Electronic Supplementary Information

Iodosylbenzene and Iodylbenzene Adducts of Cerium(IV) Complexes Bearing Chelating Oxygen Ligands

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Experimental

General Considerations

All manipulations were carried out under nitrogen by standard Schlenk techniques. Solvents were purified by standard procedures and distilled before usage. NMR spectrum were recorded on a Bruker ARX 400 spectrometer operating at 400 and 162 MHz for ^{1}H and ^{31}P, respectively. Chemical shifts (δ, ppm) were reported with reference to $SiMe_4$ (^{1}H), $CF_3C_6H_5$ (^{19}F) and H_3PO_4 (^{31}P), respectively. Gas chromatograms were obtained on a HP6850 Chromatograph equipped with a FID detector. Elemental analyses were performed by Medac Ltd, Surrey, UK. The compounds $[(L_{OEt})_2Ce^{IV}Cl_2]$[1], $[Ce^{IV}_2(\mu\text{-}O)\{N(Pr^i_2PO)_2\}_4Cl_2]$[2], PhIO[3], and $PhIO_2$[4] were prepared according to literature methods. All other reagents were purchased from standard commerical sources and used without further purification.

Synthesis of $[(L_{OEt})_2Ce^{IV}\{OI(Cl)Ph\}_2]$ (1)

To a solution of $[(L_{OEt})_2CeCl_2]$ (30 mg, 0.024 mmol) in MeCN (5 mL) was added PhIO (11 mg, 0.05 mmol), and the mixture was stirred at room temperature until all the PhIO was dissolved (ca. 10 min). The solvent was removed *in vacuo*, and the product was extracted with 5 mL of CH_2Cl_2/hexane (v/v 1:3). Slow evaporation of the solution gave single orange crystals suitable for X-ray structure determination. Yield: 36.3 mg, 90%. ^{1}H NMR (400 MHz, CD_3CN, 25 ^{o}C) δ 1.22 (t, J = 7.2 Hz, 36H, CH_3), 4.09 (m, 24H, CH_2), 5.06 (s, 10H, Cp), 7.69 (m, 2H, H_p of Ph), 7.71 – 7.76 (m, 4H, H_m of Ph), 8.22 (d, J = 4.8 Hz, 4H_o of Ph). ^{31}P $\{^{1}H\}$ NMR (162 MHz, CD_3CN, 25 ^{o}C): δ 117.4 (s). Anal. Calcd for $C_{46}H_{80}CeCl_2Co_2I_2O_{20}P_6 \cdot CH_2Cl_2$: C, 31.25; H, 4.57. Found: C, 31.91; H, 4.56.

Reaction of $[(L_{OEt})_2CeCl_2]$ with 1 equivalent of PhIO

To a solution of $[(L_{OEt})_2CeCl_2]$ (30 mg, 0.024 mmol) in MeCN (5 mL) was added ca. 1

equivalent of PhIO (5.5 mg, 0.025 mmol), and the mixture was stirred at room temperature until all the PhIO was dissolved (ca. 10 min). The solvent was removed *in vacuo*, and the product was extracted with 5 mL of CH_2Cl_2/hexane (v/v 1:3). Slow evaporation of the solution gave single orange crystals that were characterized as **1** by NMR spectroscopy and X-ray diffraction. Yield: 15 mg, 38%.

Synthesis of $[(L_{OEt})_2Ce^{IV}\{OI(OTs)Ph\}_2]$

To a solution of $[(L_{OEt})_2Ce(OTs)_2]$ (30 mg, 0.019 mmol) in MeCN (5 mL) was added ca. 2 equivalents of PhIO (8.50 mg, 0.040 mmol), and the mixture was stirred at room temperature until all the PhIO were dissolved (ca. 30 min). The solvent was removed in *vacuo* and the residue was extracted with CH_2Cl_2/THF/hexane (20 mL, v/v 1:1:1). Slow evaporation of the solution gave orange crystals. Yield: 34.2 mg, 89%. ^{1}H NMR (400MHz, CD_3CN, 25 ^{o}C): δ 1.17 (t, J = 6.8 Hz, 36H,CH_3), δ 2.34 (s, 6H,CH_3) 4.04 (m, 24H, CH_2), 5.10 (s, 10H, Cp), 7.15 – 7.18 (m, 6H_m & H_p, Ph), 7.37 – 7.41 (m, 4H_o, Ph), 7.70 (dd, 8H, Ph, OTs) . ^{31}P {^{1}H} NMR (162 MHz, CD_3CN, 25^{o}C): δ 120.1 (s). IR (KBr, cm^{-1}): 1139 [ν(S-O)]. Anal. Calcd for $C_{60}H_{94}CeCo_2I_2O_{26}P_6S_2$: C, 36.16; H, 4.75. Found: C, 35.09 ; H, 4.77.

Synthesis of $[(L_{OEt})_2Ce^{IV}\{OI(OTf)Ph\}_2]$

To a solution of $[(L_{OEt})_2Ce(OTf)_2]$ (30 mg, 0.020 mmol) in MeCN (5 mL) was added ca. 2 equivalents of PhIO (8.74 mg, 0.040 mmol), and the mixture was stirred at room temperature until all the PhIO were dissolved (ca. 30 min). The solvent was removed in *vacuo* and the residue was extracted with CH_2Cl_2/THF/hexane (20 mL, v/v 1:1:1). Slow evaporation of the solution gave orange crystals. Yield: 31.7 mg, 82%. ^{1}H NMR (400MHz, CD_3CN, 25 ^{o}C): δ 1.23 (t, J = 6.8 Hz, 36H, CH_3), 4.06 (m, 24H, CH_2), 5.16 (s, 10H, Cp), 7.18 (t, J = 8.0 Hz, 4H_m, Ph), 7.39 (d , J = 7.6 Hz, 2H_p, Ph), 7.74 (d , J = 7.2 Hz, 4H_o, Ph). ^{31}P {^{1}H} NMR (162 MHz, CD_3CN, 25^{o}C): δ 121.2. ^{19}F NMR (376 MHz, CD_3CN, 25 ^{o}C): δ -77.0 (s). IR (KBr,

cm^{-1}): 1269 [ν(S-O)]. Anal. Calcd for $C_{46}H_{80}CeCo_2F_6I_2O_{26}P_6S_2$: C, 29.58 ; H, 4.14. Found: C, 29.67 ; H, 4.17.

Synthesis of $[Ce^{IV}\{OI(Cl)Ph\}\{N(Pr^i_2PO)_2\}_3]$ (2)

To a solution of $[Ce^{IV}_2(\mu\text{-}O)\{N(Pr^i_2PO)_2\}_4Cl_2]$ (50 mg, 0.034 mmol) in MeCN (5 mL) was added PhIO (10 mg, 0.046 mmol), and the mixture was stirred at room temperature until all the PhIO was dissolved (ca. 30 min). The volatiles were removed in *vacuo*, and the product was extracted with 5 mL of hexanes. Concentration of the solution gave single orange crystals suitable for X-ray structure determination. Yield: 16.6 mg, 40%. ^{1}H NMR (400 MHz, C_6D_6, 25 ^{o}C): δ 1.19 – 1.24 (m, 36H, CH_3), 1.27 – 1.33 (m, 36H, CH_3), 1.97 – 2.08 (m, 12H, CH), 6.91 (t, J = 7.2 Hz, 1H, H_p, Ph), 7.04 (t, J = 8 Hz, 2H, H_m, Ph) , 8.47 (d, J = 8 Hz, 2H, H_o, Ph). ^{31}P $\{^1H\}$ NMR (62 MHz, C_6D_6, 25^{o}C): δ 49.49 (s). Anal. Calcd for $C_{42}H_{89}CeClIN_3O_7P_6$: C, 40.80 ; H, 7.25; N, 3.4. Found: C, 40.91; H, 7.36; N, 3.3.

