Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Spectrally-Resolved Third-Harmonic Generation and Fundamental Role of O-H···Cl Hydrogen Bonding in O_h, T_d-Cobalt(II) Tetraphenylmethane-based Coordination Polymer

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PXRD traces

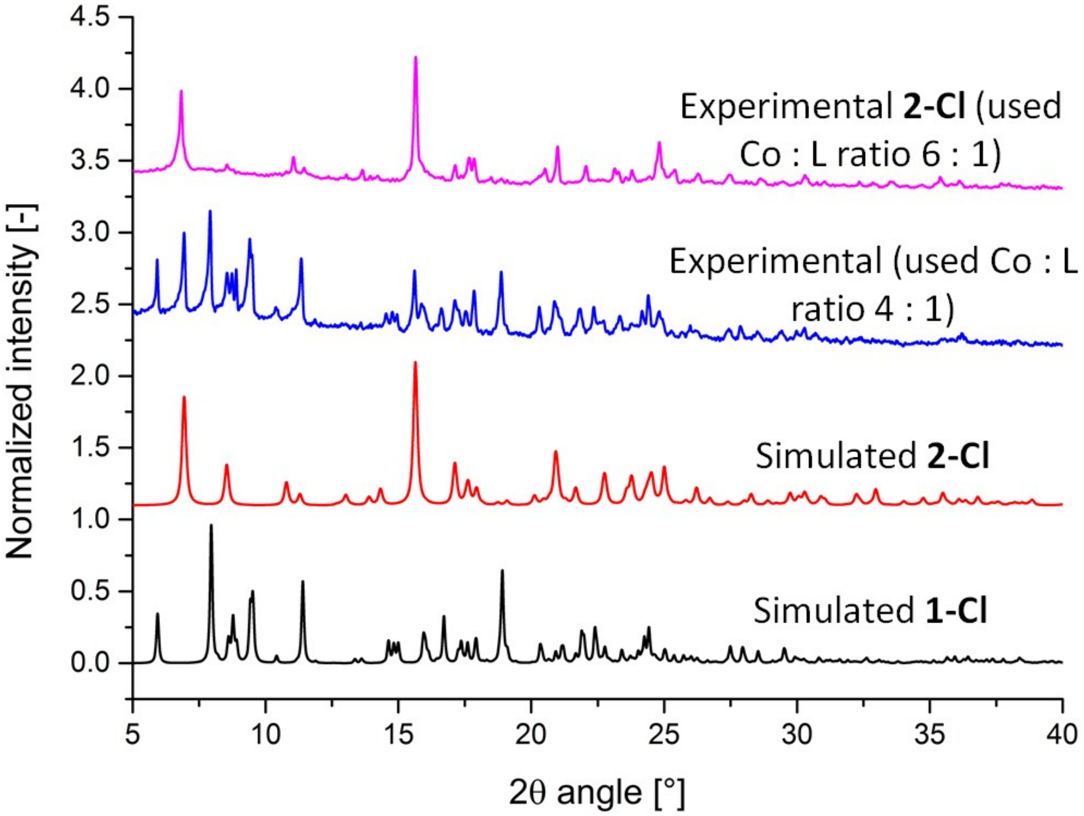

Fig. S1. The PXRD spectra of bulk materials obtained using different cobalt(II) salt to ligand ratios (pink and blue traces) and PXRD spectra simulated from crystallographic files.

Crystallographic tables

Table S1. Selected bond lengths (Å)

Coord. environment of Co1		Coord. environment of Co2	
Bond	Length [Å]	Bond	Length [Å]
Co1 - Cl1	2.2728(5)	Co2 - O1	2.0656(13)
Co1 - Cl2	2.2716(6)	Co2 - O1W	2.0835(16)
Co1 - Cl1$^{(i)}$	2.2728(5)	Co2 - O2W	2.073(2)
Co1 - Cl2$^{(i)}$	2.2716(6)	Co2 - O3W	2.052(2)
		Co2 - O1$^{(ii)}$	2.0656(13)
		Co2 - O1W$^{(ii)}$	2.0835(16)

Symmetry codes: (i) 1-x,y,1/2-z (ii) 3/2-x,1-y,z

Table S2. Hydrogen bonds

Bond D-H···A	Length D-H [Å]	Length H···A [Å]	Length D···A [Å]	Angle D-H···A [°]
O1W-H1W1···Cl2	0.82(2)	2.43(2)	3.2422(17)	171(2)
O1W-H2W1···Cl2	0.822(18)	2.34(2)	3.1344(16)	164(2)
O2W-H1W2···Cl1	0.82(3)	2.46(3)	3.2405(16)	159(2)
O3W-H2W3···Cl1	0.822(19)	2.34(2)	3.1304(13)	162(2)

