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Lanthanide(III) Complexes of a Mono(methylphosphonate) Analogue of H₄dota: The Influence of Protonation of the Phosphonate Moiety on the TSAP/SAP Isomer Ratio and the Water Exchange Rate

Jakub Rudovský,^[a] Petr Cígler,^[a] Jan Kotek,^[a] Petr Hermann,^[a] Pavel Vojtíšek,^[a]
Ivan Lukeš,^{*[a]} Joop A. Peters,^{*[b]} Luce Vander Elst,^[c] and Robert N. Muller^[c]

^[a] *Department of Inorganic Chemistry, Charles University, Hlavova 2030, 128 40 Prague 2, Czech Republic. Fax: (+420)22195-1253 E-mail: lukeš@natur.cuni.cz*

^[b] *Laboratory of Applied Organic Chemistry and Catalysis, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands. Fax: (+31)152-784-289 E-mail: J.A.Peters@tmw.tudelft.nl*

^[c] *NMR Laboratory, Department of Organic Chemistry, University of Mons-Hainaut, Avenue du champ de Mars 24, B-7000 Mons, Belgium*

Table S1
ES/MS data of selected Ln^{III} complexes of H₅do3aP

complex	negative mode	positive mode	calculated
[La(do3aP)] ²⁻	577	575	576
[Nd(do3aP)] ²⁻	580	582	582
[Eu(do3aP)] ²⁻	589	590	589
[Tb(do3aP)] ²⁻	595	597	596
[Dy(do3aP)] ²⁻	599	601	600
[Lu(do3aP)] ²⁻	611	613	612

Figure S1A

^1H NMR spectrum of $[\text{Nd}(\text{H}_2\text{O})(\text{do3aP})]^{2-}$ (pH 7, 25 °C)

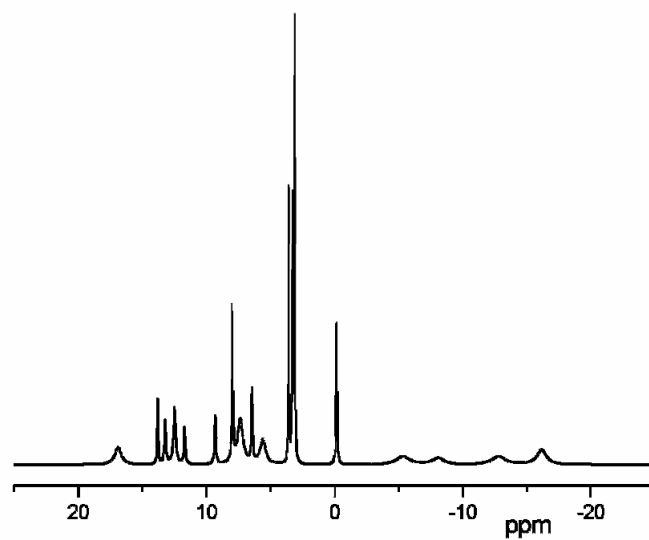


Figure S1B

^1H NMR spectrum of $[\text{Eu}(\text{H}_2\text{O})(\text{do3aP})]^{2-}$ (pH 7, 25 °C)

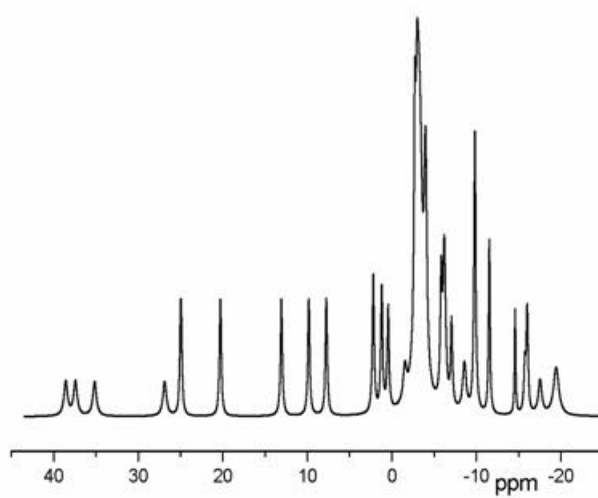


Figure S1C

^1H NMR spectrum of $[\text{Yb}(\text{H}_2\text{O})(\text{do3aP})]^{2-}$ (pH 7, 25 °C)

