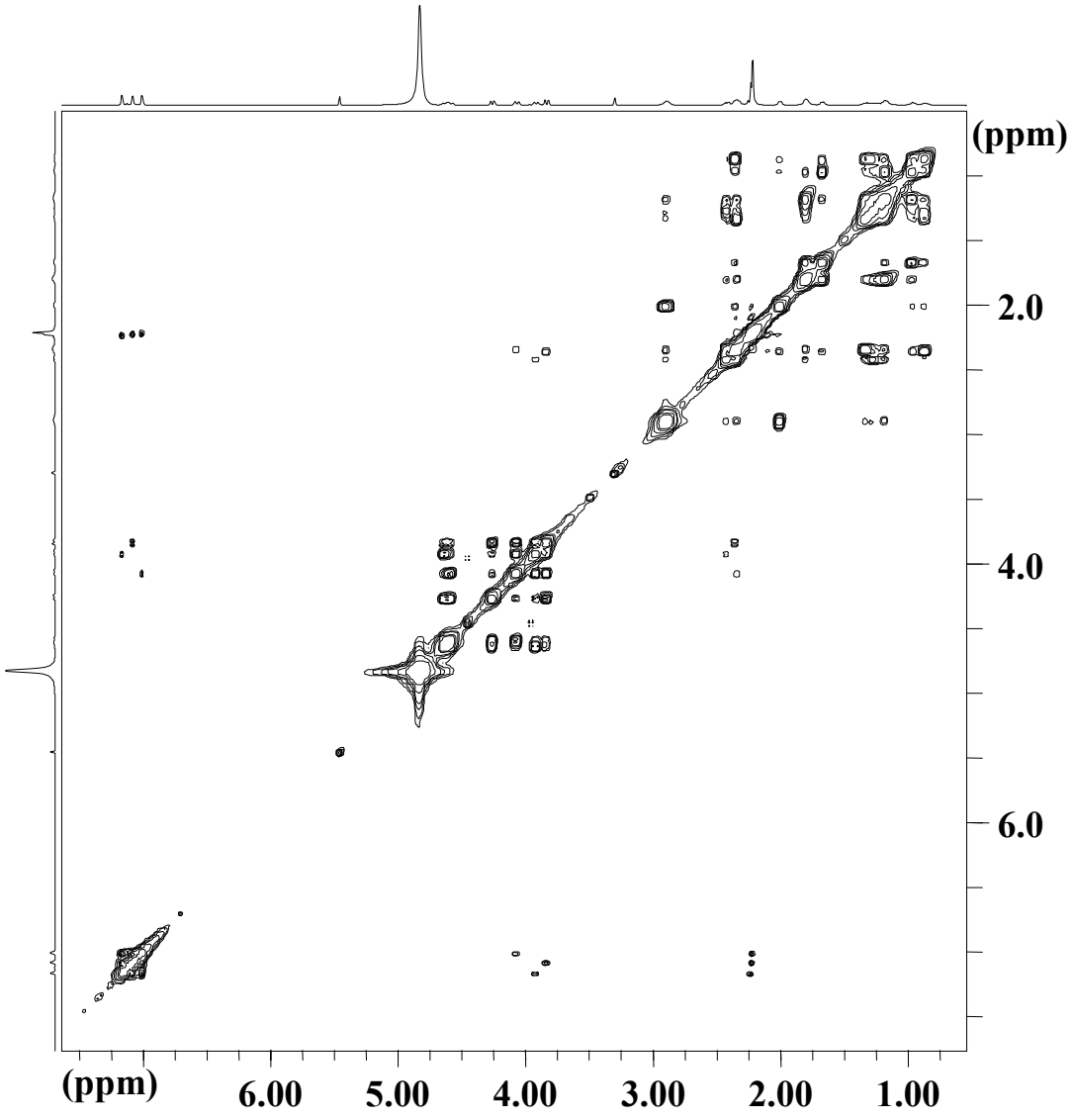
Supplementary Figure 3. ROESY spectrum (negative) of solution containing H_3L and 1.9 equivalents of $LuCl_3 \cdot 6H_2O$ (298 K, D_2O/CD_3OD 2:1 v/v).