Asymmetric unit projection

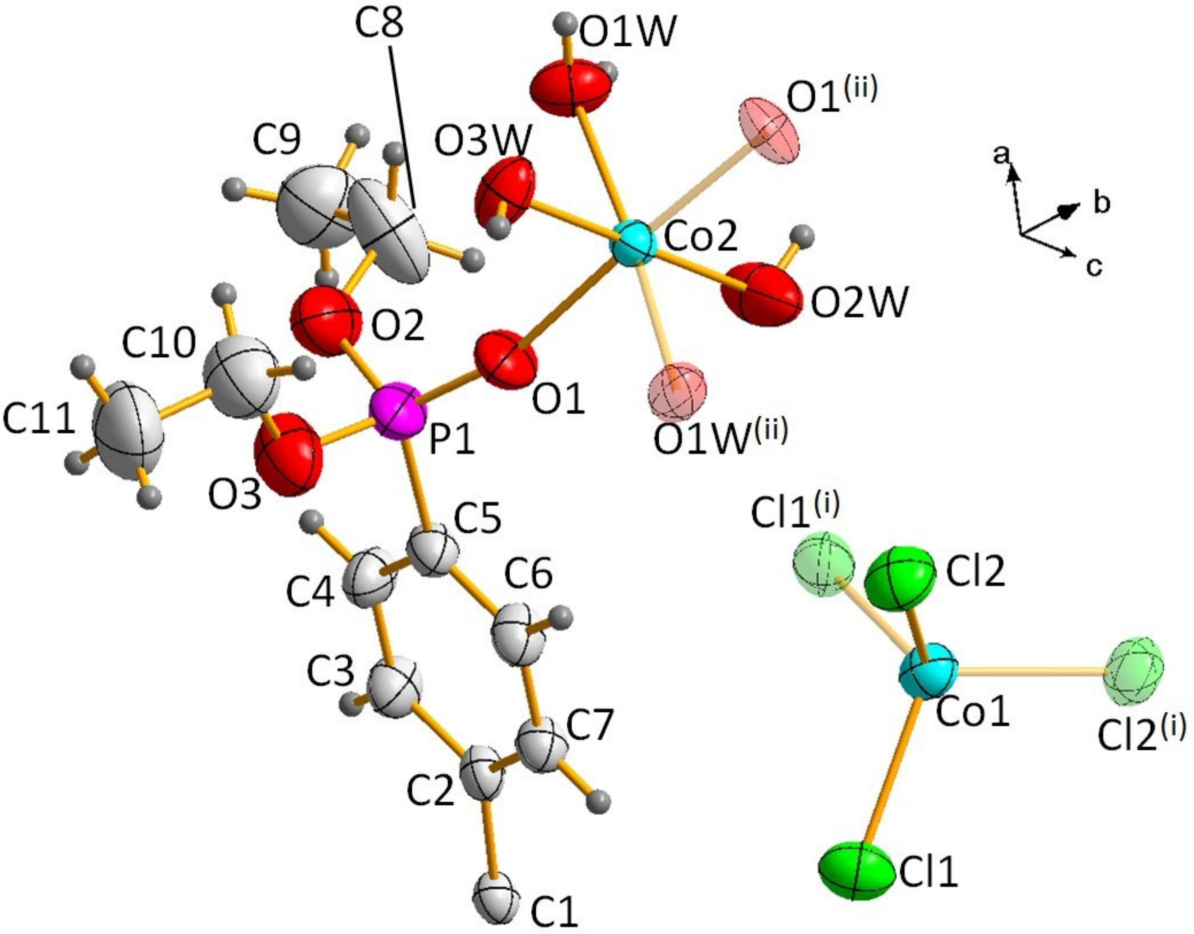

Fig. S2 The asymmetric unit of 2-Cl. Displacement ellipsoids are drawn at 50% probability. Atoms obtained by symmetry operations are drawn in semitranparent representation. Symmetry codes: (i) 1-x, y, 0.5-z; (ii) 1.5-x, 1-y, z.