Decomposition of 1 in D_2O

The decomposition of **1** (5 mg, 0.0029 mmol) in D_2O (0.5 mL) at room temperature was monitored by ^{1}H and ^{31}P $\{^1H\}$ NMR spectroscopy. During the course of the reaction, the signals due to **1** dropped while the signals attributable to $[(L_{OEt})_2CeCl_2]$ appeared. Meanwhile, the insoluble PhIO polymer (yellowish-white solid) was precipitated out gradually. The signals of **1** disappeared in ca. 2 h.

Reaction of 1 with $AgNO_3$ or $NaNO_3$

To a solution of **1** (50 mg, 0.029 mmol) in MeCN (5 mL) was added $AgNO_3$ (10 mg, 0.059 mmol) or $NaNO_3$ (5 mg, 0.059 mmol), and the mixture was stirred at room temperature for 30 min. The AgCl or NaCl formed was filtered off and the volatiles were removed *in vacuo* to give an orange solid. Recrystallization from CH_2Cl_2/hexanes afforded red single crystals,

which were identified as the reported dinitrate compound $[Ce(L_{OEt})_2(NO_3)_2]$.[6] Yield: 34 mg (88%) for $AgNO_3$, 28.6 mg (74%) for $NaNO_3$.

Synthesis of $[Ce^{IV}(L_{OEt})_2\{OI(O)(Cl)Ph\}_2]\cdot 0.2H_2O$ (3·0.2H$_2$O)

To a solution of $[(L_{OEt})_2CeCl_2]$ (30 mg, 0.024 mmol) in MeCN (5 mL) was added ca. 2 equivalents of $PhIO_2$ (11.8 mg, 0.047 mmol), and the mixture was stirred at room temperature until all the $PhIO_2$ were dissolved (ca. 30 min). The solvent was removed *in vacuo* and the residue was extracted with CH_2Cl_2/THF/hexane (20 mL, v/v 1:1:1). Slow evaporation of the solution gave orange single crystals suitable for X-ray structure determination. Yield: 36.3 mg, 87%. ^{1}H NMR (400MHz, CD_3CN, 25 ^{o}C): δ 1.16 (t, *J* = 7.2 Hz, 36H,CH_3), 4.01 – 4.10 (m, 24H, CH_2), 5.08 (s, 10H, Cp), 7.57 – 7.65 (m, 6H, Ph), 8.28 (d , *J* = 6 Hz, 4H, Ph) . ^{31}P {^{1}H} NMR (162 MHz, CD_3CN, 25^{o}C): δ 116.3 (s). IR (KBr, cm^{-1}): 3444 br. [ν(O-H)]. Anal. Calcd for $C_{46}H_{80}CeCl_2Co_2I_2O_{22}P_6\cdot 0.2H_2O$: C, 31.44 ; H, 4.61. Found: C, 31.27 ; H, 4.27. Alternatively, **3** can be synthesized by the treatment of $[(L_{OEt})_2CeCl_2]$ (30 mg, 0.024 mmol) with excess PhIO (22.4 mg, 0.102 mmol) in MeCN (5 mL). The mixture was stirred at room temperature for 30 min. The solvent was removed *in vacuo* and the residue was extracted with CH_2Cl_2/THF/hexane (20 mL, v/v 1:1:1). Slow evaporation of the solution gave single orange crystals suitable for X-ray structure determination. Yield: 39.6 mg, 97%.

Stoichiometric oxidation of PPh_3 by Ce^{IV} hypervalent iodine complexes

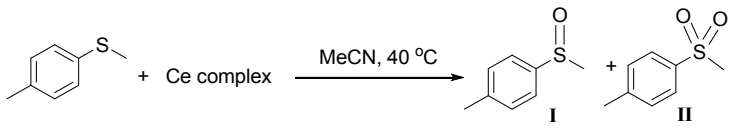
To a solution of freshly prepared **1** or **2** (12.5 μmol) in CD_3CN (2 mL) were added PPh_3 (for **1**: 6.6 mg, 25 μmol; for **2**: 3.3 mg, 12.5 μmol), and the mixture was stirred at room temperature for 5 min. NMR spectroscopy indicated that triphenylphosphine oxide ($O{=}PPh_3$) quantitatively was produced almost quantitatively (ca. 200% and 100% for **1** and **2**, respectively). Then the solvent was removed in vacuo and the residue was extracted with hexane. Slow evaporation of the hexane solution gave red or yellow crystals that were

characterized as the known compound $[(L_{OEt})_2CeCl_2]$[1] or $[Ce^{IV}\{N(Pr^i_2PO)_2\}_3Cl]$[2].

Stoichiometric oxidation of *p*-tolyl methylsulfide by Ce^{IV} hypervalent iodine complexes

To a solution of freshly prepared **1** or **3** (12.5 μmol) in MeCN (5 mL) were added 4 equivalents of *p*-tolyl methylsulfide (6.7 μL, 50 μmol), and the mixture was stirred at 40 °C. The progress of the reaction was monitored by GLC analysis. At a given time, an aliquot (0.5 mL) was removed by a syringe, and filtered through a pad of celite, and the yield of product (*p*-tolyl methylsulfide) was determined by GLC using bromobenzene as internal standard.

Table S1. Stoichiometric oxidation of *p*-tolyl methylsulfide by **1** - **3**[a]



+ Ce(IV) chloride + n PhI

n = 2 (**1** or **3**), 1 (**2**)

Complex[b]	Temp (°C)	Time (min)	Product (% yield[c])	
			I	**II**
1	40	5	200	nil
2	40	5	100	nil
3	40	5	380	10

[a] Experimental conditions: Ce complex (12.5 μmol), *p*-tolyl methylsulfide (50 μmol), MeCN (5mL), 40 °C. [b] Ce complexes: $[Ce(L_{OEt})_2\{OI(Cl)Ph\}_2]$ (**1**), $[Ce^{IV}\{N(Pr^i_2PO)_2\}_3\{OI(Cl)Ph\}]$ (**2**), $[Ce(L_{OEt})_2\{OI(Cl)(O)Ph\}_2]$ (**3**). [c] Yield relative to the Ce complex determined by GLC.

Reaction of cyclooctene with Ce^{IV} hypervalent iodine complexes

To a solution of freshly prepared **1** or **3** (12.5 μmol) in MeCN (5 mL) were added cyclooctene (6.5 μL, 50 μmol), and the mixture was stirred at 40 °C. The progress of the reaction was monitored by GLC analysis. At a given time, an aliquot (0.5 mL) was removed by a syringe, and filtered through a pad of celite, and the yield of product (*p*-tolyl methylsulfide) was determined by GLC using bromobenzene as internal standard. No reaction was found between **1** and cyclooctene.

Ce-catalyzed oxidation of *p*-tolyl methylsulfide

To a solution of $[(L_{OEt})_2Ce^{IV}Cl_2]$ (3 mg, 2.34 μmol) and 20 equivalents of PhIO (10.4 mg, 47.3 μmol) in MeCN (5 mL) were added 10 equivalents of *p*-tolyl methylsulfide (6.4 μL, 47.6 μmol), and the mixture was stirred at 40 °C for ca. 15 min. The solvent was removed by a rotavapor, and the residue was extracted with MeCN and filtered through a celite pad. The product was determined by GLC analysis using bromobenzene as the internal standard.

NMR monitoring of the Ce-catalyzed oxidation of *p*-tolyl methylsulfide

To a solution of $[(L_{OEt})_2Ce^{IV}Cl_2]$ (10 mg, 7.81 μmol) and 10 equivalents of *p*-tolyl methylsulfide (10.7 μL, 78.2 μmol) in CD_3CN (1 mL) were added 10 equivalents of PhIO (17.2 mg, 78.2 μmol), and the mixture was stirred at 40 °C. ^1H and $^{31}P\{^1H\}$ NMR spectra of the mixture at 0, 5, 10 and 15 min after the addition of PhIO were recorded.