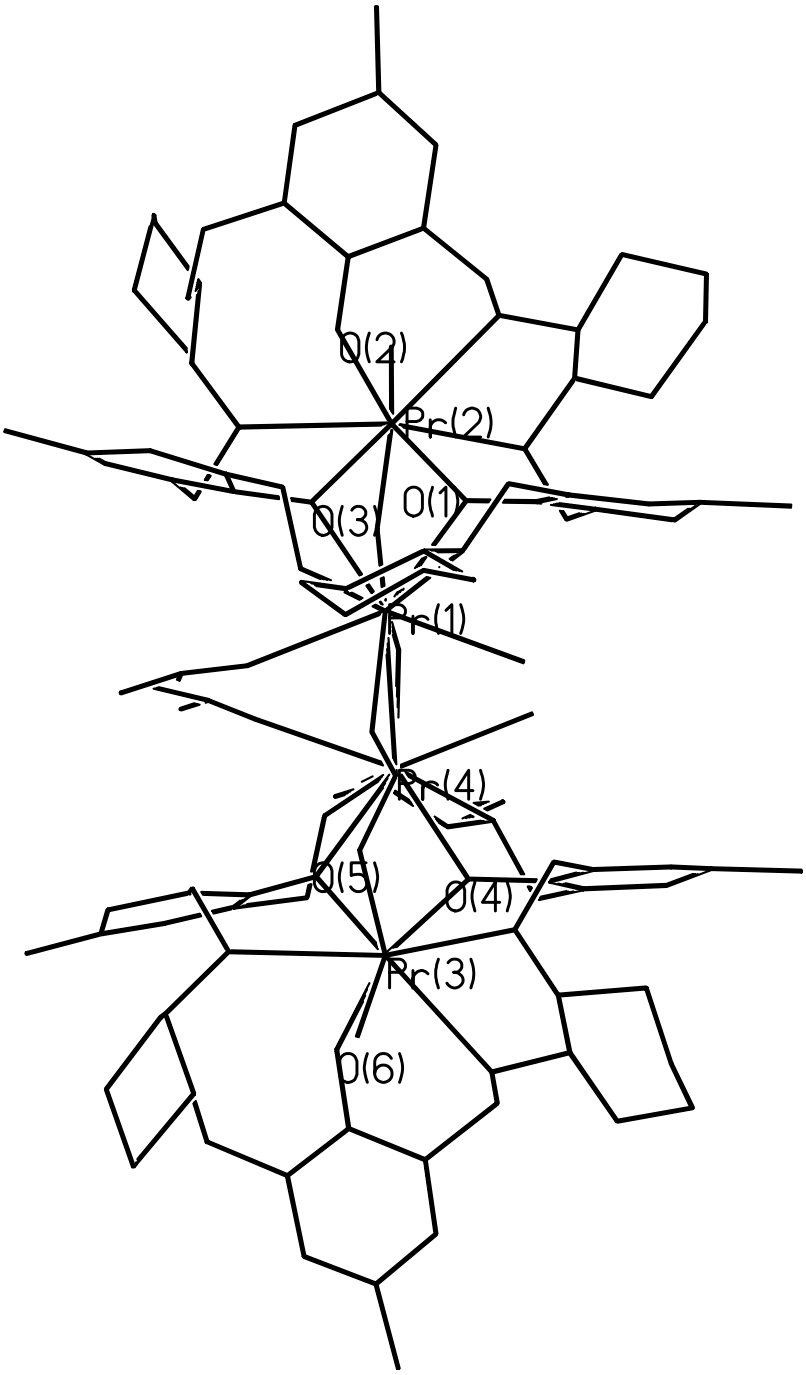
Supplementary Figure 4. COSY spectrum of solution containing H_3L and 1.9 equivalents of $LuCl_3 \cdot 6H_2O$ (298 K, D_2O/CD_3OD 2:1 v/v).