Additional NLO characterization

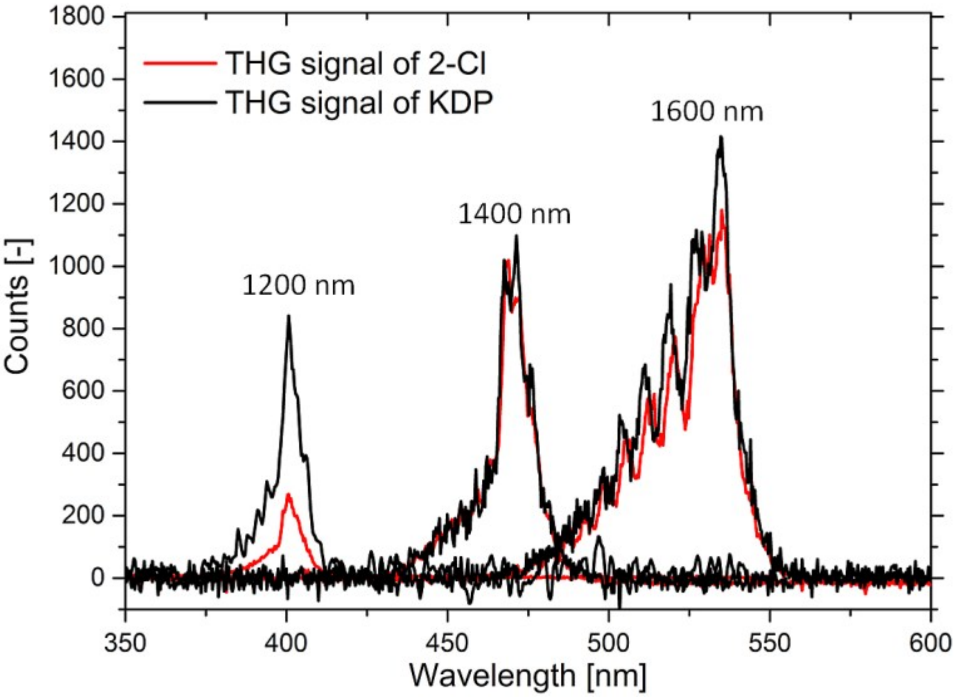

Fig. S3 Spectra of THG emissions for 2-Cl (red spectra) and KDP (black spectra). THG emission was obtained using fundamental wavelengths marked over the resulting traces.

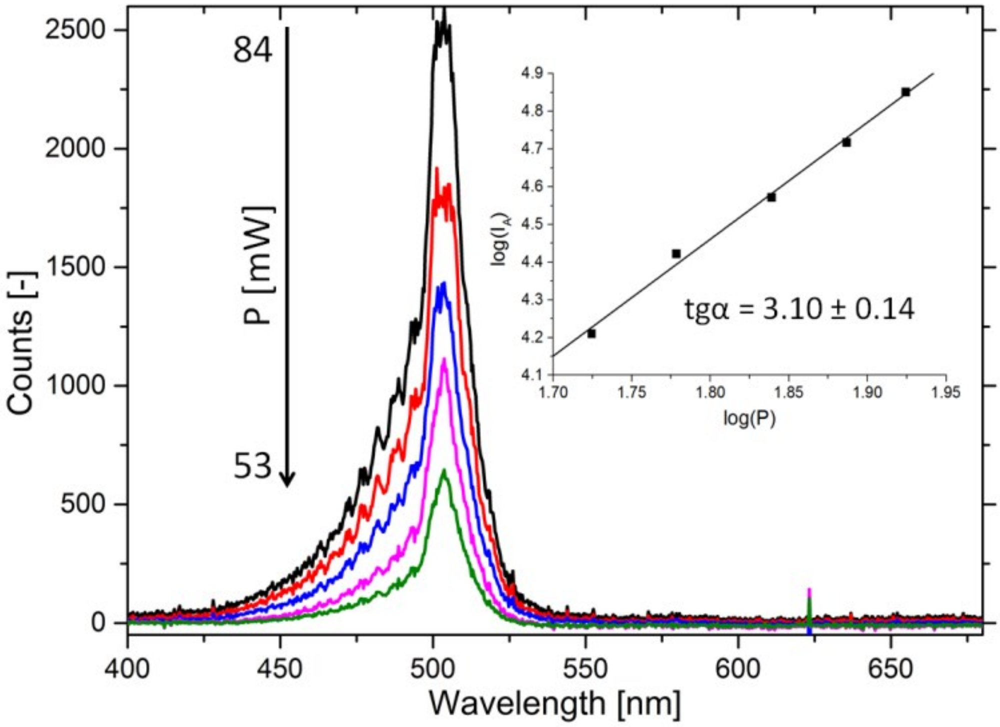

Fig. S4 Power dependence spectra of THG collected by pumping at 1500 nm in the range from 53 to 84 mW. Inset shows the log-log plot of integral THG intensities in the function of applied laser power density.