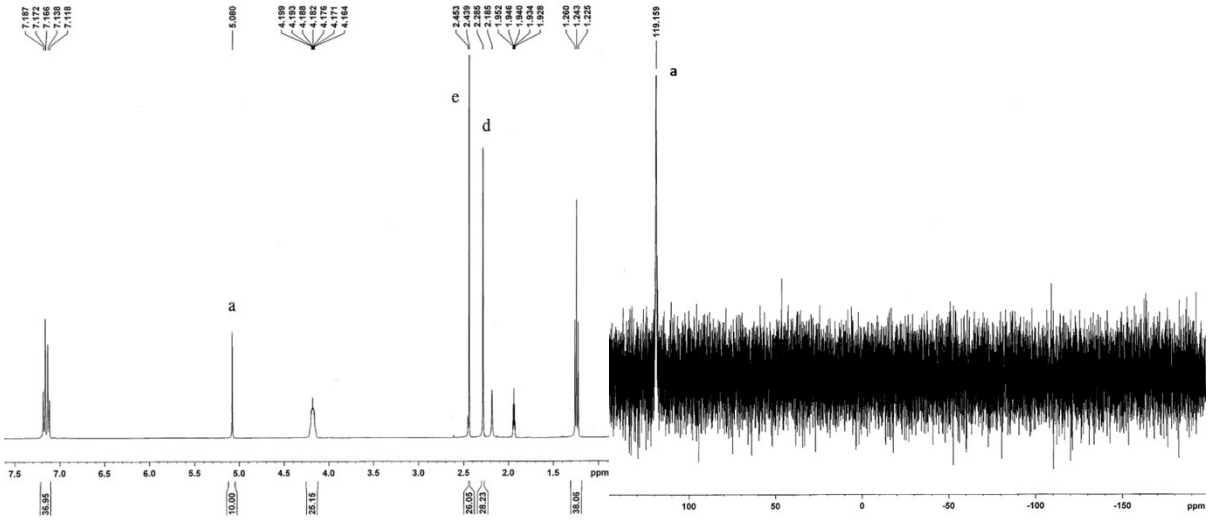
References

1. Y.-M. So, G.-C. Wang, Y. Li, H. H.-Y. Sung, I. D. Williams, Z. Lin and W.-H. Leung, *Angew. Chem. Int. Ed.*, 2014, **53**, 1626.
2. G.-C. Wang, H. H.-Y. Sung, I. D. Williams and W.-H. Leung, *Inorg. Chem.*, 2012, **51**, 3640.
3. H. J. Lucas and E. R. Kennedy, *Org. Synth.*, 1943, **coll. vol. 2**, 351.
4. H. J. Lucas and E. R. Kennedy, *Org. Synth.*, 1939, **19**, 55.
5. V. V. Zhdankin, *Hypervalent Iodine Chemistry: Preparation, Structure and Synthetic Applications of Polyvalent Iodine Compounds*, John Wiley & Sons, 2014.
6. Y.-X. Yi, T. C.-H. Lam, I. D. Williams and W.-H. Leung, *Inorg. Chem.*, 2010, **49**, 2232.

NMR monitoring of the Ce-catalysed oxidation of *p*-tolyl methylsulfide with PhIO

^{1}H (left) and ^{31}P $\{^{1}H\}$ (right) NMR spectra of a mixture of $[(L_{OEt})_2CeCl_2]$ and *p*-tolyl methylsufide (10 equiv.) in CD_3CN (1 mL) at 40 °C at 0, 5, 10 and 15 min after the addition of PhIO (10 equiv.). The signals due to $[(L_{OEt})_2CeCl_2]$, **1** and **3** are indicated by **a**, **b**, and **c**, respectively. The ^{1}H NMR signals of $(C\underline{H}_3C_6H_4)SCH_3$, $(CH_3C_6H_4)SC\underline{H}_3$, $(C\underline{H}_3C_6H_4)S(O)CH_3$, $(CH_3C_6H_4)S(O)C\underline{H}_3$ are indicated by **d**, **e**, **d'** and **e'**, respectively.

t = 0 min



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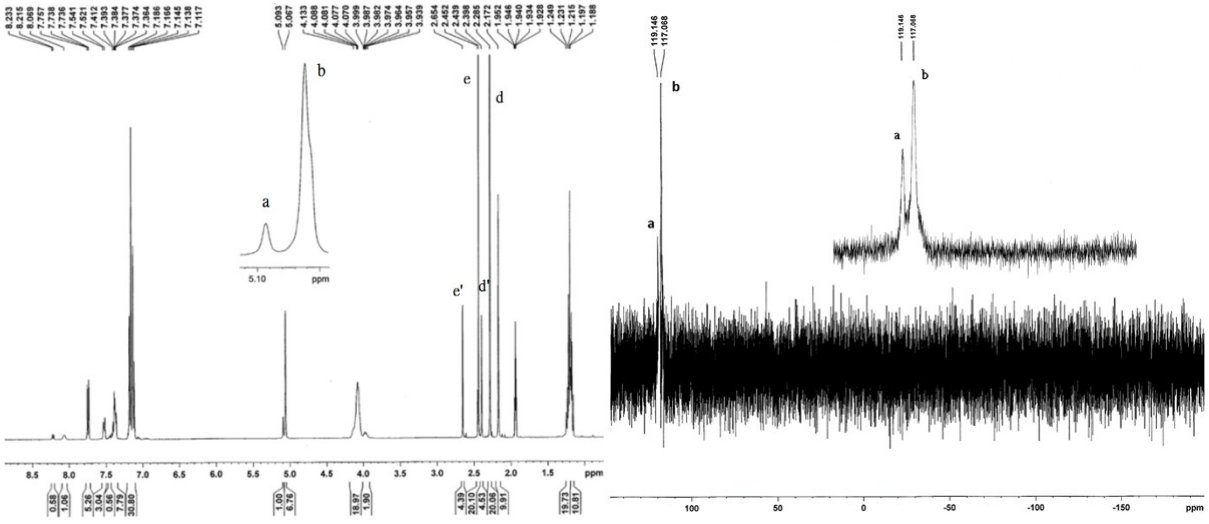