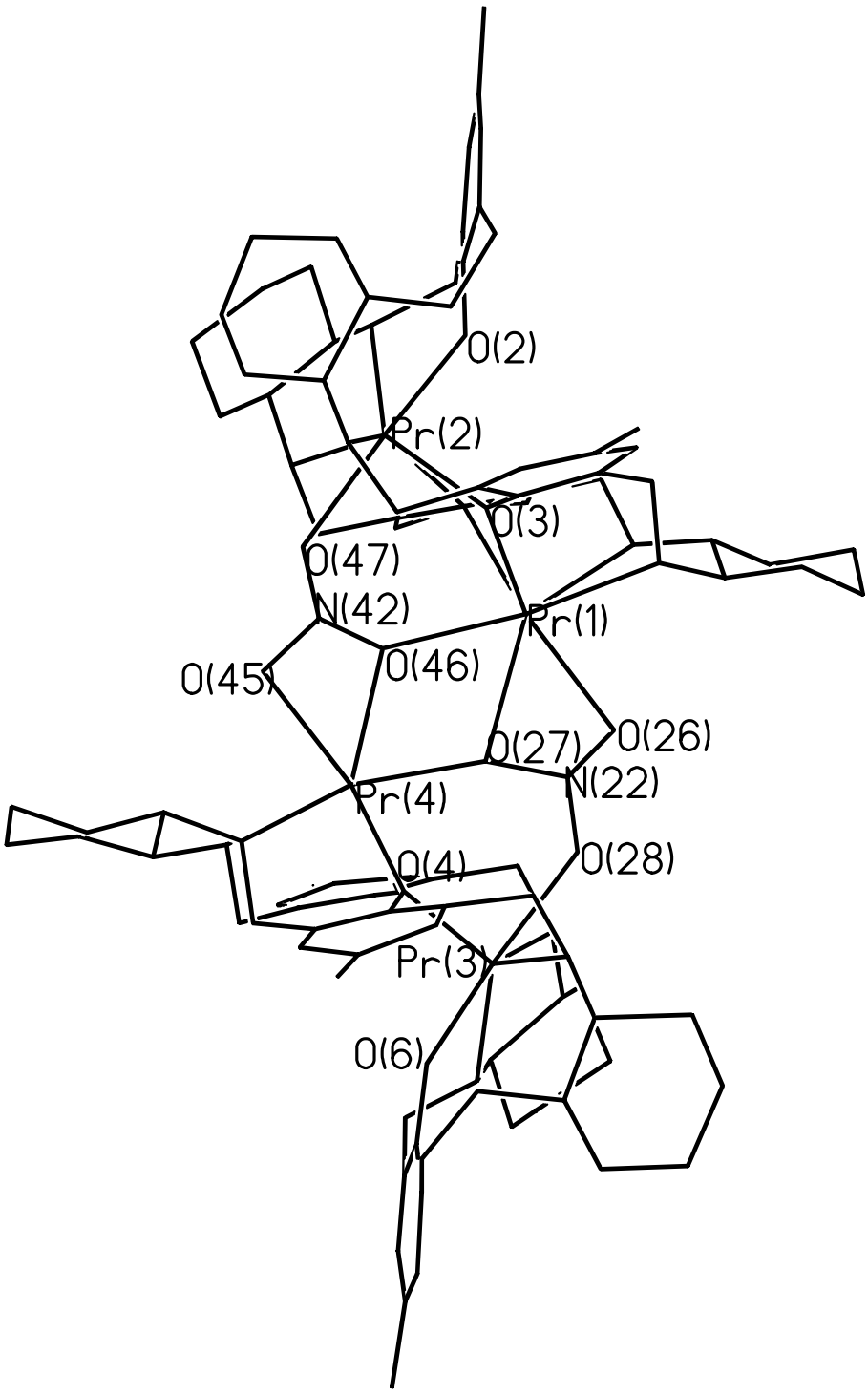
Supplementary Figure 5. ROESY spectrum (positive) of solution containing H_3L and 1.9 equivalents of $LuCl_3 \cdot 6H_2O$ (298 K, D_2O/CD_3OD 2:1 v/v).



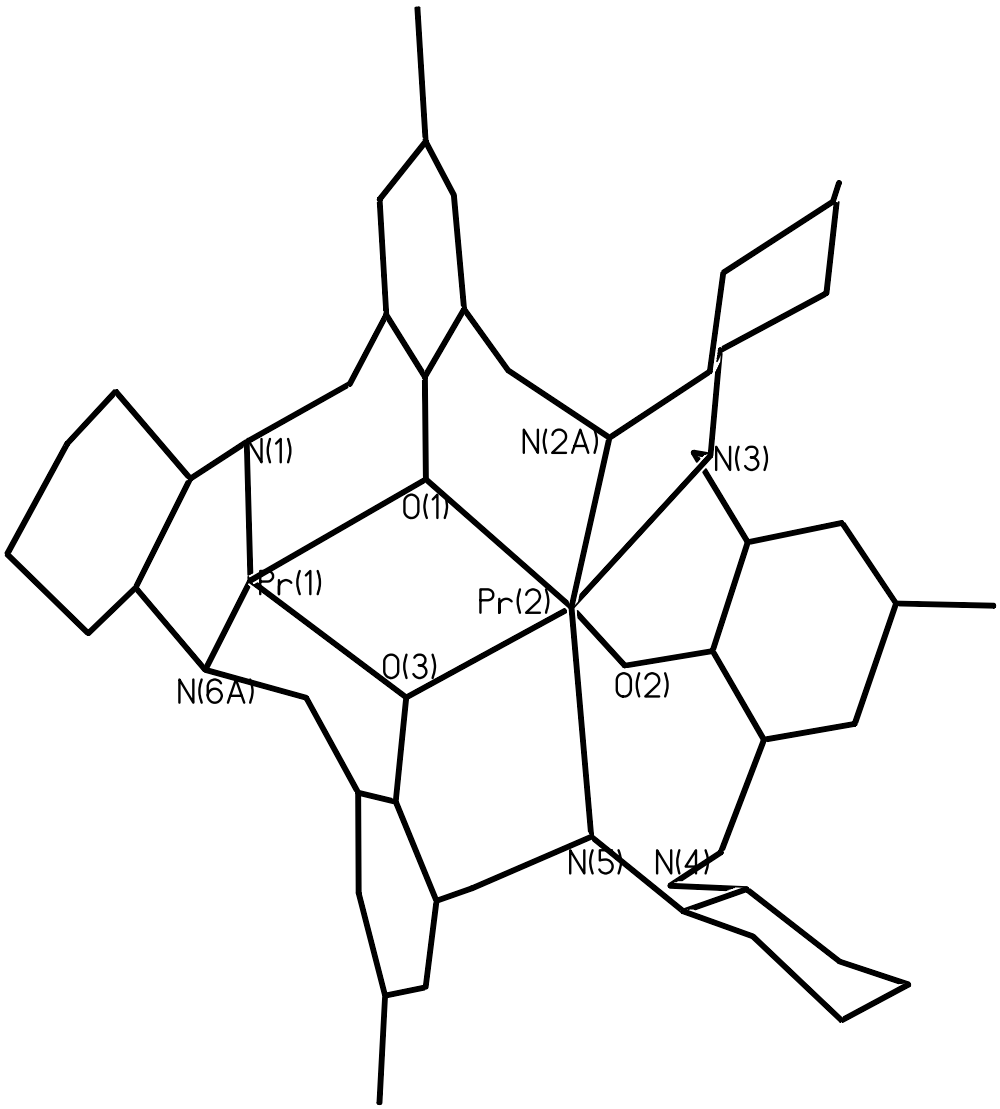
Supplementary Figure 6. NOESY spectrum (positive) of solution containing H_3L and 1.9 equivalents of $LuCl_3 \cdot 6H_2O$ (298 K, D_2O/CD_3OD 2:1 v/v).