Description of solid-state absorption spectrum

In Fig. S5 has been presented solid-state absorption spectrum recalculated from reflectance data using Kubelka-Munk relation. It is easily noticeable, that **2-Cl** shares absorption properties of cobalt(II) ions of both geometries. The spectrum is dominated by Laporte-allowed *d-d* transitions coming from tetrahedral Co1 ion. In the visible range $^4A_2 \rightarrow {}^4T_1(P)$ band, consisting from at least three weakly resolved components, is present (maximum at 676 nm, noticeable components are located at 614 and 640 nm), while in the IR region $^4A_2 \rightarrow {}^4T_1(F)$ transition is located (approximately at 1600 nm). The octahedral Co2 ion imparts much weaker bands resulting from $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ forbidden transitions (at 445 nm and 526 nm).

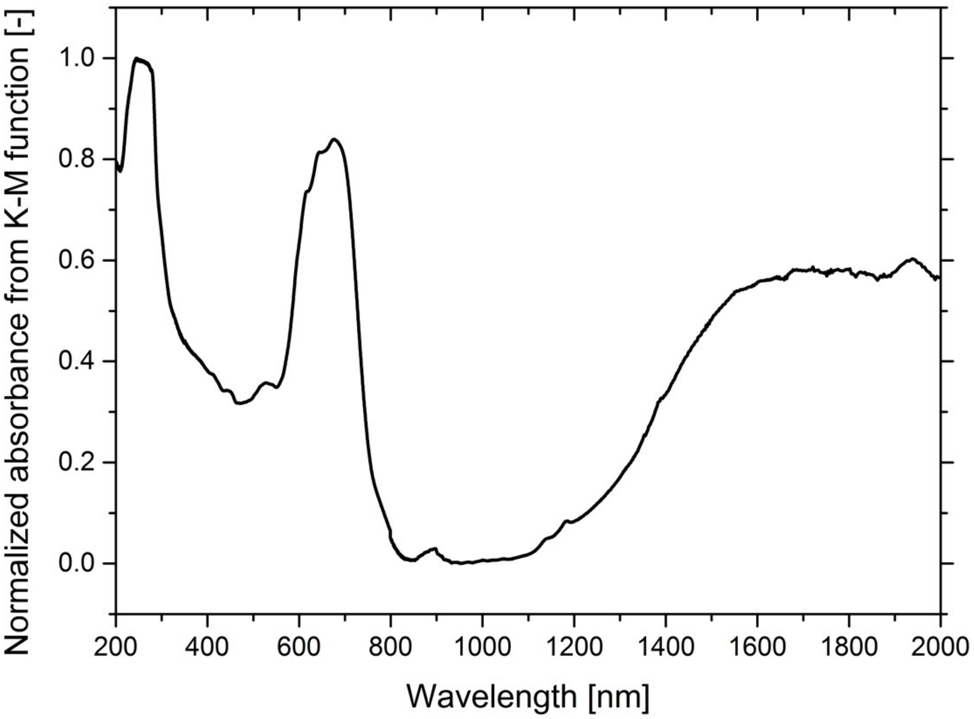

Fig. S5 The solid state absorption spectrum of 2-Cl.