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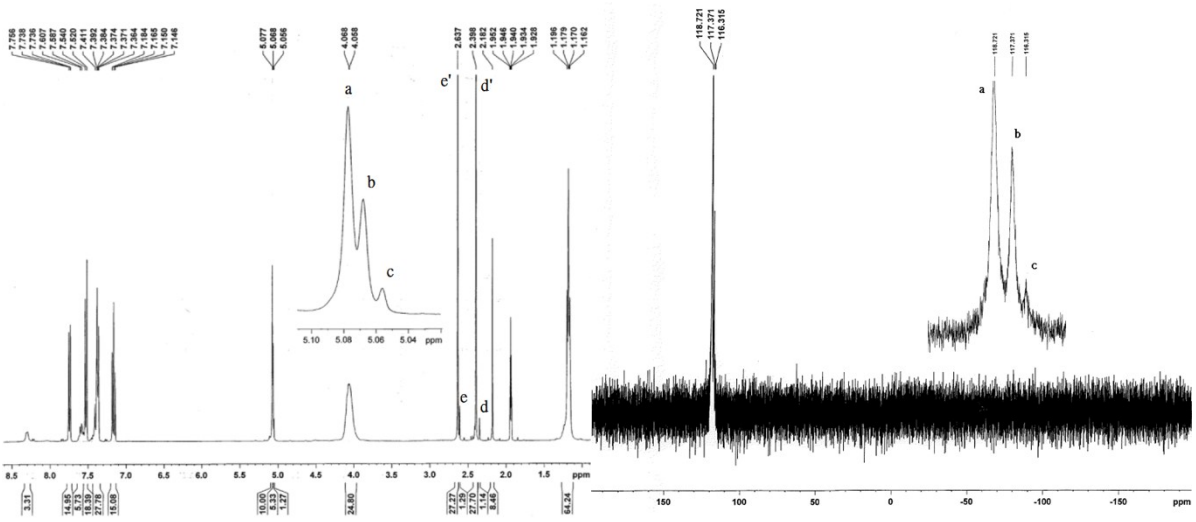
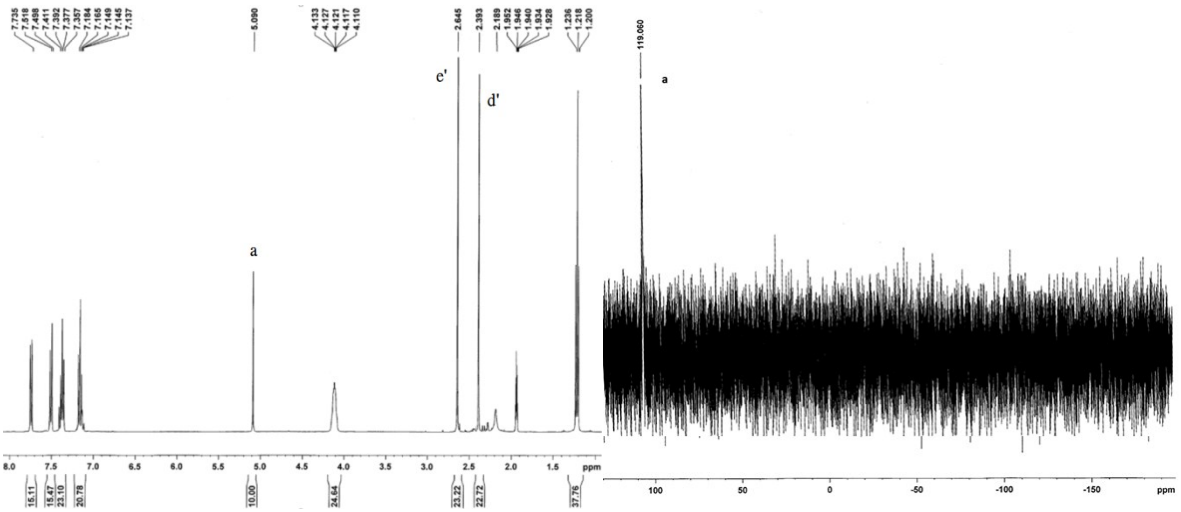


t =15 min



2. X-ray Crystallography

Crystallographic data and refinement details for complexes **1**, **2** and **3**·0.2H_2O are listed in Table S1. The diffraction intensity data of **1** and **3**·0.2H_2O were collected with a Rigaku SuperNova Atlas X-ray Diffractometer with monochromated Mo-Kα radiation (λ = 0.71073 Å) at 100 K. The diffraction intensity data of **2** was collected with a Rigaku Gemini™ S Ultra X-ray Diffractometer with monochromatized Cu-Kα radiation (λ = 1.54178Å) at 100K. Diffraction data of **1**, **2** and **3**·0.2H_2O were collected and processed using the CrysAlisPro software (Rigaku, 2012). Empirical absorption corrections were performed using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm in the CrysAlisPro software suite. Structure solution and refinement for all complexes were performed using the Olex2 software package[1] (which embedded SHELXTL[2]). All the structures were solved by direct methods, expanded by difference Fourier syntheses and refined by full matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically with a riding model for the hydrogen atoms except noted separately. All the pictures of molecules were made using XP implemented in SHELXTL.[2] CCDC 1451299, 1432570 and 1432572 contain the supplementary crystallography data for complexes **1**, **2** and **3**·0.2H_2O respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

References

1. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339. OLEX2: A complete structure solution, refinement and analysis program.
2. G. M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112.

Table S2. Crystallographic data and refinement details for complexes **1**, **2** and **3**·0.2H_2O.

	1	**2**	**3**·0.2H_2O
Formula	$C_{47}H_{82}CeCl_4Co_2I_2O_{20}P_6$	$C_{42}H_{89}CeClIN_3O_7P_6$	$C_{46}H_{80.4}CeCl_2Co_2I_2O_{22.2}P_6$
F_w	1806.52	1236.45	1757.20
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2/c	Cc	Pn
a (Å)	24.8983(5)	21.8270(2)	12.0266(4)
b (Å)	12.6591(2)	12.71458(13)	12.5297(4)
c (Å)	44.0778(11)	20.51840(19)	21.8315(6)
α (°)	90	90	90
β (°)	104.574(2)	93.3517(8)	90.136(2)
γ (°)	90	90	90
V (Å^3)	13445.9(5)	5684.56(9)	3289.77(18)
Z	8	4	2
ρ_{calcd} (g cm^{-1})	1.785	1.445	1.774
T (K)	100	100	100
F(000)	7200	2544	1752
μ (mm^{-1})	2.439	12.835	2.413
No. of reflns	78576	11724	25725
No. of indep reflns	26365	7434	13080
R_{int}	0.0849	0.0850	0.0396
GoF[a]	1.004	1.003	1.001
R_1[b],wR_2[c] (I>2σ(I))	0.0579, 0.1063	0.0582, 0.1058	0.0361, 0.0542
R_1, wR_2 (all data)	0.1082, 0.1265	0.1086, 0.1258	0.0457, 0.0571

[a] $R1 = \Sigma \left| |F_o| - |F_c| \right| / \Sigma |F_o|$. [b] $wR2 = [\Sigma w(|F_o^2| - |F_c^2|)^2 / \Sigma w |F_o^2|^2]^{1/2}$. [c] GoF $= [\Sigma w(|F_o| - |F_c|)^2 / (N_{obs} - N_{param})]^{1/2}$.

Figure S1. Molecular structure of **1**. Hydrogen atoms are omitted for clarity. The ellipsoids are drawn at 30% probability level.

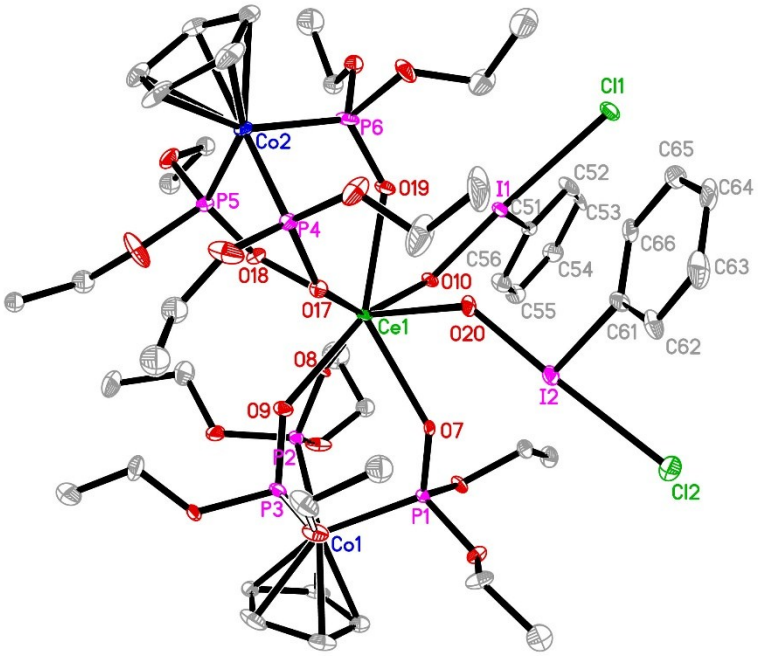


Table S3. Selected bond lengths [Å] and angles [°] for **1**.