Supplementary Figure 7. View of the $[Pr_2L(NO_3)_2(OH)_2]_2^{2-}$ complex anion.



Supplementary Figure 8. Side view of the $[Pr_2L(NO_3)_2(OH)_2]_2^{2-}$ complex anion. Axial ligands, except bridging nitrates, are omitted.



Supplementary Figure 9. View of the dinuclear macrocyclic subunit of the tetranuclear $[Pr_2L(NO_3)_2(OH)_2]_2^{2-}$ complex anion. Axial ligands are omitted.

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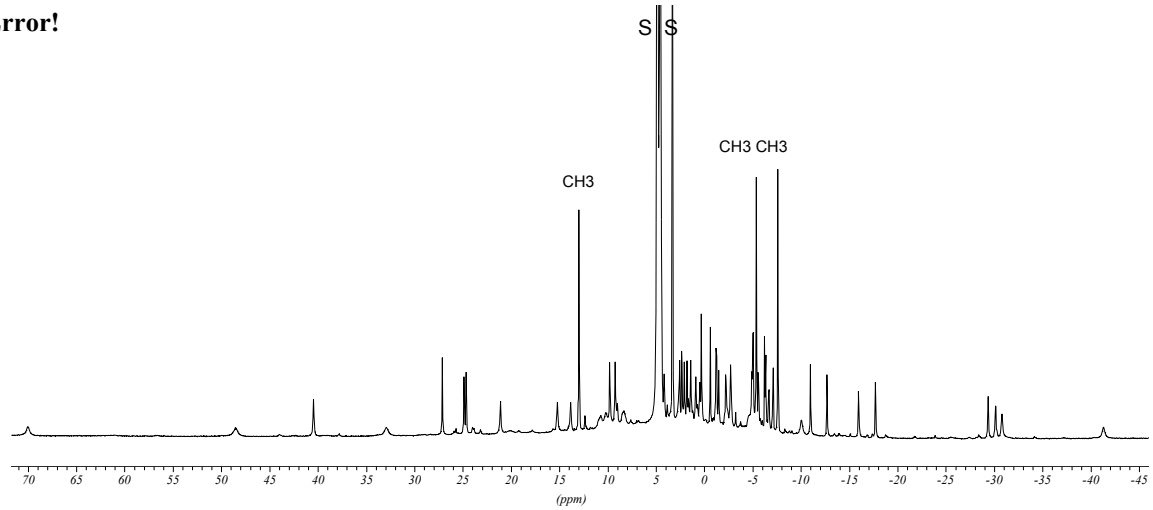

Supplementary Figure 10. ^{1}H NMR spectrum (298K) of CD_3OD/ D_2O (v/v 3:1) solution of $Na_3[Pr_2L(NO_3)_2(OH)_2]_2NO_3*5H_2O$ complex. s-solvent, CH3-methyl groups of the macrocycle.