NMR spectra

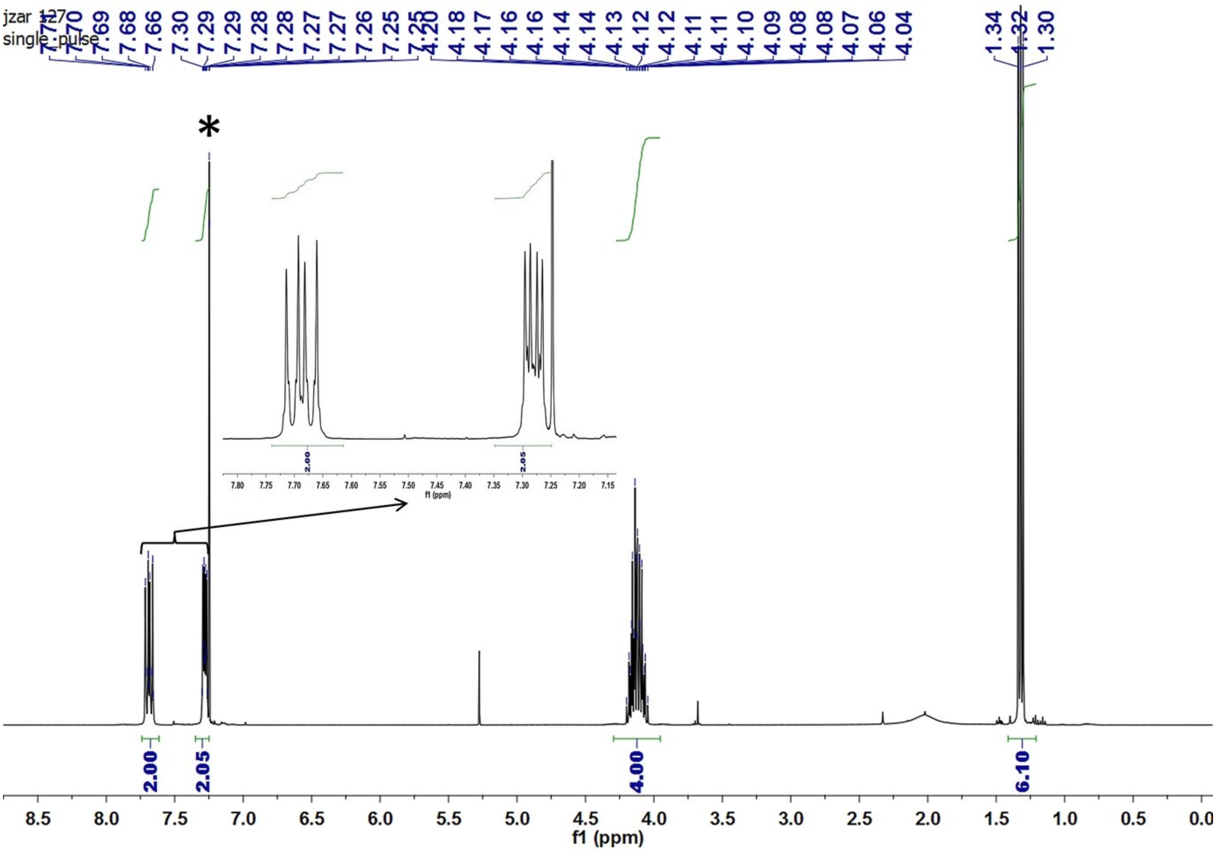

Fig. S6 ^{1}H NMR (400 MHz, CDCl$_3$, 300K) spectrum of ligand L. Inset shows the aromatic signals in the 7.80 – 7.15 ppm region in more detail. With an asterisk is indicated the signal from residual CHCl$_3$.