Ce(1)-O(7)	2.446(4)	I(1)-Cl(1)	2.8195(18)
Ce(1)-O(8)	2.360(5)	I(1)-O(10)	1.918(4)
Ce(1)-O(9)	2.370(4)	I(1)-C(51)	2.124(8)
Ce(1)-O(17)	2.345(5)	I(2)-Cl(2)	2.718(2)
Ce(1)-O(18)	2.352(4)	I(2)-O(20)	1.950(4)
Ce(1)-O(19)	2.411(4)	I(2)-C(61)	2.109(8)
Ce(1)-O(10)	2.262(5)		
Ce(1)-O(20)	2.202(5)		
O(10)-I(1)-Cl(1)	175.91(15)	O(20)-I(2)-Cl(2)	177.63(15)
O(10)-I(1)-C(51)	92.3(2)	O(20)-I(2)-C(61)	91.6(2)
C(51)-I(1)-C(11)	89.39(19)	O(22)-I(2)-Cl(2)	86.1(2)
I(1)-O(10)- Ce(1)	122.1 (2)	I(2) -O(20)- Ce(1)	129.4 (2)
O(20)-Ce(1)-O(10)	83.17(18)		

Figure S2. Molecular structure of **2**. Hydrogen atoms are omitted for clarity. The ellipsoids are drawn at 30% probability level.

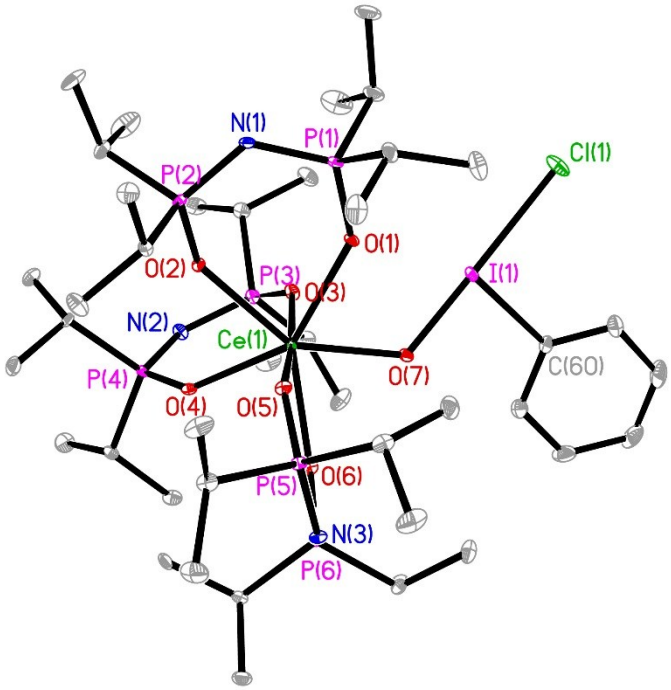
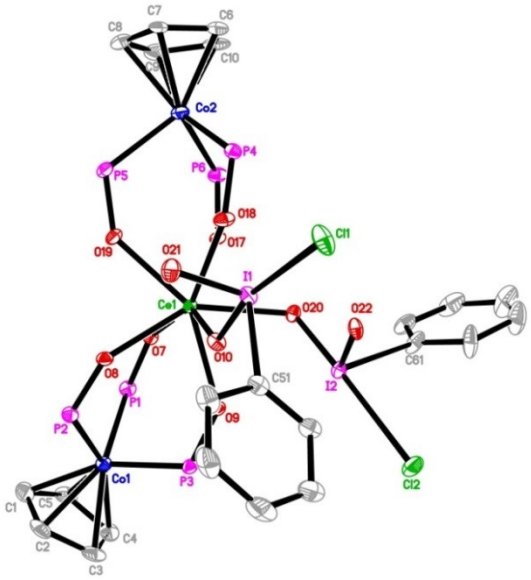


Table S4. Selected bond lengths [Å] and angles [°] for **2**

Ce(1)-O(1)	2.383(2)	Ce(1)-O(4)	2.294(2)
Ce(1)-O(2)	2.299(2)	Ce(1)-O(5)	2.288(2)
Ce(1)-O(3)	2.299(2)	Ce(1)-O(6)	2.296(2)
Ce(1)-O(7)	2.171(2)	I(1)-O(7)	1.966(2)
I(1)-Cl(1)	2.6711(10)	I(1)-C(60)	2.135(4)
I(1)-O(7)-Ce(1)	124.92(12)	O(7)-I(1)-Cl(1)	177.93(8)
O(7)-I(1)-C(60)	90.64(13)	C(60)-I(1)-Cl(1)	89.22(11)

Figure S3. Molecular structure of **3**·0.2H_2O. Hydrogen atoms and Ethoxy groups on L_{OEt}^- and the co-crystallized H_2O molecule are omitted for clarity. The ellipsoids are drawn at 30% probability level.



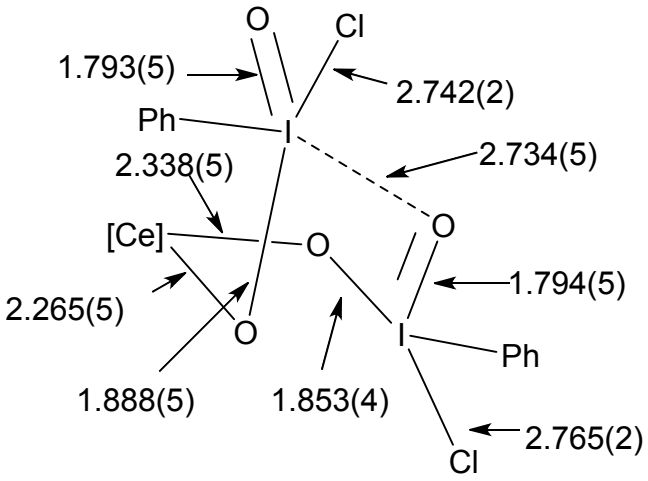


Table S5. Selected bond lengths [Å] and angles [°] for **3**·0.2H_2O.

Ce(1)-O(7)	2.313(5)	I(1)-Cl(1)	2.742(2)
Ce(1)-O(8)	2.308(5)	I(1)-O(10)	1.888(5)
Ce(1)-O(9)	2.415(4)	I(1)-O(21)	1.793(5)
Ce(1)-O(10)	2.265(5)	I(1)-C(51)	2.124(7)
Ce(1)-O(17)	2.304(4)	I(2)-Cl(2)	2.765(2)
Ce(1)-O(18)	2.442(5)	I(2)-O(20)	1.853(4)
Ce(1)-O(19)	2.314(5)	I(2)-O(22)	1.794(5)
Ce(1)-O(20)	2.338(5)	I(2)-C(61)	2.105(8)
I(2)-O(22)···I(1)	2.734(5)		
I(1)-O(10)- Ce(1)	128.6(2)	I(2)-O(20)- Ce(1)	121.2(2)
O(10)-I(1)-Cl(1)	167.41(16)	O(20)-I(2)-Cl(2)	170.37(15)
O(10)-I(1)-C(51)	89.7(2)	O(20)-I(2)-C(61)	91.6(3)
O(21)-I(1)-Cl(1)	93.33(18)	O(22)-I(2)-Cl(2)	88.86(16)
O(21)-I(1)-O(10)	98.2(2)	O(22)-I(2)-O(20)	100.4(2)
O(21)-I(1)-C(51)	96.8(3)	O(22)-I(2)-C(61)	96.9(3)
C(51)-I(1)-Cl(1)	84.0(2)	C(61)-I(2)-Cl(2)	84.6(2)
O(10)-Ce(1)-O(20)	79.02(17)	I(2)-O(22)-I(1)	113.9(2)

