# Supplementary information

**to**

## Union is Strength: π…π Stacking Interactions are Capable to Prevent Solid State Racemization of *tris*-chelate Complexes

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The first reliable observation of temperature- and desolvation-induced solid phase racemization of the entire *tris*-chelates complex is reported. The capability of π…π stacking interactions to prevent such processes was revealed for the first time.

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**Keywords**: *Tris*-chelate complexes; Racemization; Secondary interactions; π…π stacking

## 1. Experimental

### *1.1. Materials*

The following commercial reagents and solvents were used without further purification: hydrated lanthanide nitrates, $Ln(NO_3)_3 \cdot 6H_2O$ (99.99%, Lanhit); $Co(NO_3)_2 \cdot 6H_2O$ (pure for analysis, Chimmed); $Ni(NO_3)_2 \cdot 6H_2O$ (99,999%, Sigma-Aldrich); $Zn(NO_3)_2 \cdot 6H_2O$ (99%, Alfa Aesar); monohydrate of 1,10-phenanthroline, phen$\cdot H_2O$ (99%, Sigma-Aldrich); acetonitrile MeCN (99,9%, LabScan).

### *1.2. Methods*

The X-ray data sets for complexes were collected on a Bruker D8 Venture, Bruker SMART APEX II, and Bruker SMART APEX III diffractometers (graphite monochromated $MoK_\alpha$ radiation sources) [1]. Semi-empirical absorption corrections were applied [2].

The structures were solved by direct methods and using Fourier techniques and were refined by the full-matrix least squares against $F^2$. The hydrogen atoms in compounds were positioned geometrically and refined using the riding model. All calculations were carried out with the use of the SHELX program package [3]. The crystallographic parameters and the refinement statistics are given in Tables S1, S2, S5-S7.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC 2212844, 2212845, 2295260-2295262, 2295266, 2295269, 2295270-2295276, 2295278, 2295280-2295283, 2295285, 2295286, 2295288, 2295291, 2295292, 2295294, 2295295, 2295321, 2295322, 2313463-2313465. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

The powder X-ray diffraction patterns were recorded on Bruker D8 ADVANCE X-Ray Diffractometer ($CuK_\alpha$, Ni-filter, LYNXEYE detector, reflection geometry).

### *1.3. Synthesis of complexes*

Complex *$[Co(phen)_3][Tb(NO_3)_5] \cdot 3MeCN$* (**CoTb_3MeCN**) and other **MLn_3MeCN** species were prepared similarly to the previously reported procedure [4,5], namely *via* the interaction of $M(NO_3)_2 \cdot 6H_2O$ (0.7 mmol) with phen$\cdot H_2O$ (0.41 g; 2.1 mmol) and then $Ln(NO_3)_3 \cdot 6H_2O$ (0.7 mmol) in hot (80 °C) MeCN followed by the evaporation of this solution by means of water jet pump. On cooling to room temperature, well crystalline single phase (powder XRD, Fig. S3a,S6) complexes precipitated in moderate yields of 50-60 %.

Single crystals of *[Co(phen)$_3$][Tb(NO$_3$)$_5$] (***CoTb***)* and other *[M(phen)$_3$][Ln(NO$_3$)$_5$] (***MLn***)* suitable for unambiguous structural determination were isolated from the syntheses performed similarly to that of **MLn_3MeCN** except for the replacement of MeCN with MeOH.

Complexes *[M(phen)$_3$][La(NO$_3$)$_5$(Phen)]·3MeCN (***CoLaPhen_3MeCN***)* and other **MLnPhen_3MeCN** species were prepared as follows. Solid M(NO$_3$)$_2$·6H$_2$O (0.17 mmol) were dissolved in 40 ml of MeCN on heating to 80 °C. In the resulting hot solutions, solid phen·H$_2$O (0.135 g; 0.68 mmol) was dissolved on stirring. After that, a solution of La(NO$_3$)$_3$·6H$_2$O (0.074 g; 0.17 mmol) in 10 ml of MeCN was quickly added. In 1-2 minutes, rapid and almost quantitative precipitation of fine-crystalline products began. According to powder XRD (Fig. S10-S15), **MLnPhen_3MeCN** phases initially formed in the syntheses start to rapidly lose lattice MeCN molecules just after the isolation from the mother liquor yielding pure **MLnPhen** phases.

Single crystals of **CoLaPhen_3MeCN** and other *[M(phen)$_3$][La(NO$_3$)$_5$(phen)]·3MeCN* species were obtained upon the interaction of the mentioned amounts of reactants in the joint mother liquor of three repeated syntheses performed in the above described manner with the addition of few crystals of corresponding complex along with 3 drops of H$_2$O.

*References*


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3. G. Sheldrick, Acta Crystallogr C, 2015, 71, 3-8.
4. A.V. Gavrikov, A.B. Ilyukhin, E.V. Belova, A.D. Yapryntsev, Zh.V. Dobrokhotova, A.V. Khrushcheva, N.N. Efimov, *Ceram. Int.* **2020**, 46, 13014.
5. A.V. Gavrikov, A.B. Ilyukhin, E.V. Belova, A.D. Yapryntsev, A.V. Khrushcheva, A.S. Loktev, *Appl. Organomet. Chem.* **2022**, 36, e6519.

## 2. Discussion of the synthesis

Complexes **MLn_3MeCN** were produced according to the reported procedures [1]. For each of studied M/Ln combinations, the solubility of corresponding complex was sufficient to isolate well-crystalline species, although in moderate yields. Given the results of [1], one can conclude that complexes of $[M(phen)_3][Ln(NO_3)_5]\cdot 3MeCN$ type are formed for both light and heavy lanthanides when 3 equivalents of phen ligand per 1 equivalent of both $M^{2+}$ and $Ln^{3+}$ are involved in the syntheses. The only previously known known exception is lanthanum triply charged cation of which possesses largest radii among the $Ln^{3+}$ series [2,3]. As a result, binding with additional ligands takes place yielding $[M(phen)_3][La(NO_3)_5(Solv)_2]\cdot xSolv$ (Solv = $H_2O$, MeCN) complexes with 12-coordinated $La^{3+}$ [4].

This difference was exploited upon the elaboration of $[M(phen)_3][Ln(NO_3)_5(phen)]\cdot 3MeCN$ (**MLnPhen_3MeCN**) complexes in which higher coordination requirements of $Ln^{3+}$ are fulfilled due to fourth equivalent of phen introduced in the syntheses. Noteworthy, although such complexes can be formed by cations of other light lanthanides ($Nd^{3+}$, $Sm^{3+}$) along with $La^{3+}$, these cations do not form $[M(phen)_3][Ln(NO_3)_5(Solv)_2]\cdot xSolv$ complexes with two monodentate molecules of donating solvents as monodentate auxilary ligands. This is apparently due to the fact that coordination of phen ligands yielding stable 5-membered chelating cycles is much more favorable compared to the coordination of monodentate ligands.

For **MLaPhen_3MeCN** series, structure was previously established for Ni derivative [4]. This allowed identifying formation of these species by powder XRD. However, it turns out to be a challenge to grow single crystals of sufficient quality for all these systems. Almost quantitative precipitation of **MLnPhen_3MeCN** as tiny (tens of mm) and thin flake-like crystals rapidly occurred in the initial syntheses without any evaporation, and we failed to isolate single crystals suitable for XRD from these samples. Moreover, repeating syntheses did not yield appropriate single crystals as well. Such low solubility, compared to **MLn_3MeCN** series, is apparently due to fourth phen molecule forming $[La(NO_3)_5(phen)]^{2-}$ moieties. As will be shown below, this phen ligand participates in the π…π stacking with phen of $[M(phen)_3]^{2+}$ moieties. Given the similarity in compositions and structures of two studied series, we believe it is the joint effect of π…π stacking which determines low solubility of $[M(phen)_3][La(NO_3)_5(phen)]\cdot 3MeCN$ series. The addition of $H_2O$ upon the syntheses of well crystalline *$[M(phen)_3][La(NO_3)_5(phen)]\cdot 3MeCN$* were made to considerably increase the solubility of complexes. As a result, single crystals suitable for structural studies were isolated in each the case.