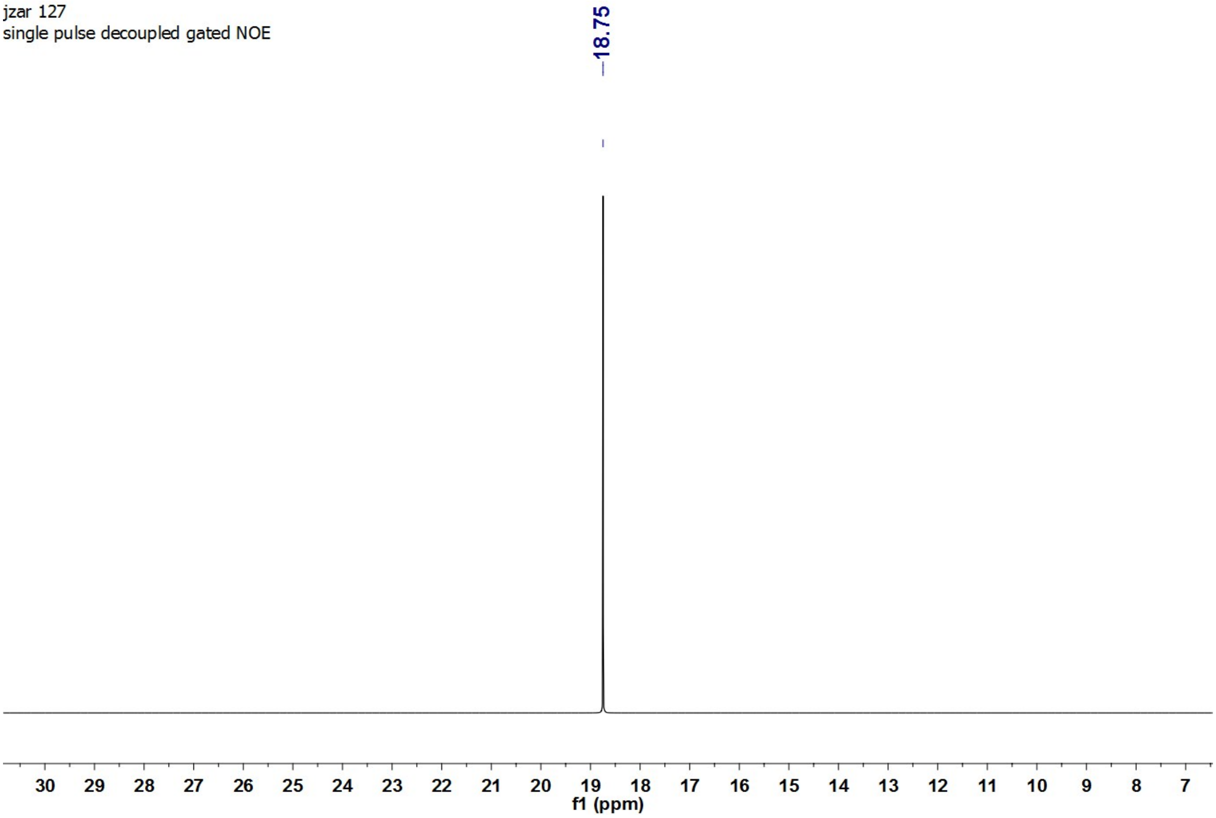

Fig. S7 $^{31}P\{^1H\}$ **NMR (162 MHz, CDCl$_3$, 300K) spectrum of ligand L.**

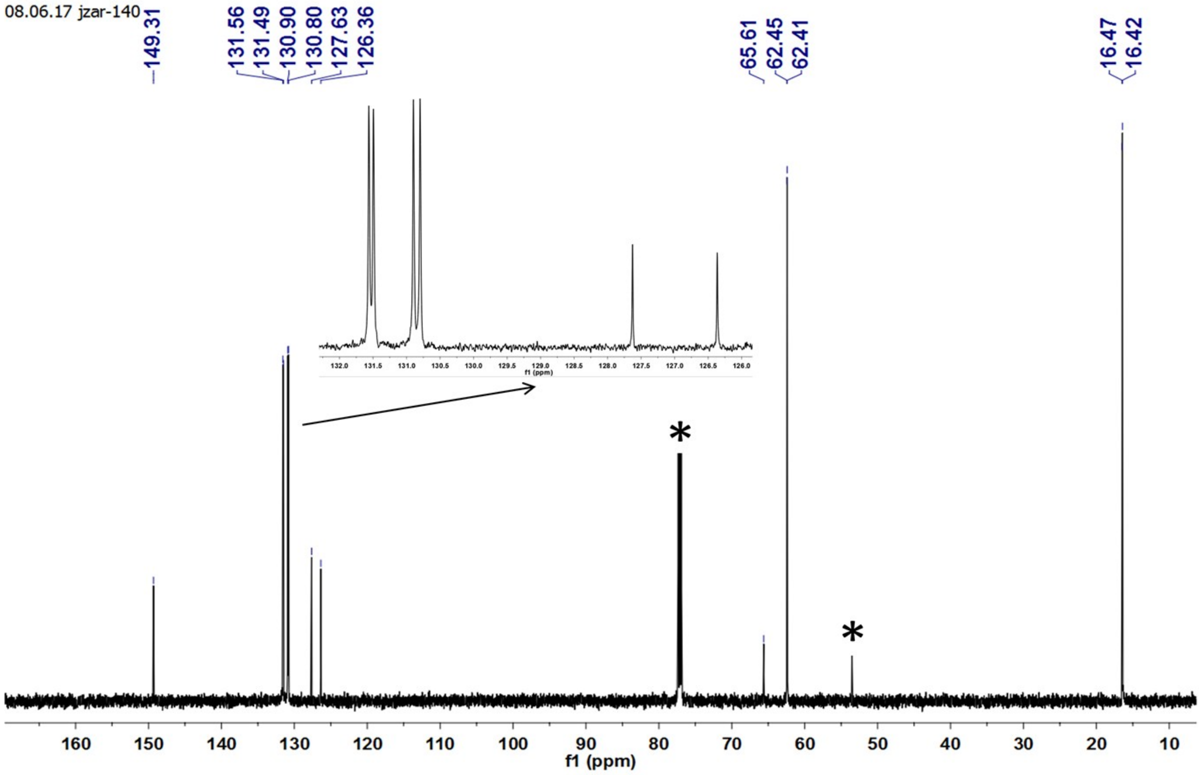

Fig. S8 $^{13}C\{^1H\}$ **NMR (151 MHz, CDCl$_3$, 300K) spectrum of ligand L. Inset shows the aromatic signals in the 132 – 126 ppm region in more detail. With asterisks are indicated signals from CDCl$_3$ and residual CH$_2$Cl$_2$ (77.16 and 53.52 ppm, respectively).**