3. NMR and IR Spectra

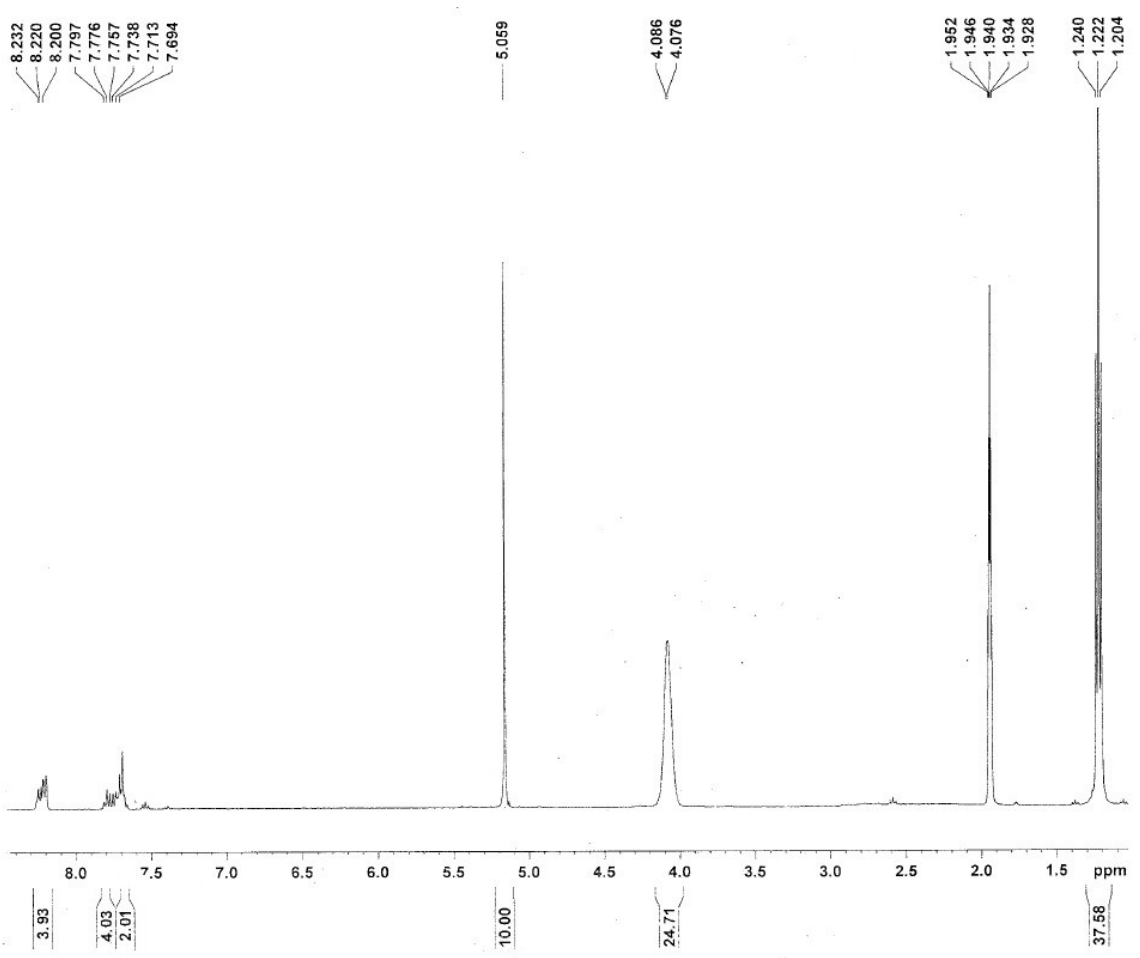


Figure S4. ^{1}H NMR (400 MHz, 25 ^{o}C) spectrum of **1** in CD_3CN.

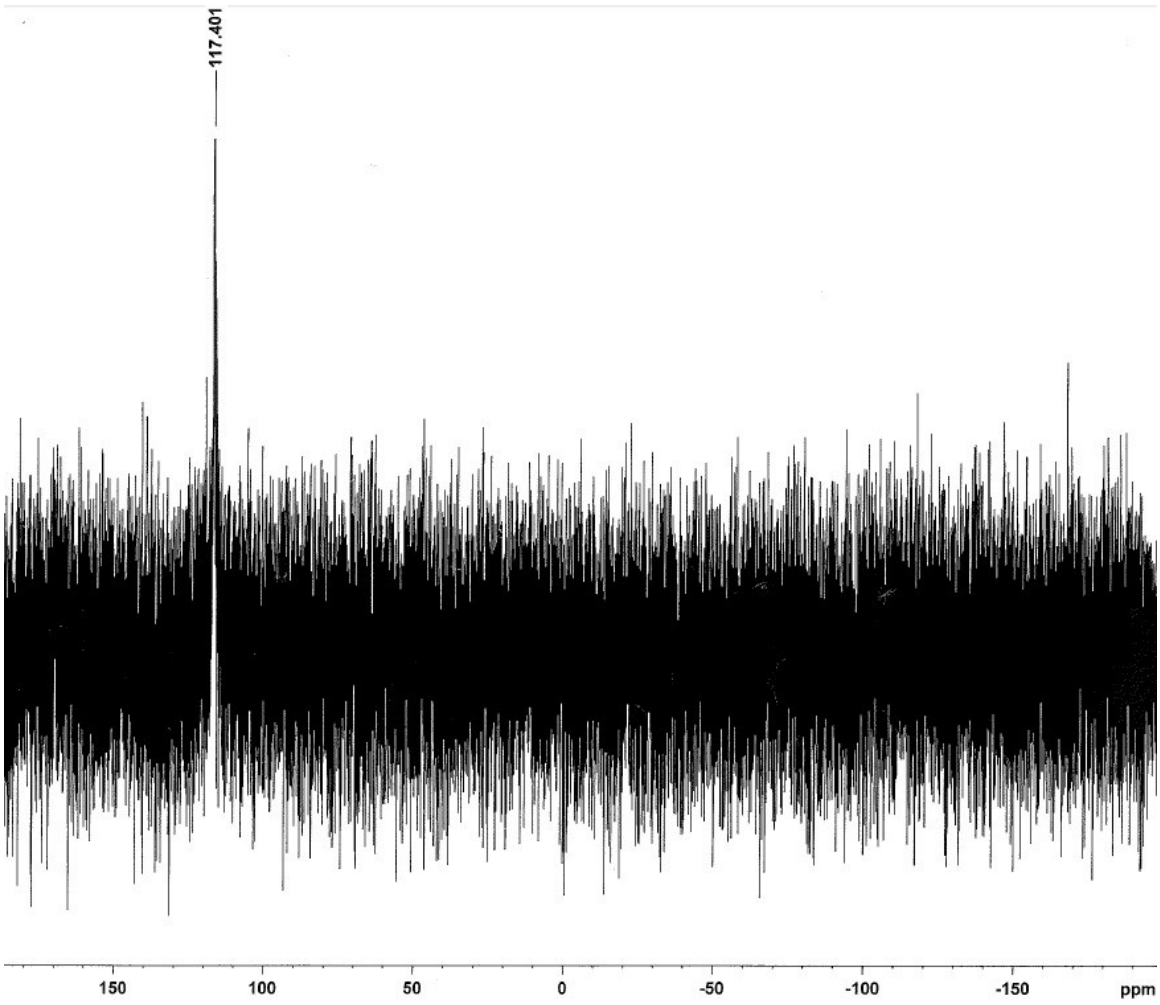


Figure S5. ^{31}P $\{^{1}H\}$ NMR (162 MHz, 25 ^{o}C) spectrum of **1** in CD_3CN.