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**Table S1.** Crystal data and structure refinement for **MLn_3MeCN** and corresponding desolvated structures.

| Identification code | **CoTb_3MeCN** | **CoTb_MeCN** | **CoTb** * | **CoTb** ** |
|---|---|---|---|---|
| Empirical formula | $C_{42}H_{33}CoN_{14}O_{15}Tb$ | $C_{38}H_{27}CoN_{14}O_{15}Tb$ | $C_{36}H_{24}CoN_{14}O_{15}Tb$ | $C_{36}H_{24}CoN_{14}O_{15}Tb$ |
| Formula weight | 1191.67 | 1109.56 | 1068.51 | 1068.51 |
| Temperature, K | 150(2) | 150(2) | 100(2) | 150(2) |
| Wavelength, Å | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | Orthorhombic | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P2_12_12_1$ | C2 | $P2_1/n$ | $P2_1/n$ |
| a, Å | 12.6274(9) | 27.417(2) | 17.849(3) | 17.8139(6) |
| b, Å | 17.4622(13) | 13.0209(12) | 12.469(2) | 12.4929(4) |
| c, Å | 21.5945(16) | 27.138(2) | 19.337(3) | 19.4102(7) |
| β, ° | 90 | 104.446(3) | 110.991(5) | 110.7820(10) |
| Volume, $Å^3$ | 4761.6(6) | 9381.8(13) | 4018.0(11) | 4038.6(2) |
| Z | 4 | 8 | 4 | 4 |
| D (calc), $Mg/m^3$ | 1.662 | 1.571 | 1.766 | 1.757 |
| μ, $mm^{-1}$ | 1.905 | 1.926 | 2.244 | 2.233 |
| F(000) | 2380 | 4408 | 2116 | 2116 |
| Crystal size, mm | 0.36 x 0.24 x 0.12 | 0.24 x 0.18 x 0.10 | 0.26 x 0.18 x 0.12 | 0.30 x 0.24 x 0.14 |
| θ range, ° | 2.202, 28.306 | 2.201, 25.525 | 2.040, 20.813 | 2.038, 32.607 |
| Index ranges | -16<=h<=16<br>-23<=k<=23<br>-28<=l<=28 | -33<=h<=33<br>-15<=k<=15<br>-32<=l<=32 | -17<=h<=17<br>-12<=k<=12<br>-19<=l<=19 | -26<=h<=26<br>-18<=k<=18<br>-29<=l<=28 |
| Reflections collected | 67606 | 70199 | 33340 | 61178 |
| Independent reflections, Rint | 11827, 0.0425 | 17064, 0.0918 | 4259, 0.2299 | 14431, 0.0479 |
| Completeness to θ = 25.242° | 99.9 % | 99.8 % | 99.8 % | 100.0 % |
| Absorption correction | Semi-empirical from equivalents | Semi-empirical from equivalents | none | Semi-empirical from equivalents |
| Max,. min. transmission | 0.7457, 0.5769 | 0.7452, 0.6248 | | 0.7464, 0.4828 |
| Refinement method | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 11827 / 12 / 647 | 17064 / 271 / 1152 | 4259 / 0 / 268 | 14431 / 54 / 629 |
| Goodness-of-fit | 1.075 | 1.179 | 1.365 | 0.993 |
| R1, wR2 [I>2sigma(I)] | 0.0296, 0.0727 | 0.0836, 0.1960 | 0.1549, 0.3743 | 0.0316, 0.0691 |
| R1, wR2 (all data) | 0.0337, 0.0744 | 0.1071, 0.2126 | 0.1665, 0.3876 | 0.0495, 0.0763 |
| Absolute structure parameter | -0.011(3) | | | |
| Largest diff. peak and hole, $e.Å^{-3}$ | 0.592, -0.660 | 3.267, -1.954 | 3.943, -2.575 | 1.734, -0.698 |
| CCDC Number | 2212845 | 2295260 | | 2212844 |

***** Experimental data were obtained on "single crystal" formed *via* the desolvation of **CoTb_3MeCN** single crystal.

****** Experimental data were obtained on single crystal grown in MeOH (see *p. 1.2.* of SI).

| Identification code | **CoY_3MeCN** | **CoY** | **NiY_3MeCN_100K** | **NiY_3MeCN_300K** | **NiY** |
|---|---|---|---|---|---|
| Empirical formula | $C_{42}H_{33}CoN_{14}O_{15}Y$ | $C_{36}H_{24}CoN_{11}O_{15}Y$ | $C_{42}H_{33}N_{14}NiO_{15}Y$ | $C_{42}H_{33}N_{14}NiO_{15}Y$ | $C_{36}H_{24}N_{11}NiO_{15}Y$ |
| Formula weight | 1121.66 | 998.50 | 1121.44 | 1121.44 | 998.28 |
| Temperature, K | 100(2) | 150(2) | 100(2) | 300(2) | 150(2) |
| Wavelength, Å | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | Orthorhombic | Monoclinic | Orthorhombic | Orthorhombic | Monoclinic |
| Space group | $P2_12_12_1$ | $P2_1/n$ | $P2_12_12_1$ | $P2_12_12_1$ | $P2_1/n$ |
| a, Å | 12.6020(5) | 17.7823(6) | 12.6828(4) | 12.8340(6) | 17.7131(4) |
| b, Å | 17.3989(7) | 12.4756(4) | 17.3643(6) | 17.5509(9) | 12.4943(3) |
| c, Å | 21.5392(10) | 19.4154(7) | 21.4063(8) | 21.6296(12) | 19.3020(5) |
| β, ° | 90 | 110.8480(10) | 90 | 90 | 110.6110(10) |
| Volume, $Å^3$ | 4722.7(3) | 4025.2(2) | 4714.3(3) | 4872.0(4) | 3998.35(17) |
| Z | 4 | 4 | 4 | 4 | 4 |
| D (calc), $Mg/m^3$ | 1.578 | 1.648 | 1.580 | 1.529 | 1.658 |
| μ, $mm^{-1}$ | 1.658 | 1.932 | 1.708 | 1.653 | 2.001 |
| F(000) | 2276 | 2012 | 2280 | 2280 | 2016 |
| Crystal size, mm | 0.22 x 0.14 x 0.12 | 0.30 x 0.30 x 0.12 | 0.30 x 0.24 x 0.16 | 0.30 x 0.24 x 0.16 | 0.40 x 0.32 x 0.18 |
| θ range, ° | 2.208, 28.347 | 2.109, 28.727 | 2.204, 31.518 | 2.180, 26.391 | 2.112, 29.598 |
| Index ranges | -16<=h<=16 | -24<=h<=24 | -18<=h<=18 | -16<=h<=16 | -24<=h<=24 |
| | -23<=k<=23 | -16<=k<=16 | -25<=k<=25 | -21<=k<=21 | -17<=k<=17 |
| | -28<=l<=28 | -26<=l<=26 | -31<=l<=31 | -27<=l<=27 | -26<=l<=26 |
| Reflections collected | 73220 | 51084 | 60288 | 47337 | 53619 |
| Independent reflections, Rint | 11750, 0.0795 | 10422, 0.0641 | 15187, 0.0485 | 9958, 0.0843 | 11238, 0.0565 |
| Completeness to θ = 25.242° | 99.9 % | 99.9 % | 99.8 % | 99.9 % | 99.9 % |
| Absorption correction | Semi-empirical | Semi-empirical | Semi-empirical | Semi-empirical | Semi-empirical |
| | from equivalents | from equivalents | from equivalents | from equivalents | from equivalents |
| Max,. min. transmission | 0.7457, 0.6137 | 0.7458, 0.5637 | 0.7462, 0.6624 | 0.7454, 0.5936 | 0.7459, 0.526 |
| Refinement method | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 11750 / 12 / 649 | 10422 / 18 / 593 | 15187 / 12 / 648 | 9958 / 12 / 621 | 11238 / 36 / 593 |
| Goodness-of-fit | 1.086 | 0.958 | 1.009 | 1.023 | 1.002 |
| R1, wR2 [I>2sigma(I)] | 0.0463, 0.0948 | 0.0398, 0.0869 | 0.0387, 0.0781 | 0.0592, 0.1350 | 0.0387, 0.0868 |
| R1, wR2 (all data) | 0.0568, 0.0984 | 0.0714, 0.0998 | 0.0566, 0.0842 | 0.1107, 0.1592 | 0.0691, 0.0985 |
| Absolute structure parameter | -0.007(3) | | 0.456(4) | 0.481(11) | |
| Largest diff. peak and hole, $e.Å^{-3}$ | 0.687, -0.544 | 0.591, -0.483 | 0.528, -0.597 | 0.703, -0.405 | 0.648, -0.565 |
| CCDC Number | 2295274 | 2295269 | 2295272 | 2295270 | 2295266 |