IR analysis

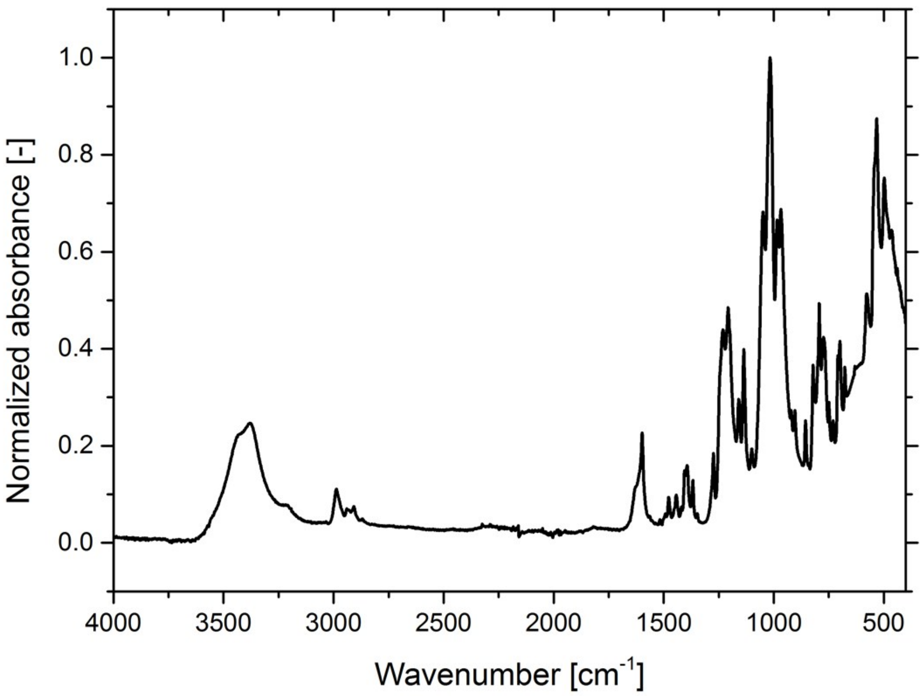

Fig. S9 The medium-infrared (4000 – 400 cm^{-1}) spectrum of 2-Cl.

Table S3. Tentative IR assignments for structure 2-Cl.

2-Cl	**Tentative assignment**
cm^{-1}	
3439.9(vw)	**υ(O-H)**
3381.0(w)	
3210.3(w)	
2987.6(w)	**υ_{as}(C$_{ar}$-H)**
2939.4(vw)	**υ_{symm}(C$_{ar}$-H)**
2931.6(vw)	
2908.5(vw)	**υ_{as}(C$_{aliph}$-H)**
2869.9(vw)	**υ_{sym}(C$_{aliph}$-H)**
1629.4(w)	**δ(H-O-H)**
1597.9(w)	**υ(C=C)**
1491.9(vw)	**ρ(CH$_2$) + ρ(CH$_3$)**
1405.0(w)	**δ(CH$_2$) + δ(CH$_3$) + δ(C$_{ar}$-H)**
1393.5(w)	
1230.5(m)	**υ(P=O)**
1207.4(m)	
1136.0(s)	**breathing**
1049.2(s)	**υ(C-O)**
1016.4(s)	**δ(ring) in plane**
984.6(m)	**υ(PO$_2$)**
968.2(m)	

821.6(m)	**υ(P-O) + δ(ring) + δ(CH$_3$)**
773.4(s)	
708.8(m)	**δ(ring)**
699.2(m)	
577.7(m)	**δ(C-H$_{ar}$) out of plane + δ(PO$_3$)**
532.2(vs)	**δ(C-H) out of plane + δ(PO$_3$)**