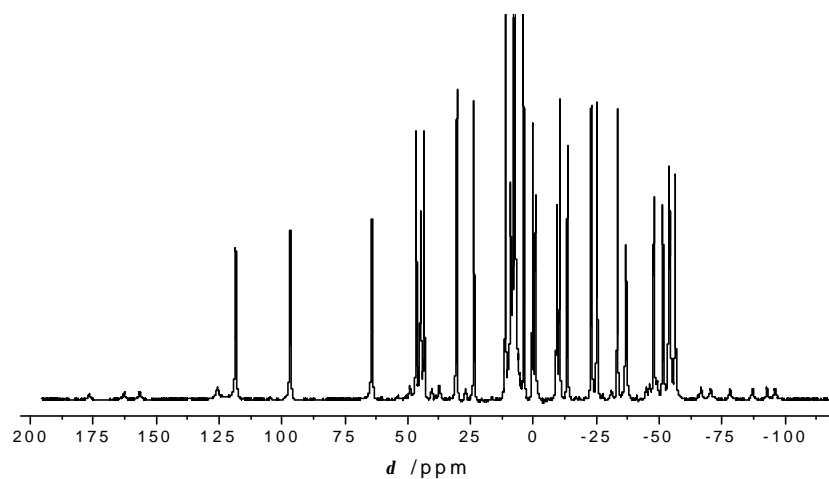


Figure S1D

The H4 part of ^1H EXSY spectrum of $[\text{Eu}(\text{H}_2\text{O})(\text{do3aP})]^{2-}$ (pH 7, 25 °C)

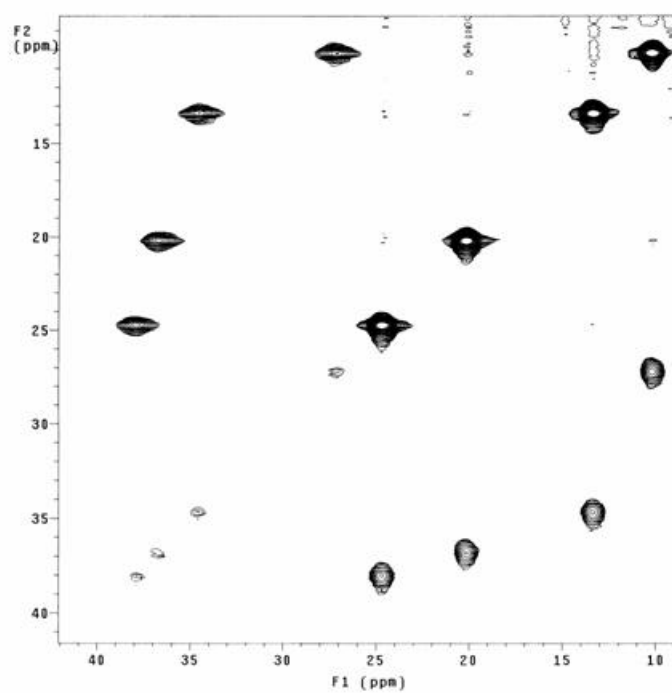


Figure S2

Linearization of ^{31}P NMR lanthanide induced shifts of $[\text{Ln}(\text{do3aP})(\text{H}_2\text{O})]^{2-}$ (pH = 7, 25 °C) for isomer SAP.