| Identification code | **ZnY_3MeCN_100K** | **ZnY_3MeCN_200K** | **ZnY** | **CoDy_3MeCN_100K** | **CoDy_3MeCN_173K** | **CoDy** |
|---|---|---|---|---|---|---|
| Empirical formula | $C_{42}H_{33}N_{14}O_{15}YZn$ | $C_{42}H_{33}N_{14}O_{15}YZn$ | $C_{36}H_{24}N_{11}O_{15}YZn$ | $C_{42}H_{33}CoDyN_{14}O_{15}$ | $C_{42}H_{33}CoDyN_{14}O_{15}$ | $C_{36}H_{24}CoDyN_{11}O_{15}$ |
| Formula weight | 1128.10 | 1128.10 | 1004.94 | 1195.25 | 1195.25 | 1072.09 |
| Temperature, K | 100(2) | 200(2) | 150(2) | 103(2) | 173(2) | 150(2) |
| Wavelength, Å | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | Orthorhombic | Orthorhombic | Monoclinic | Orthorhombic | Orthorhombic | Monoclinic |
| Space group | $P2_12_12_1$ | $P2_12_12_1$ | $P2_1/n$ | $P2_12_12_1$ | $P2_12_12_1$ | $P2_1/n$ |
| a, Å | 12.6890(7) | 12.7677(7) | 17.8105(5) | 12.5969(5) | 12.6343(3) | 17.7940(4) |
| b, Å | 17.3285(8) | 17.4140(8) | 12.4596(5) | 17.4194(7) | 17.4984(4) | 12.4847(3) |
| c, Å | 21.5711(9) | 21.6944(10) | 19.4286(6) | 21.5508(9) | 21.6439(5) | 19.4090(4) |
| β, ° | 90 | 90 | 110.5440(10) | 90 | 90 | 110.8510(10) |
| Volume, $Å^3$ | 4743.1(4) | 4823.5(4) | 4037.2(2) | 4728.9(3) | 4785.03(19) | 4029.38(16) |
| Z | 4 | 4 | 4 | 4 | 4 | 4 |
| D (calc), $Mg/m^3$ | 1.580 | 1.553 | 1.653 | 1.679 | 1.659 | 1.767 |
| μ, $mm^{-1}$ | 1.807 | 1.777 | 2.110 | 2.003 | 1.979 | 2.337 |
| F(000) | 2288 | 2288 | 2024 | 2384 | 2384 | 2120 |
| Crystal size, mm | 0.32 x 0.24 x 0.24 | 0.32 x 0.24 x 0.24 | 0.16 x 0.12 x 0.04 | 0.22 x 0.18 x 0.16 | 0.40 x 0.24 x 0.18 | 0.36 x 0.3 x 0.2 |
| θ range, ° | 2.202, 30.111 | 2.189, 28.346 | 2.239, 27.104 | 2.208, 28.319 | 2.200, 31.508 | 2.040, 31.010 |
| Index ranges | -17<=h<=17 | -17<=h<=17 | -22<=h<=22 | -16<=h<=16 | -18<=h<=18 | -25<=h<=24 |
| | -24<=k<=24 | -23<=k<=23 | -15<=k<=12 | -23<=k<=23 | -25<=k<=24 | -17<=k<=18 |
| | -30<=l<=30 | -28<=l<=28 | -24<=l<=24 | -28<=l<=28 | -31<=l<=31 | -27<=l<=27 |
| Reflections collected | 67727 | 68170 | 35818 | 80282 | 68854 | 56647 |
| Independent reflections, Rint | 13866, 0.0793 | 11884, 0.0711 | 8877, 0.0743 | 11731, 0.0909 | 15064, 0.0409 | 12597, 0.0350 |
| Completeness to θ = 25.242° | 99.9 % | 99.8 % | 99.8 % | 99.9 % | 99.9 % | 100.0 % |
| Absorption correction | Semi-empirical from equivalents | Semi-empirical from equivalents | Semi-empirical from equivalents | Semi-empirical from equivalents | Semi-empirical from equivalents | Semi-empirical from equivalents |
| Max,. min. transmission | 0.746, 0.5777 | 0.7457, 0.5913 | 0.7455, 0.6354 | 0.7457, 0.6649 | | 0.7462, 0.461 |
| Refinement method | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 13866 / 12 / 653 | 11884 / 12 / 653 | 8877 / 66 / 614 | 11731 / 12 / 653 | 15064 / 12 / 652 | 12597 / 36 / 593 |
| Goodness-of-fit | 1.040 | 1.053 | 1.080 | 1.039 | 0.993 | 1.068 |
| R1, wR2 [I>2sigma(I)] | 0.0420, 0.0779 | 0.0397, 0.0766 | 0.0429, 0.0683 | 0.0365, 0.0791 | 0.0287, 0.0664 | 0.0273, 0.0699 |
| R1, wR2 (all data) | 0.0683, 0.0890 | 0.0671, 0.0878 | 0.0827, 0.0765 | 0.0487, 0.0883 | 0.0344, 0.0688 | 0.0363, 0.0741 |
| Absolute structure parameter | 0.062(6) | 0.071(6) | | 0.090(11) | -0.004(3) | |
| Largest diff. peak and hole, $e.Å^{-3}$ | 0.579, -0.468 | 0.359, -0.380 | 0.570, -0.596 | 0.977, -1.161 | 0.793, -0.515 | 1.432, -0.876 |
| CCDC Number | 2295271 | 2295275 | 2295261 | 2295276 | 2295273 | 2295262 |