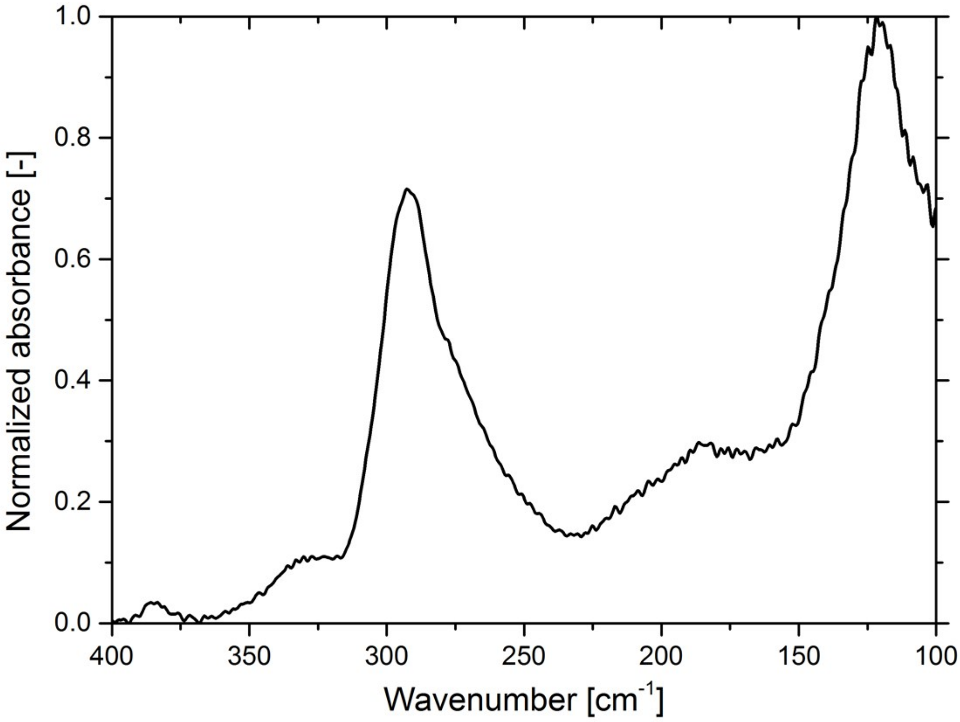

Fig. S10 The far-infrared spectrum (400 – 100 cm^{-1}) of 2-Cl.

Thermogravimetry

Thermal decomposition of **2-Cl** was investigated by heating of the sample in air (80% nitrogen-20% oxygen) atmosphere from 20 to 800 °C is presented in Fig. S11. In general, there are four steps of material decomposition. The first step, which starts just below 100 °C unambiguously corresponds to thermal release of coordination water (for 8 water molecules per $2Co(H_2O)_4^{2+}$•$2CoCl_4^{2-}$·L formula calculated loss is 9.4 %, experimental 9.5 %), which is also confirmed by strong endothermic peak in DTA trace. Next decomposition step, beginning around 120 °C is ascribed to the dissociation of chloride ions, which are probably released in the form of Cl_2 (calculated loss of 8Cl is 18.6 %, experimental 18.2 %). Dissociation of halogen atoms at this temperature from cobalt(II) center has been noted by us previously, and pointed as limiting factor for stability of CPs of this type.[1] Further increase of temperature triggers dealkylation of ligand (which starts at 230 °C, assisted my small peak at DTA trace), and is in agreement with thermal behaviour of the ligand alone.[1] Oxidative atmosphere allows for burning of organic part, which in consequence leads to strong broad exothermic peak in DTA plot.

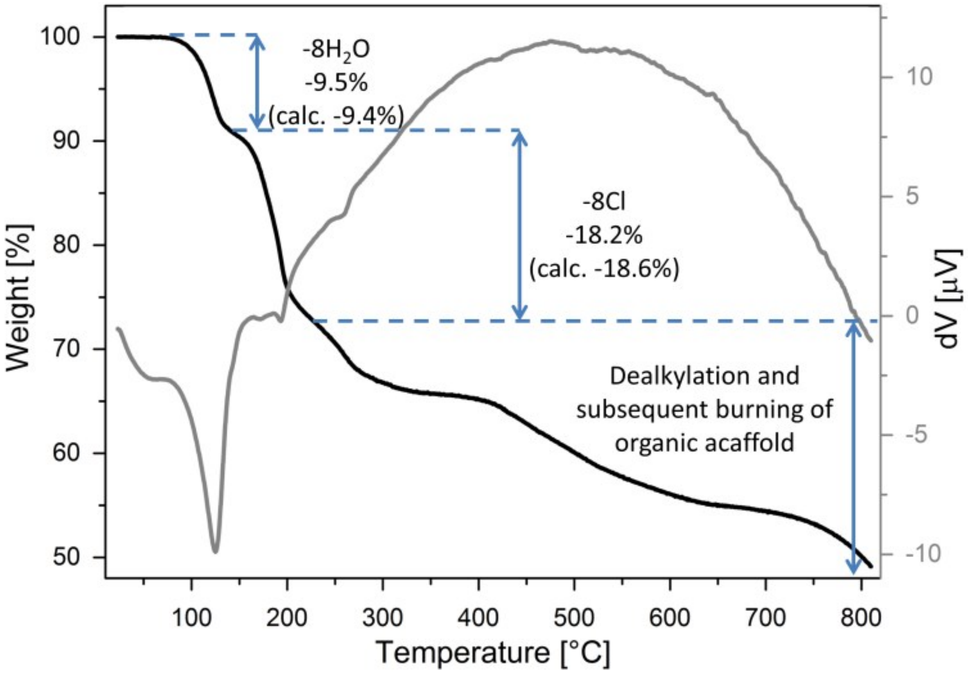

Fig. S11 TGA and DTA curves of 2-Cl with indicated mass losses.

References

1. Zaręba, J. K.; Białek, M. J.; Janczak, J.; Nyk, M.; Zoń, J.; Samoć, M., Beyond Single-Wavelength SHG Measurements: Spectrally-Resolved SHG Studies of Tetraphosphonate Ester Coordination Polymers. *Inorg. Chem.* **2015,** *54*, 10568-10575.