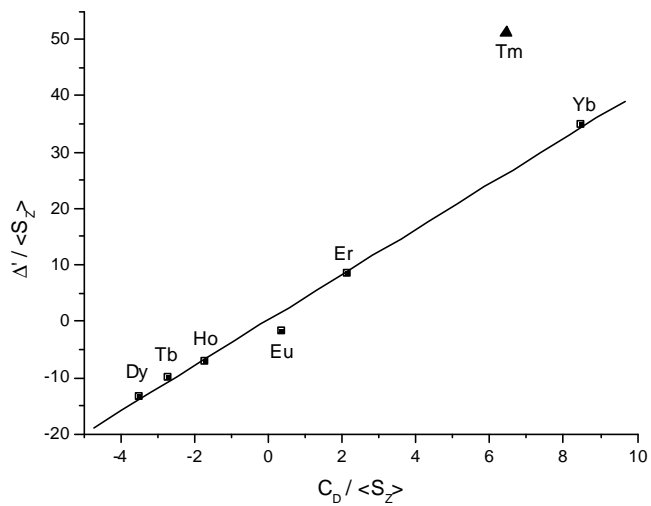


Figure S3

Linearization of ^{31}P NMR lanthanide induced shifts of $[\text{Ln}(\text{do3aP})(\text{H}_2\text{O})]^{2-}$ (pH = 7, 25 °C) for isomer TSAP.

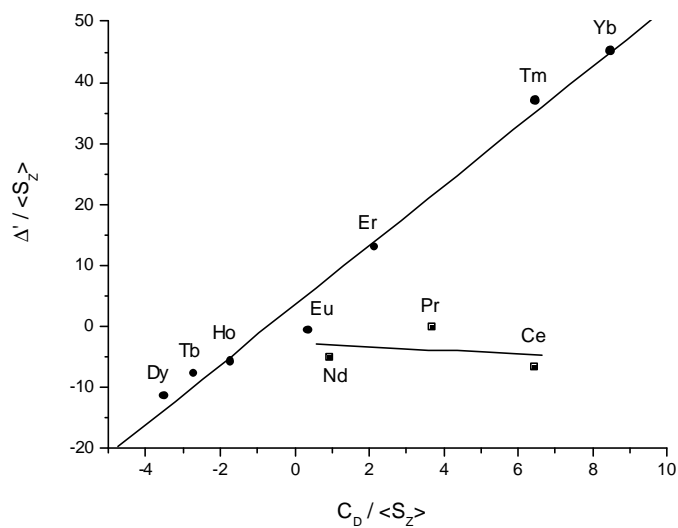
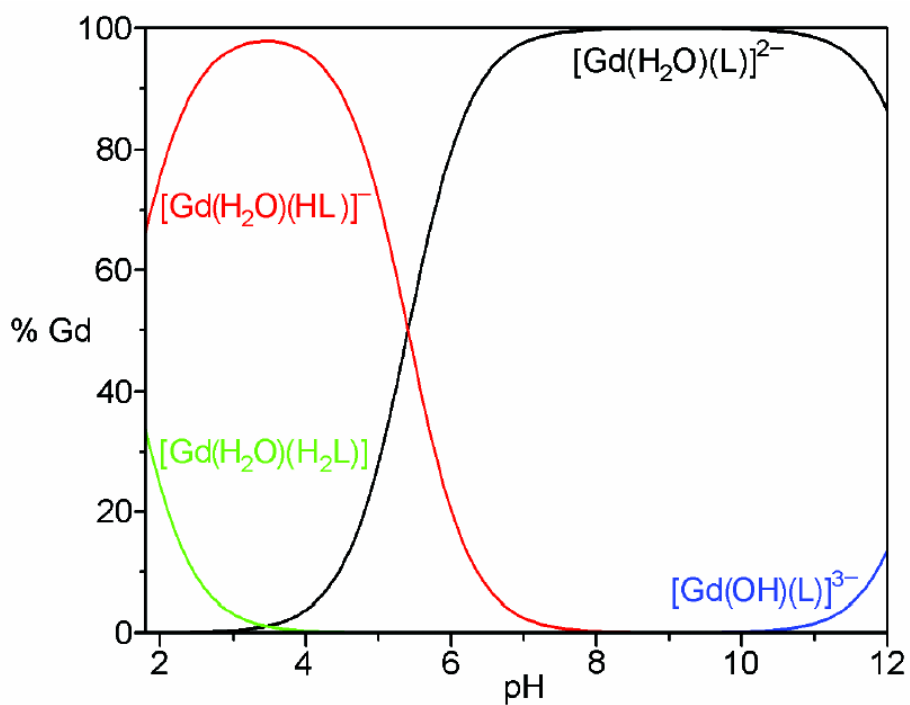