**Table S2.** Crystal data and structure refinement for **MLnPhen_3MeCN** and corresponding desolvated structures.

| Identification code | **CoLaPhen_3MeCN_150K** | **CoLaPhen_3MeCN_250K** | **CoLaPhen_3MeCN_350K** | **CoLaPhen_400K** | **CoLaPhen_400_150K*** |
|---|---|---|---|---|---|
| Empirical formula | $C_{54}H_{41}CoLaN_{16}O_{15}$ | $C_{54}H_{41}CoLaN_{16}O_{15}$ | $C_{54}H_{41}CoLaN_{16}O_{15}$ | $C_{48}H_{32}CoLaN_{16}O_{15}$ | $C_{48}H_{32}CoLaN_{16}O_{15}$ |
| Formula weight | 1351.87 | 1351.87 | 1351.87 | 1228.70 | 1228.70 |
| Temperature, K | 150(2) | 250(2) | 350(2) | 400(2) | 150(2) |
| Wavelength, Å | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | Orthorhombic | Orthorhombic | Orthorhombic | Orthorhombic | Orthorhombic |
| Space group | $P2_12_12_1$ | $P2_12_12_1$ | $P2_12_12_1$ | $P2_12_12_1$ | $P2_12_12_1$ |
| a, Å | 12.4723(8) | 12.5205(4) | 12.5614(18) | 12.6555(6) | 12.4652(6) |
| b, Å | 20.1964(10) | 20.2855(5) | 20.372(3) | 17.9417(8) | 17.7628(8) |
| c, Å | 22.0456(11) | 22.2201(6) | 22.451(3) | 22.6477(10) | 22.4407(10) |
| Volume, $Å^3$ | 5553.2(5) | 5643.6(3) | 5745.1(13) | 5142.4(4) | 4968.7(4) |
| Z | 4 | 4 | 4 | 4 | 4 |
| D (calc), $Mg/m^3$ | 1.617 | 1.591 | 1.563 | 1.587 | 1.643 |
| μ, $mm^{-1}$ | 1.142 | 1.124 | 1.104 | 1.223 | 1.266 |
| F(000) | 2724 | 2724 | 2724 | 2460 | 2460 |
| Crystal size, mm | 0.28 x 0.24 x 0.20 | 0.28 x 0.24 x 0.20 | 0.28 x 0.24 x 0.20 | 0.28 x 0.24 x 0.20 | 0.28 x 0.24 x 0.20 |
| θ range, ° | 2.105, 30.528 | 2.090, 27.114 | 2.071, 26.470 | 2.127, 26.422 | 2.147, 26.398 |
| Index ranges | -17<=h<=17<br>-28<=k<=24<br>-31<=l<=31 | -16<=h<=16<br>-26<=k<=22<br>-28<=l<=28 | -15<=h<=15<br>-25<=k<=22<br>-27<=l<=28 | -15<=h<=15<br>-20<=k<=22<br>-28<=l<=28 | -15<=h<=15<br>-19<=k<=22<br>-27<=l<=28 |
| Reflections collected | 63103 | 52511 | 45248 | 39963 | 39790 |
| Independent reflections, Rint | 16863, 0.0474 | 12440, 0.0399 | 11750, 0.0974 | 10561, 0.0654 | 10164, 0.0869 |
| Completeness to θ = 25.242° | 99.9 % | 99.9 % | 99.7 % | 99.9 % | 99.9 % |
| Absorption correction | Semi-empirical from equivalents | Semi-empirical from equivalents | Semi-empirical from equivalents | Semi-empirical from equivalents | Semi-empirical from equivalents |
| Max,. min. transmission | 0.7461, 0.6662 | 0.7455, 0.6817 | 0.7454, 0.5958 | 0.7454, 0.6251 | 0.7454, 0.6391 |
| Refinement method | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 16863 / 0 / 787 | 12440 / 0 / 787 | 11750 / 3 / 788 | 10561 / 0 / 703 | 10164 / 0 / 703 |
| Goodness-of-fit | 1.022 | 1.000 | 1.201 | 1.044 | 1.038 |
| R1, wR2 [I>2sigma(I)] | 0.0347, 0.0588 | 0.0281, 0.0503 | 0.0972, 0.2523 | 0.0499, 0.0648 | 0.0348, 0.0683 |
| R1, wR2 (all data) | 0.0478, 0.0629 | 0.0346, 0.0527 | 0.1297, 0.2720 | 0.1175, 0.0791 | 0.0429, 0.0715 |
| Absolute structure parameter | -0.013(4) | -0.025(4) | 0.05(5) | -0.009(6) | -0.008(7) |
| Largest diff. peak and hole, $e.Å^{-3}$ | 0.383, -0.580 | 0.268, -0.324 | 3.596, -1.410 | 0.390, -0.348 | 0.751, -0.779 |
| CCDC Number | 2295321 | 2295283 | 2295295 | 2295288 | 2295322 |

*These data were obtained from the single crystal heated to 400 K, then cooled to 150 K.

**Table S2 (continued)**

| Identification code | **NiLaPhen_3MeCN_100K** | **NiLaPhen_3MeCN_340K** | **NiLaPhen_3MeCN_360K** | **NiLaPhen_400K** |
|---|---|---|---|---|
| Empirical formula | $C_{54}H_{41}LaN_{16}NiO_{15}$ | $C_{54}H_{41}LaN_{16}NiO_{15}$ | $C_{54}H_{41}LaN_{16}NiO_{15}$ | $C_{48}H_{32}LaN_{13}NiO_{15}$ |
| Formula weight | 1351.65 | 1351.65 | 1351.65 | 1228.48 |
| Temperature, K | 100(2) | 340(2) | 360(2) | 400(2) |
| Wavelength, Å | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | Orthorhombic | Orthorhombic | Orthorhombic | Orthorhombic |
| Space group | $P2_12_12_1$ | $P2_12_12_1$ | $P2_12_12_1$ | $P2_12_12_1$ |
| a, Å | 12.4224(4) | 12.5426(18) | 12.555(2) | 12.660(2) |
| b, Å | 20.0351(9) | 20.322(4) | 20.342(4) | 17.879(4) |
| c, Å | 22.1111(10) | 22.424(4) | 22.458(5) | 22.640(5) |
| Volume, $Å^3$ | 5503.1(4) | 5715.7(17) | 5735.6(19) | 5124.5(18) |
| Z | 4 | 4 | 4 | 4 |
| D (calc), $Mg/m^3$ | 1.631 | 1.571 | 1.565 | 1.592 |
| μ, $mm^{-1}$ | 1.193 | 1.149 | 1.145 | 1.271 |
| F(000) | 2728 | 2728 | 2728 | 2464 |
| Crystal size, mm | 0.20 x 0.20 x 0.12 | 0.20 x 0.20 x 0.12 | 0.20 x 0.20 x 0.12 | 0.20 x 0.20 x 0.12 |
| θ range, ° | 2.104, 26.387 | 2.074, 26.474 | 2.072, 26.431 | 2.129, 25.443 |
| Index ranges | -14<=h<=14<br>-25<=k<=23<br>-27<=l<=27 | -14<=h<=15<br>-25<=k<=24<br>-27<=l<=27 | -14<=h<=14<br>-25<=k<=24<br>-27<=l<=27 | -14<=h<=14<br>-20<=k<=21<br>-27<=l<=27 |
| Reflections collected | 30715 | 31681 | 31642 | 26141 |
| Independent reflections, Rint | 10215, 0.1508 | 10684, 0.1252 | 10690, 0.1515 | 8797, 0.1253 |
| Completeness to θ = 25.242° | 96.8 % | 97.0 % | 96.7 % | 94.3 % |
| Absorption correction | Semi-empirical from equivalents | Semi-empirical from equivalents | Semi-empirical from equivalents | Semi-empirical from equivalents |
| Max,. min. transmission | 0.7453, 0.6190 | 0.7443, 0.6421 | 0.7441, 0.5979 | 0.7441, 0.5761 |
| Refinement method | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 10215 / 12 / 787 | 10684 / 0 / 737 | 10690 / 8 / 737 | 8797 / 456 / 703 |
| Goodness-of-fit | 0.856 | 0.858 | 0.909 | 0.735 |
| R1, wR2 [I>2sigma(I)] | 0.0442, 0.0917 | 0.0508, 0.0912 | 0.0572, 0.1060 | 0.0472, 0.1103 |
| R1, wR2 (all data) | 0.0604, 0.0995 | 0.1233, 0.1106 | 0.1527, 0.1285 | 0.1588, 0.1608 |
| Absolute structure parameter | -0.025(12) | -0.049(15) | 0.010(17) | 0.008(15) |
| Largest diff. peak and hole, $e.Å^{-3}$ | 0.642, -0.493 | 0.545, -0.487 | 0.504, -0.494 | 0.313, -0.397 |
| CCDC Number | 2295282 | 2295291 | 2295292 | 2295278 |