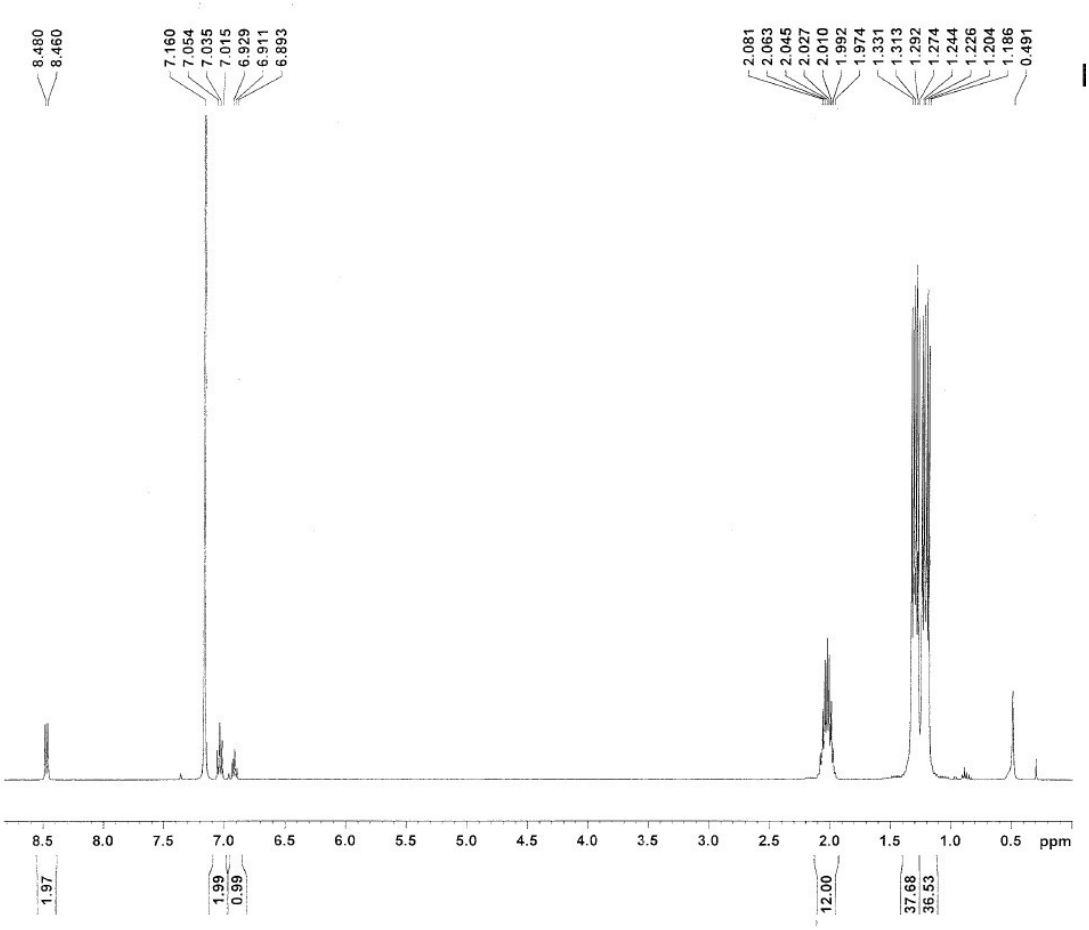


Figure S6. ^{1}H NMR (400 MHz, 25 ^{o}C) spectrum of **2** in C_6D_6.

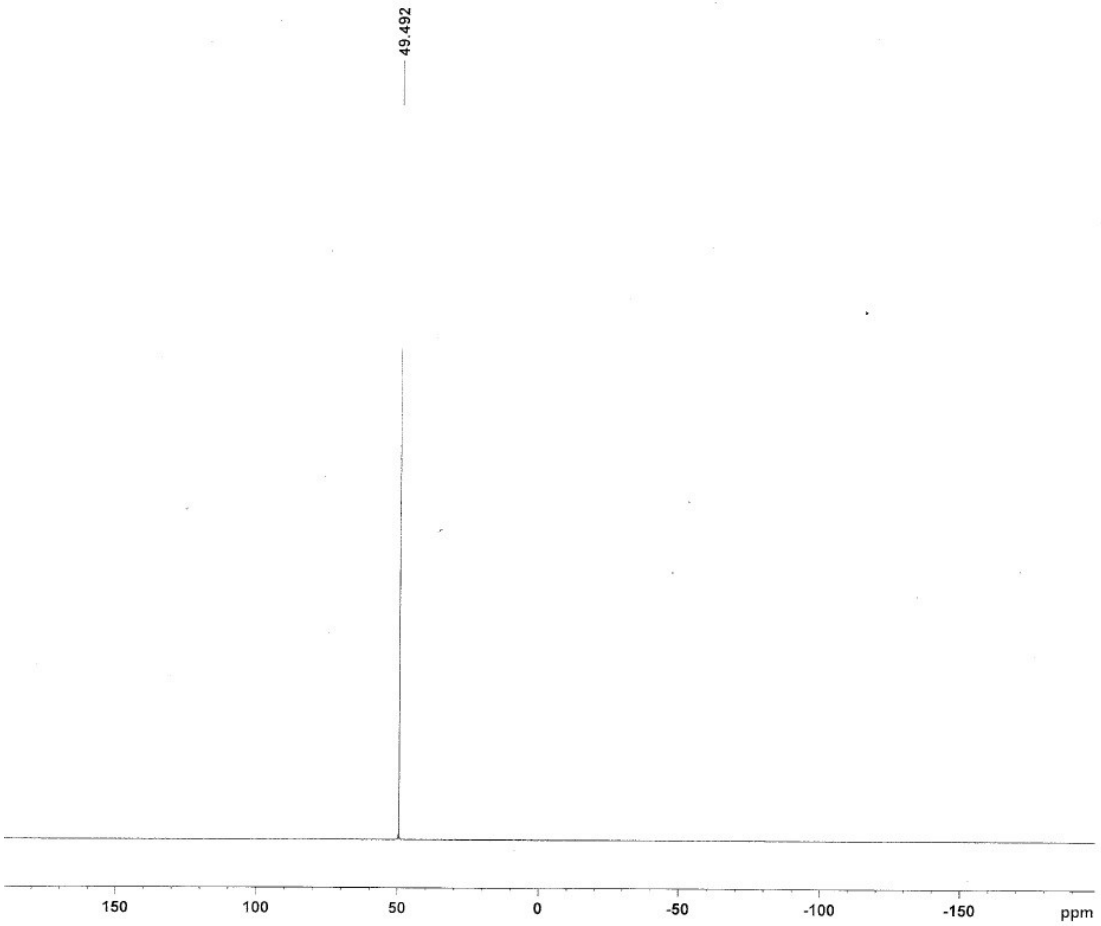


Figure S7. ^{31}P $\{^{1}H\}$ NMR (162 MHz, 25 ^{o}C) spectrum of **2** in C_6D_6.