Figure S4

Distribution diagram of system $\text{H}^+ - [\text{Gd}(\text{H}_2\text{O})(\text{do3aP})]^{2-}$ (calculated from data obtained from potentiometric titration of $[\text{Gd}(\text{H}_2\text{O})(\text{do3aP})]^{2-}$ complex; $I = 0.1 \text{ M NMe}_4\text{Cl}$, $25 \text{ }^\circ\text{C}$).



Equations:

// Equations used for the Fit of NMRD and 17O T2 data in Scientist format

IndVars: T,B

DepVars: R2o,R1h

Params:delta,Hm,tm0,Hr,tr0,Hv,tv0,acc,ro,rh,n,a,trsf,rsf,Hmss,tm0ss,n1

// Parameters and variables used

// T - temperature at °K

// B - used field at MHz

// R2o - 17O transversal relaxivity at ms⁻¹ (unreduced)

// R1h- 1H longitudinal relaxivity at ms⁻¹/mmol (reduced)

// delta - Δ2 trace of ZFS matrix

// tm0 - water residence time at 298°K

// Hm - water exchange free energy

// tr0 - rotation corelation time at 298°K

// Hr -rotation free energy

// tv0 - coralation time of modulation of ZFS matrix ???

// Hv - modulation of ZFS free energy

// acc - hyperfine Gd-O coupling constant A/hbar

// ro - Gd-O distance at m

// rh - Gh-H distance at m

// n number of water molecule coordinated at Gd

// conc - milimolar concentration for unreduced 17O data

// s - multiplicity of Gd - fixed to 3.5

// a - shortest distance form outer sphere to gadolinium - for OS contribution

// D - diffusion coeeficient at 298°K

// n1 - number of water molecules at second sphere

// rsf - Gd-SF distance

// trsf - rotation corelation time of second sphere

// Hmss - water exchange free energy for second sphere contribution

// tm0ss - water residence time at 298°K for second sphere

// Physical constants implicitly used

// univ - universal gass constant R = 8.31441

// μB - Bohr magneton μB = 9.274e-24

// μ0 - vaccum magnetic susceptibilty μ0 = 4πe-7

// h - Planck constant h = 6.62617e-34

// hbar = 1.0546e-34

// NA - Avogadro constant NA = 6.023e23

// k - Boltzman constant k = 1.38066e-23

// γo - gyromagnetic ratio of 17O γo = -3.626e7

// γh - gyromagnetic ration of 1H γh = 2.675e8

// gs - elektrononic gyromagnetic ratio gs = 1.75977e11

// Notes

// magnetic field is in Larmor fraquencies - omegas (Wo a WS) are calculated as 2*pi*B*ratio of gyros