**Table S2 (continued)**

| Identification code | **ZnLaPhen_3MeCN_100K** | **ZnLaPhen_350_100K** | **CoNdPhen_3MeCN_100K** | **CoNdPhen_3MeCN_296K** | **CoNdPhen_390_100K** |
|---|---|---|---|---|---|
| Empirical formula | $C_{54}H_{41}LaN_{16}O_{15}Zn$ | $C_{48}H_{32}LaN_{13}O_{15}Zn$ | $C_{54}H_{41}CoN_{16}NdO_{15}$ | $C_{54}H_{41}CoN_{16}NdO_{15}$ | $C_{48}H_{32}CoN_{13}NdO_{15}$ |
| Formula weight | 1358.31 | 1235.14 | 1357.20 | 1357.20 | 1234.03 |
| Temperature, K | 100(2) | 100(2) | 100(2) | 296(2) | 100(2) |
| Wavelength, Å | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | Orthorhombic | Orthorhombic | Orthorhombic | Orthorhombic | Orthorhombic |
| Space group | $P2_12_12_1$ | $P2_12_12_1$ | $P2_12_12_1$ | $P2_12_12_1$ | $P2_12_12_1$ |
| a, Å | 12.4889(8) | 12.4662(18) | 12.4132(7) | 12.5118(16) | 12.453(4) |
| b, Å | 20.1897(13) | 17.717(3) | 20.1554(12) | 20.320(3) | 17.820(6) |
| c, Å | 21.9131(17) | 22.612(3) | 22.0770(13) | 22.341(3) | 22.217(8) |
| Volume, $Å^3$ | 5525.3(7) | 4994.2(13) | 5523.5(6) | 5680.0(13) | 4930(3) |
| Z | 4 | 4 | 4 | 4 | 4 |
| D (calc), $Mg/m^3$ | 1.633 | 1.643 | 1.632 | 1.587 | 1.663 |
| μ, $mm^{-1}$ | 1.282 | 1.408 | 1.315 | 1.279 | 1.462 |
| F(000) | 2736 | 2472 | 2736 | 2736 | 2472 |
| Crystal size, mm | 0.24 x 0.20 x 0.04 | 0.24 x 0.20 x 0.04 | 0.20 x 0.14 x 0.12 | 0.28 x 0.20 x 0.16 | 0.20 x 0.14 x 0.12 |
| θ range, ° | 2.115, 30.080 | 2.137, 26.528 | 2.104, 28.304 | 2.080, 28.274 | 2.160, 20.815 |
| Index ranges | -17<=h<=17<br>-26<=k<=28<br>-30<=l<=30 | -15<=h<=15<br>-22<=k<=21<br>-27<=l<=27 | -16<=h<=16<br>-26<=k<=26<br>-29<=l<=29 | -16<=h<=16<br>-27<=k<=27<br>-27<=l<=29 | -12<=h<=12<br>-17<=k<=17<br>-21<=l<=22 |
| Reflections collected | 61717 | 52773 | 82157 | 109150 | 34180 |
| Independent reflections, Rint | 15620, 0.0590 | 9367, 0.1808 | 13713, 0.0703 | 13900, 0.0664 | 5162, 0.1390 |
| Completeness to θ = 25.242° | 99.9 % | 99.9 % | 99.9 % | 99.8 % | 99.8 % |
| Absorption correction | Semi-empirical from equivalents | Semi-empirical from equivalents | Semi-empirical from equivalents | Semi-empirical from equivalents | Semi-empirical from equivalents |
| Max,. min. transmission | 0.746, 0.6375 | 0.4901, 0.3935 | 0.2627, 0.1985 | 0.7457, 0.6445 | 0.7412, 0.5697 |
| Refinement method | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 15620 / 0 / 787 | 9367 / 456 / 705 | 13713 / 0 / 787 | 13900 / 0 / 787 | 5162 / 461 / 695 |
| Goodness-of-fit | 0.997 | 1.184 | 1.082 | 0.950 | 1.438 |
| R1, wR2 [I>2sigma(I)] | 0.0337, 0.0568 | 0.0938, 0.2497 | 0.0329, 0.0588 | 0.0543, 0.1105 | 0.1429, 0.3434 |
| R1, wR2 (all data) | 0.0488, 0.0617 | 0.2140, 0.2816 | 0.0429, 0.0636 | 0.0622, 0.1141 | 0.1461, 0.3452 |
| Absolute structure parameter | -0.015(5) | 0.06(6) | -0.075(5) | -0.019(4) | 0.15(10) |
| Largest diff. peak and hole, $e.Å^{-3}$ | 0.384, -0.566 | 3.183, -2.870 | 0.516, -0.452 | 1.020, -1.286 | 3.072, -2.798 |
| CCDC Number | 2295286 | 2295280 | 2295285 | 2295294 | 2295281 |