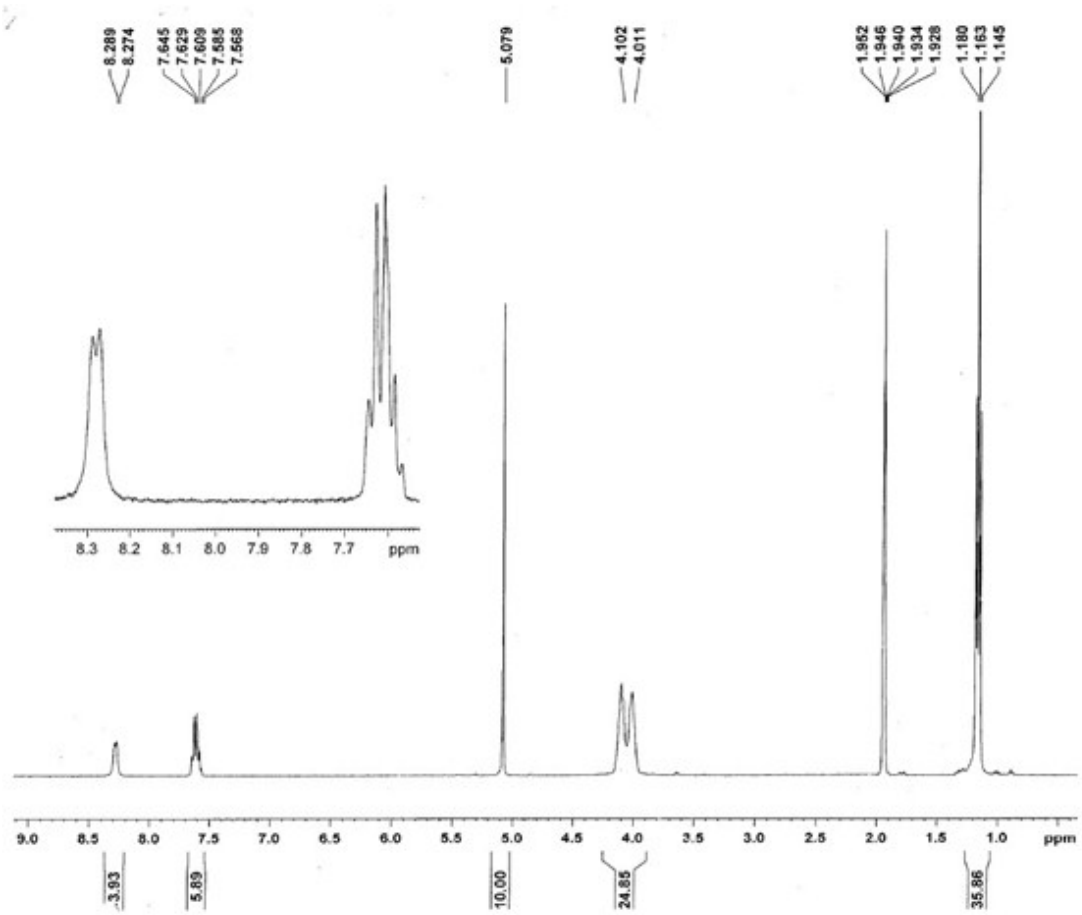


Figure S8. ^{1}H NMR (400 MHz, 25 ^{o}C) spectrum of **3**·0.2H_2O in CD_3CN.

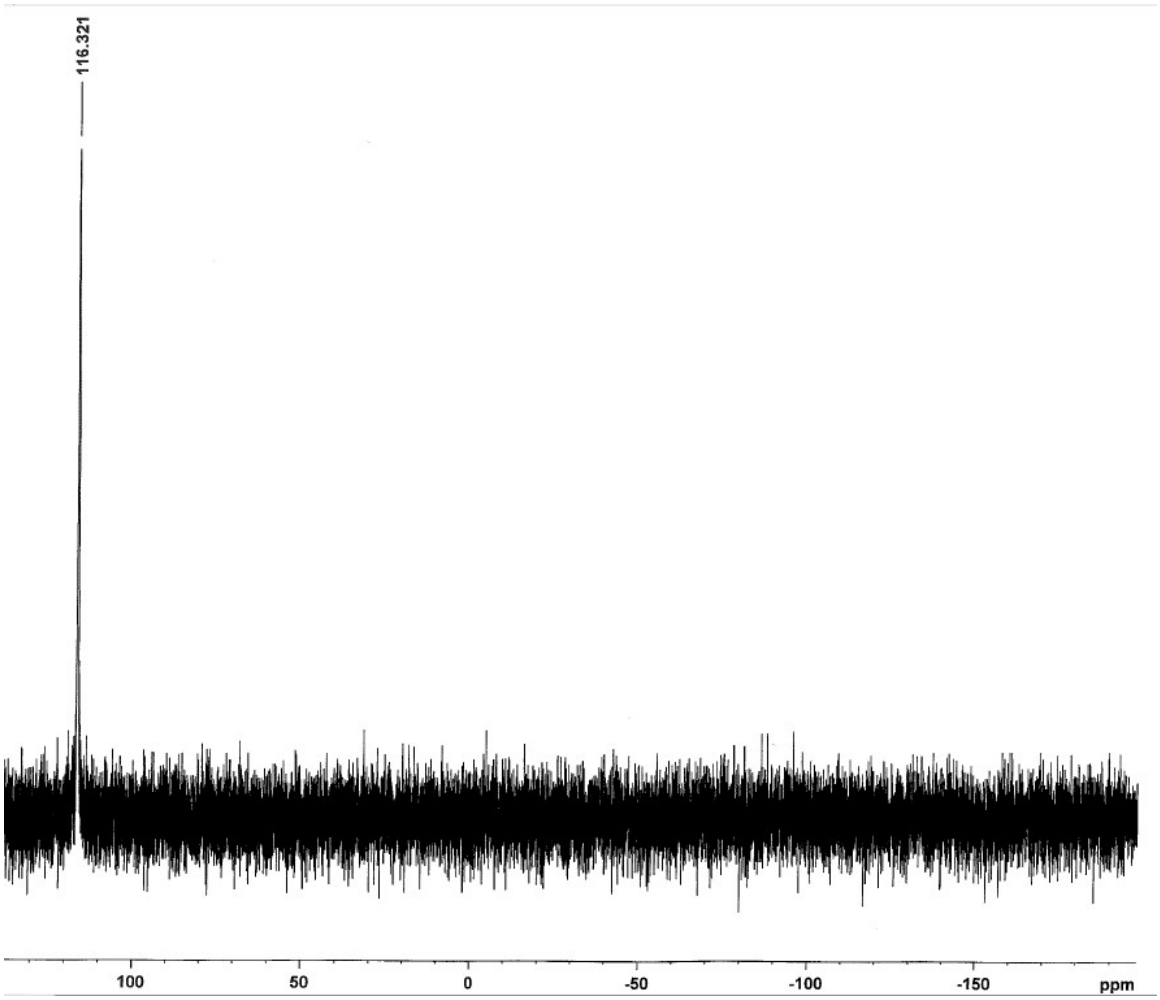


Figure S9. ^{31}P $\{^{1}H\}$ NMR (162 MHz, 25 ^{o}C) spectrum of **3**·0.2H_2O in CD_3CN.

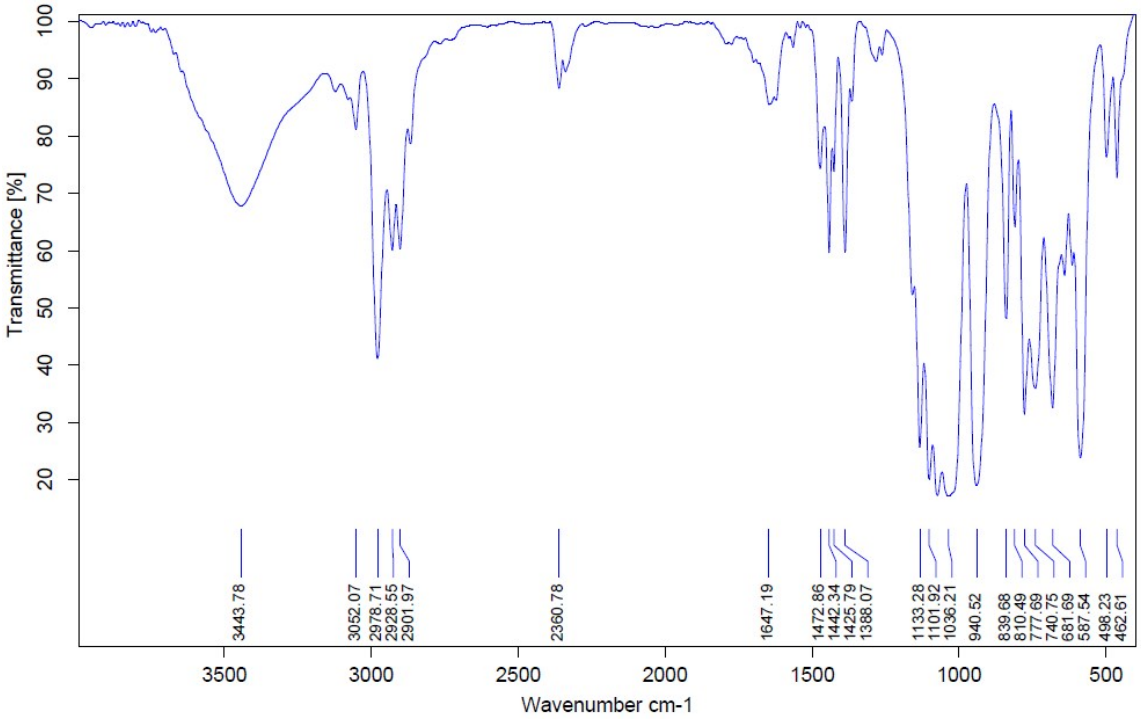


Figure S10. IR (KBr) spectrum (400-4000 cm^{-1} region) of **3**·0.2H_2O.