// **BMS equations :**

// **Definitions of constants**

s=3.5


```

univ=8.31441
sz=31.5
// Definition of omegas
wh=6.28e6*B
ws=658.21*wh
wo=-0.133557*wh
// Eyring equations
tm=((tm0^(-1))*T/298.15)*exp((Hm/univ)*(0.003354-(1/T)))^(-1)
tmss=((tm0ss^(-1))*T/298.15)*exp((Hmss/univ)*(0.003354-(1/T)))^(-1)
tr=((tr0^(-1))*T/298.15)*exp((Hr/univ)*(0.003354-(1/T)))^(-1)
tv=((tv0^(-1))*T/298.15)*exp((Hv/univ)*(0.003354-(1/T)))^(-1)
// Electronic relaxation
T1e=((1/25)*delta*tv*(4*s^2+4*s-3)*((1/(1+ws^2*tv^2))+4/(1+4*ws^2*tv^2)))^(-1)
T2e=((0.02*(4*s^2+4*s-3)*tv*delta*(3+(5/(1+(ws^2*tv^2)))+(2/(1+(4*ws^2*tv^2))))))^(-1)
tc1=(T1e^(-1)+tr^(-1)+tm^(-1))^(-1)
tc2=(T2e^(-1)+tr^(-1)+tm^(-1))^(-1)
te1=(T1e^(-1)+tm^(-1))^(-1)
te2=(T2e^(-1)+tm^(-1))^(-1)
// R2 scalar - contact contribution for 17O
cont=(1/3)*s*(s+1)*acc^2*(te1+(te2/(1+ws^2*te2^2)))
// R2 dipolar - pseudocontact contribution for 17O
dip1=((1/15)*4.535671e-45*s*(s+1))/(ro^6)
dip2=4*tc1
dip3=(13*tc2)/(1+ws^2*tc2^2)
dip4=(3*tc1)/(1+wo^2*tc1^2)
dip=dip1*(dip2+dip3+dip4)
// R2 dipolar Curie contribution for 17O
dip7=(1/5)*(wo^2*7.397e-107*7.94^4)/(9*1.9063324e-46*T^2*ro^6)
dip8=4*tr+(3*tr)/(1+wo^2*tr^2)
cur=dip7*dip8
// Total dipolar contribution to R2 of 17O
diptot=dip+cur
// Total R2 relaxation
T2m=(cont+diptot)^(-1)
// Radial frequency difference of bound and free water at rad/s
dwm=sz*9.274e-24/(3*1.38066e-23*T)*acc*(B*1E6*6.28/2.675E8)
// Overall reduced T2 relaxation of 17O
num=(T2m^(-2))+T2m*tm^(-1)+dwm^2
denom=(tm^(-1)+T2m^(-1))^2+dwm^2
scam=num/denom
pm=n*1e-3/55.56
R2o=pm*scam/tm
// R1 dipolar - pseudocontact contribution for 1H
COST2=5.16963e-43/rh^6
R1DIP=(COST2*((7*TC2/(1+WS^2*TC2^2)))+(3*TC1/(1+Wh^2*TC1^2))))
// Total inner sphere millimolar contribution to 1H relaxivity
T1M=(R1DIP)^(-1)
R1IN=(N*1E-3/55.6)/(T1M+TM)
// Calculus for diffusion coefficient according to J.C.Hindman
B1=3.118150E-04
B2=5.062560E+03
B3=1.547920E+02
B4=1.629310E+03
D=(1E-4)/((B1*EXP(B2/T))+(B3*EXP(B4/T)))
// Freed model of outer sphere contribution to 1H relaxivity
TAU=A^2/D

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// Spectral density function J(i) for proton spins
Al=TAU/T1e
Cl=[0,1]*wh*tau
z2l=ai+ci
Jl=RE((1+0.25*(z2l^0.5))/(1+z2l^0.5+(4/9)*z2l+(1/9)*(z2l^1.5)))
// Spectral density function J(s) for gadolinium electron states
AS=TAU/T2e
CS=[0,1]*ws*tau
z2S=aS+cS
JS=RE((1+0.25*(z2S^0.5))/(1+z2S^0.5+(4/9)*z2S+(1/9)*(z2S^1.5)))
// Calculation of outer sphere contribution to 1H relaxivity according to Freeds model
COST3=3.68e-20*S*(S+1)
R1OS=(COST3/(A*D))*((3*Jl)+(7*JS))
// Aime's and Bote's second sphere contribution to 1H R1 relaxivity; only dipolar R1
contribution
TC1SF=(T1E^(-1)+TRSF^(-1))^(-1)
TC2SF=(T2E^(-1)+TRSF^(-1))^(-1)
COST2SF=(5.16963e-43/RSF^6)
R1DIPSF=(COST2SF*((7*TC2SF/(1+WS^2*TC2SF^2)))+(3*TC1SF/(1+Wh^2*TC1SF^2))))
T1MSF=(R1DIPSF)^(-1)
R1SF=(N1*1e-3/55.6)/(T1MSF+tmss)
// Overall R1 proton relaxivity
R1h=R1IN+R1OS+R1SF

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