**Table S2 (continued)**

| Identification code | **CoSmPhen_3MeCN_100K** | **CoSmPhen_3MeCN_300K** | **CoSmPhen_380K** |
|---|---|---|---|
| Empirical formula | $C_{54}H_{41}CoN_{16}O_{15}Sm$ | $C_{54}H_{41}CoN_{16}O_{15}Sm$ | $C_{48}H_{32}CoN_{13}O_{15}Sm$ |
| Formula weight | 1363.31 | 1363.31 | 1240.14 |
| Temperature, K | 100(2) | 300(2) | 380(2) |
| Wavelength, Å | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | Orthorhombic | Orthorhombic | Orthorhombic |
| Space group | $P2_12_12_1$ | $P2_12_12_1$ | $P2_12_12_1$ |
| a, Å | 12.4061(10) | 12.4812(7) | 12.6065(14) |
| b, Å | 20.1133(17) | 20.2883(13) | 17.9940(17) |
| c, Å | 21.9689(19) | 22.2801(15) | 22.460(2) |
| Volume, $Å^3$ | 5481.8(8) | 5641.8(6) | 5094.9(9) |
| Z | 4 | 4 | 4 |
| D (calc), $Mg/m^3$ | 1.652 | 1.605 | 1.617 |
| μ, $mm^{-1}$ | 1.449 | 1.408 | 1.549 |
| F(000) | 2744 | 2744 | 2480 |
| Crystal size, mm | 0.32 x 0.24 x 0.12 | 0.32 x 0.24 x 0.12 | 0.28 x 0.16 x 0.10 |
| θ range, ° | 2.113, 29.154 | 2.086, 28.307 | 2.138, 28.363 |
| Index ranges | -16<=h<=16<br>-27<=k<=27<br>-30<=l<=30 | -16<=h<=16<br>-27<=k<=27<br>-29<=l<=29 | -8<=h<=16<br>-23<=k<=23<br>-28<=l<=27 |
| Reflections collected | 108991 | 111377 | 14750 |
| Independent reflections, Rint | 14750, 0.0900 | 14012, 0.0729 | 9551, 0.0444 |
| Completeness to θ = 25.242° | 99.9 % | 99.8 % | 98.0 % |
| Absorption correction | Semi-empirical<br>from equivalents | Semi-empirical<br>from equivalents | Semi-empirical<br>from equivalents |
| Max,. min. transmission | 0.4926, 0.3207 | 0.492, 0.3753 | 0.492, 0.3529 |
| Refinement method | Full-matrix<br>least-squares on $F^2$ | Full-matrix<br>least-squares on $F^2$ | Full-matrix<br>least-squares on $F^2$ |
| Data / restraints / parameters | 14750 / 0 / 787 | 14012 / 0 / 787 | 9551 / 467 / 703 |
| Goodness-of-fit | 1.010 | 1.029 | 1.110 |
| R1, wR2 [I>2sigma(I)] | 0.0324, 0.0783 | 0.0284, 0.0615 | 0.0823, 0.2057 |
| R1, wR2 (all data) | 0.0352, 0.0799 | 0.0345, 0.0641 | 0.1164, 0.2288 |
| Absolute structure parameter | -0.014(5) | -0.022(5) | 0.060(19) |
| Largest diff. peak and hole, $e.Å^{-3}$ | 1.099, -0.938 | 0.465, -0.577 | 1.184, -1.327 |
| CCDC Number | **2313464** | **2313465** | **2313463** |

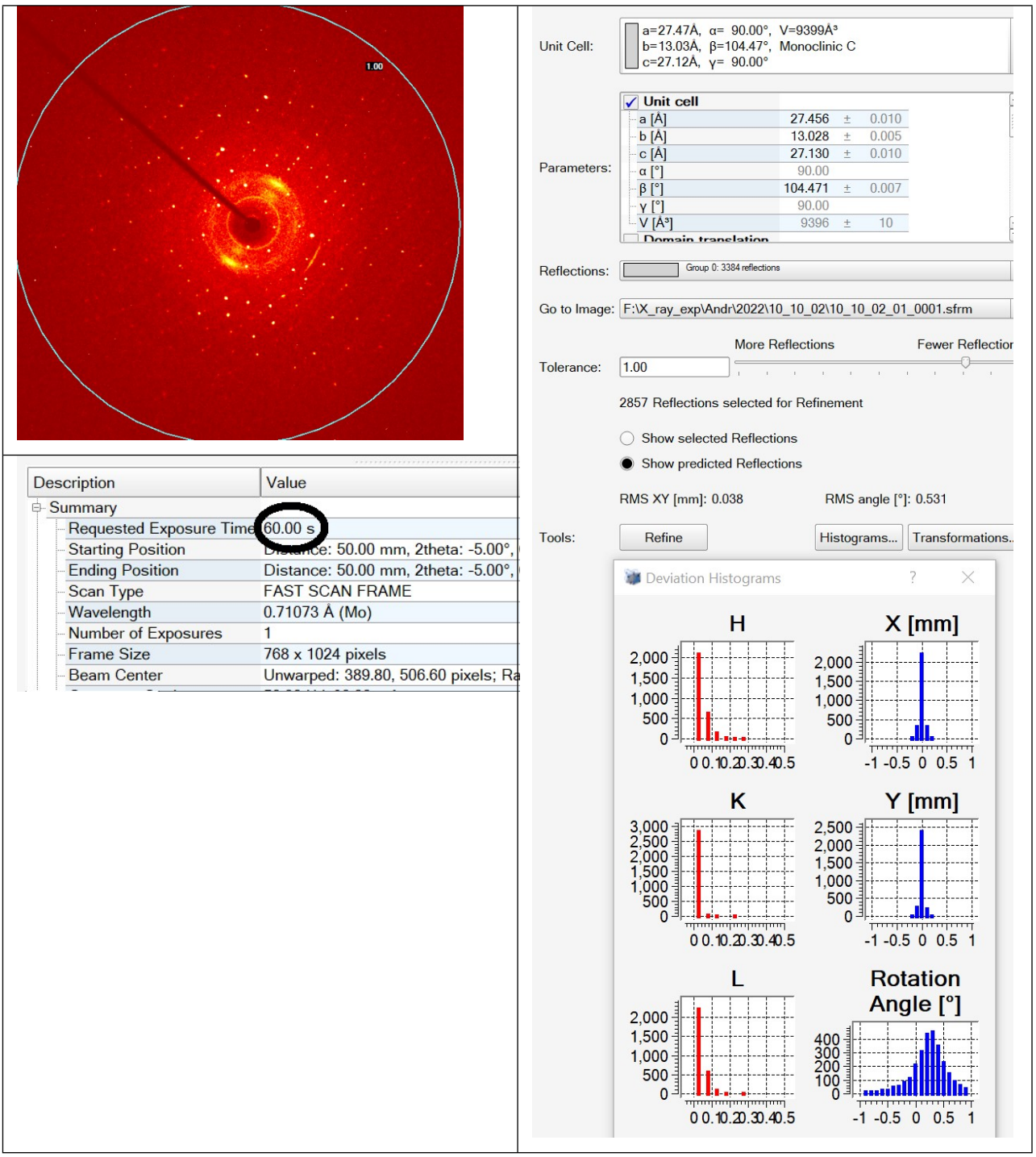



**Fig.S1.** Refinement of the unit cell parameters of **CoTb_MeCN** structure.

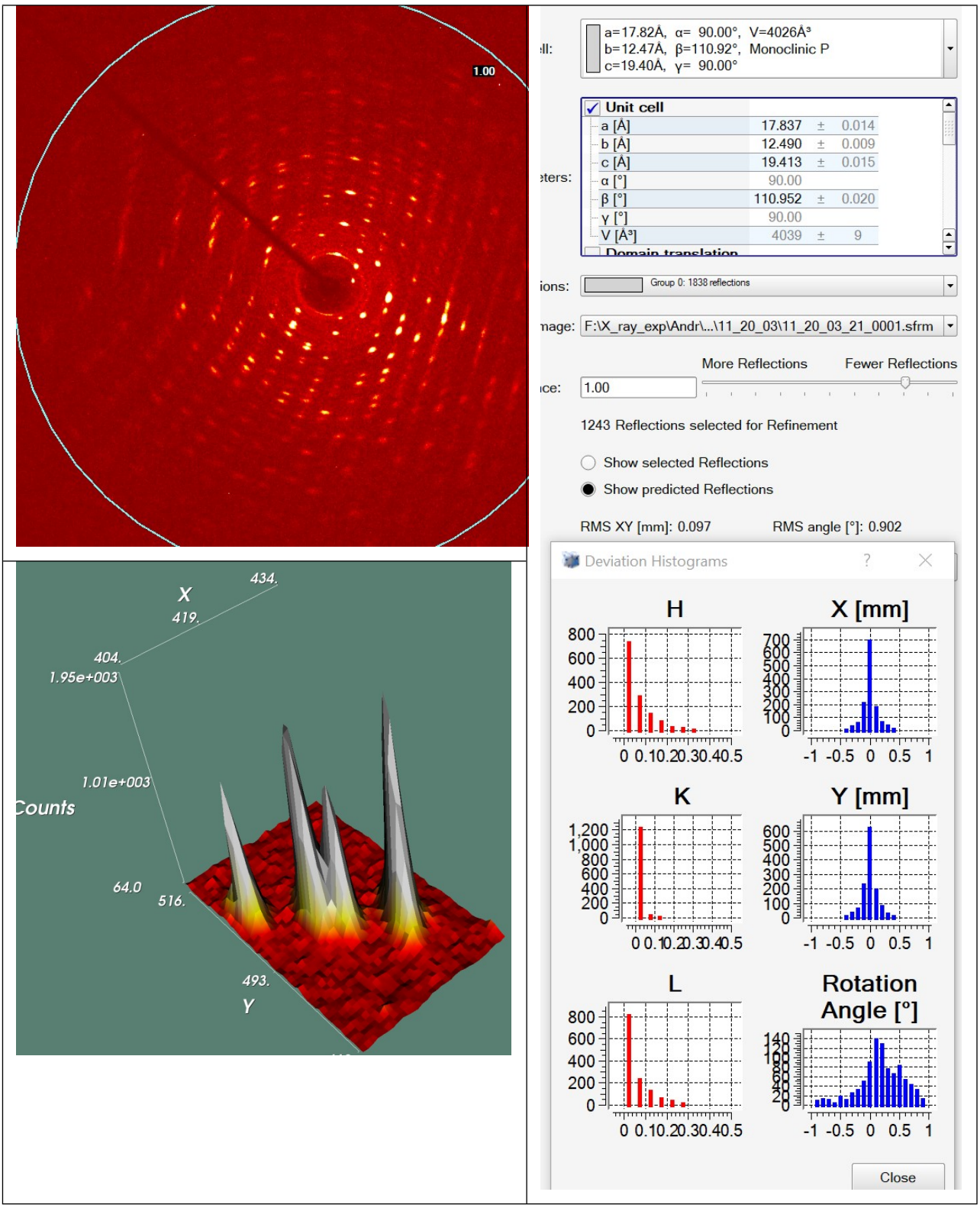



**Fig.S2**. Refinement of unit cell parameters of **CoTb** structure.

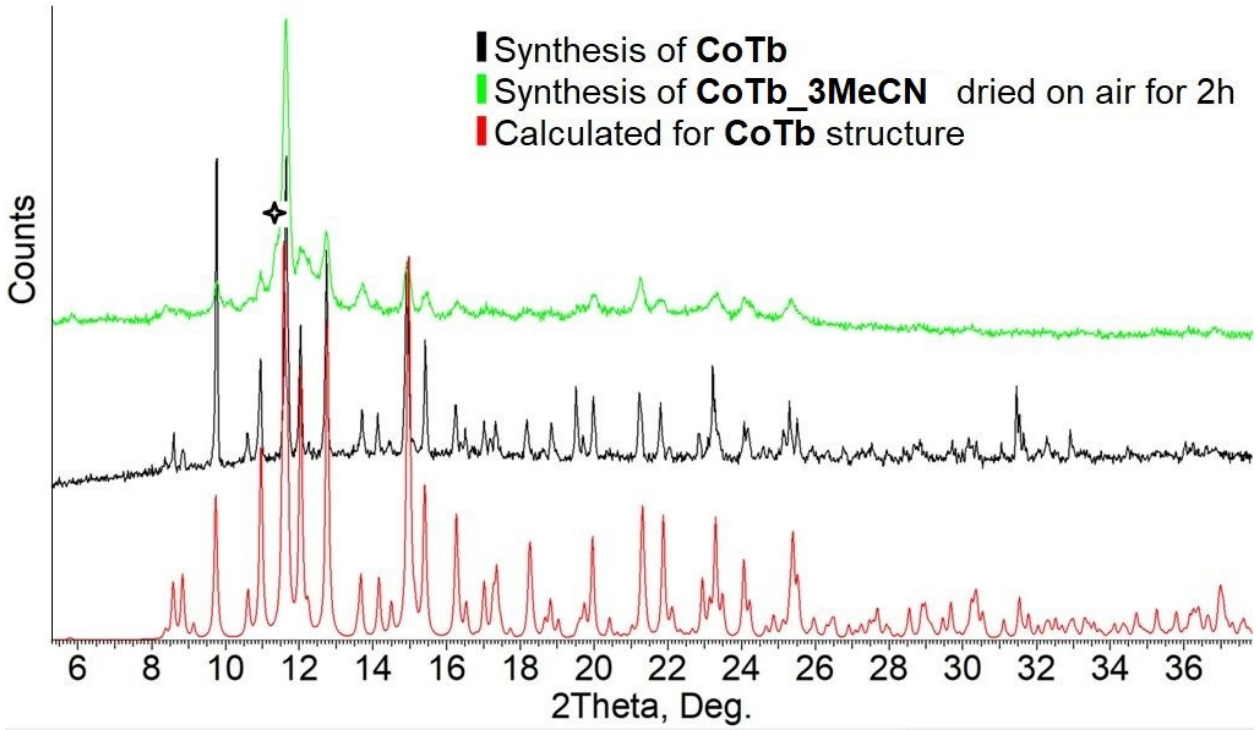


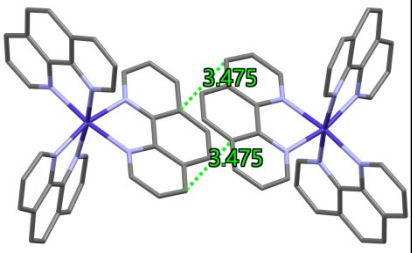

**Fig.S3.** Experimental and calculated patterns of **CoTb** prepared in MeOH compared with the pattern of the product of complete desolvation of **CoTb_3MeCN**.

**Table S3.** Hydrogen bonds in **CoTb_xMeCN** (x = 3, 1, 0) and **CoLaPhen_yMeCN** (y =3, 0) structures.

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| **CoTb_3MeCN** | | | | |
| C(13)-H(13A)…O(13) (-x+1/2, -y+1, z-1/2) | 0.95 | 2.52 | 3.241(6) | 133 |
| C(14)-H(14A)…O(4) (-x+1/2, -y+1, z-1/2) | 0.95 | 2.57 | 3.280(7) | 131 |
| C(21)-H(21A)…O(5) | 0.95 | 2.60 | 3.185(7) | 120 |
| C(22)-H(22A)…O(5) | 0.95 | 2.50 | 3.146(6) | 125 |
| C(25)-H(25A)…N(13) (x+1/2, -y+3/2, -z) | 0.95 | 2.46 | 3.260(1) | 142 |
| C(25)-H(25A)…N(132) (x+1/2, -y+3/2, -z) | 0.95 | 2.56 | 3.37(2) | 144 |
| **CoTb_MeCN** | | | | |
| C(25)-H(25A)...O(22) (-x+1, y+1, -z) | 0.95 | 2.39 | 3.09(3) | 130 |
| C(34)-H(34A)...O(7) (-x+1/2, y-1/2, -z) | 0.95 | 2.39 | 3.11(3) | 132 |
| C(50)-H(50A)...O(26a) (-x+1, y-1, -z) | 0.95 | 2.63 | 3.52(3) | 156 |
| C(61)-H(61A)...O(8) (x, y-1, z) | 0.95 | 2.53 | 3.24(3) | 132 |
| C(61)-H(61A)...O(9) (x, y-1, z) | 0.95 | 2.56 | 3.34(3) | 140 |
| C(69)-H(69A)...O(33) (x-1/2, y-1/2, z-1) | 0.95 | 2.50 | 3.29(3) | 141 |
| **CoTb** | | | | |
| C(1)-H(1A)...O(3) (-x+1/2, y+1/2, -z+1/2) | 0.95 | 2.46 | 3.159(3) | 130 |
| C(10)-H(10A)...O(1) (-x+1, -y, -z+1) | 0.95 | 2.58 | 3.257(3) | 128 |
| C(14)-H(14A)...O(11) (-x+1/2, y+1/2, -z+1/2) | 0.95 | 2.61 | 3.255(15) | 126 |
| C(26)-H(26A)...O(6) (-x+1, -y, -z+1) | 0.95 | 2.51 | 3.181(3) | 128 |
| C(33)-H(33A)...O(8) (-x+1/2, y+1/2, -z+1/2) | 0.95 | 2.46 | 3.252(3) | 141 |
| **CoLaPhen_3MeCN_150K** | | | | |
| C(1)-H(1A)...O(15) | 0.95 | 2.56 | 3.249(5) | 130 |
| C(2)-H(2A)...N(14) | 0.95 | 2.60 | 3.290(6) | 129 |
| C(10)-H(10A)...O(13) (-x+1/2, -y+1, z-1/2) | 0.95 | 2.41 | 3.082(5) | 127 |
| C(13)-H(13A)...N(1) | 0.95 | 2.60 | 3.146(5) | 117 |
| C(22)-H(22A)...O(10) (-x+1/2, -y+1, z-1/2) | 0.95 | 2.59 | 3.195(5) | 122 |
| C(22)-H(22A)...O(12) (-x+1/2, -y+1, z-1/2) | 0.95 | 2.53 | 3.340(6) | 143 |
| C(26)-H(26A)...O(9) (-x+1/2, -y+1, z-1/2) | 0.95 | 2.57 | 3.251(5) | 129 |
| C(33)-H(33A)...O(4) | 0.95 | 2.42 | 3.305(5) | 156 |
| C(34)-H(34A)...O(1) | 0.95 | 2.51 | 3.092(5) | 120 |
| C(34)-H(34A)...O(3) | 0.95 | 2.50 | 3.407(5) | 159 |
| C(37)-H(37A)...O(1) | 0.95 | 2.58 | 3.039(5) | 110 |
| C(37)-H(37A)...O(14) | 0.95 | 2.40 | 3.035(5) | 124 |

| | | | | |
|---|---|---|---|---|
| C(45)-H(45A)...O(6) (x+1/2, -y+3/2, -z+1) | 0.95 | 2.55 | 3.141(5) | 120 |
| C(46)-H(46A)...O(8) | 0.95 | 2.44 | 2.919(5) | 111 |
| **CoLaPhen_400_150K** | | | | |
| C(1)-H(1A)...O(6) (-x+1/2, -y+1, z+1/2) | 0.95 | 2.54 | 3.313(8) | 139 |
| C(14)-H(14A)...O(8) (-x+1/2, -y+1, z+1/2) | 0.95 | 2.47 | 3.313(8) | 148 |
| C(14)-H(14A)...O(9) (-x+1/2, -y+1, z+1/2) | 0.95 | 2.36 | 3.098(8) | 134 |
| C(14)-H(14A)...N(11) (-x+1/2, -y+1, z+1/2) | 0.95 | 2.58 | 3.366(8) | 140 |
| C(21)-H(21A)...O(7) | 0.95 | 2.34 | 2.911(7) | 118 |
| C(22)-H(22A)...O(7) | 0.95 | 2.40 | 2.955(7) | 117 |
| C(25)-H(25A)...O(2) | 0.95 | 2.60 | 3.114(7) | 115 |
| C(37)-H(37A)...O(11) | 0.95 | 2.39 | 2.941(7) | 117 |
| C(46)-H(46A)...O(8) | 0.95 | 2.49 | 3.160(7) | 128 |

**Table S4.** Secondary C…C contacts [Å] in **CoTb_xMeCN** (x = 3, 1, 0) and **CoLaPhen_yMeCN** (y =3, 0) structures.

| **CoTb_3MeCN** | **CoTb_MeCN** | **CoTb** |
|---|---|---|
| C(14)…C(20) 4555 3.647 | C(2)…C(65) 3655 3.817 | C(4)…C(8) 2656 3.475 |
| C(15)…C(20) 4555 3.662 | C(15)…C(54) 4555 3.743 | C(26)…C(32) 3645 3.476 |
| C(15)…C(21) 4555 3.528 | C(26)…C(63) 3665 3.838 | C(27)…C(33) 3645 3.459 |
| **The angle between RMS planes of phen ligands is 56.7°.** | C(27)…C(65) 3665 3.811 | First contact refers to π…π stacking, second and third do not. |
| | C(29)…C(38) 3665 3.808 |  |
| | C(29)…C(57) 3655 3.752 |  |
| | C(30)…C(38) 3665 3.792 | **The angle between RMS planes of phen ligands is 0°.** |
| | C(32)…C(68) 3655 3.549 | |
| | C(33)…C(51) 4555 3.737 | |
| | C(33)…C(68) 3655 3.659 | |
| | C(42)…C(54) 4544 3.780 | |

| **CoLaPhen_3MeCN** | **CoLaPhen** |
|---|---|
| C(17)…C(43) 2664 3.416 | C(9)…C(43) 2665 3.491 |
| C(17)…C(47) 2664 3.495 | C(25)…C(44) 4456 3.501 |
| C(18)…C(42) 2664 3.397 | C(26)…C(43) 4456 3.340 |
| C(18)…C(43) 2664 3.466 | C(26)…C(44) 4456 3.297 |
| C(27)…C(40) 1455 3.494 | C(27)…C(45) 4456 3.505 |
| C(29)…C(43) 1455 3.486 | C(27)…C(46) 4456 3.360 |
| C(29)…C(47) 1455 3.318 | C(32)…C(37) 1455 3.366 |
| C(30)…C(44) 1455 3.390 | **The angle between N(1,2)C(1-12) and N(7,8)C(37-C48) (2665) RMS planes is 9.5°;** |
| C(30)…C(45) 1455 3.432 | **The angle between N(5,6)C(25-36) and N(7,8)C(37-C48) (4456) RMS planes is 11.2°** |
| **The angle between N(5,6)C(25-36) and N(7,8)C(37-C48) (1455) RMS planes is 9.2°;** | **The angle between N(5,6)C(25-36) and N(7,8)C(37-C48) (1455) RMS planes is 11.0°** |
| **The angle between N(3,4)C(13-24) and N(7,8)C(37-C48) (2664) RMS planes is 10.8°** | |

**Table S5.** Shortest M…M contacts [Å] in **CoTb_xMeCN** (x = 3, 1, 0) and **CoLaPhen_yMeCN** (y =3, 0) structures.

| Structure | Ln…Ln | Ln…Co | Co…Co |
|---|---|---|---|
| **CoTb_3MeCN** | 9.272; 11.324 | 7.052; 7.270 | 10.160; 10.829 |
| **CoTb_MeCN** | 8.698; 9.180 | 7.149; 7.195 | 10.081; 10.249 |
| **CoTb** | 9.511; 9.743 | 6.899; 7.800 | 9.609; 9.691 |
| **CoLaPhen_3MeCN_150K** | 10.106; 11.686 | 6.910; 7.686 | 11.058; 11.808 |
| **CoLaPhen_400_150K** | 10.648; 11.137 | 6.931; 7.614 | 10.887; 11.217 |

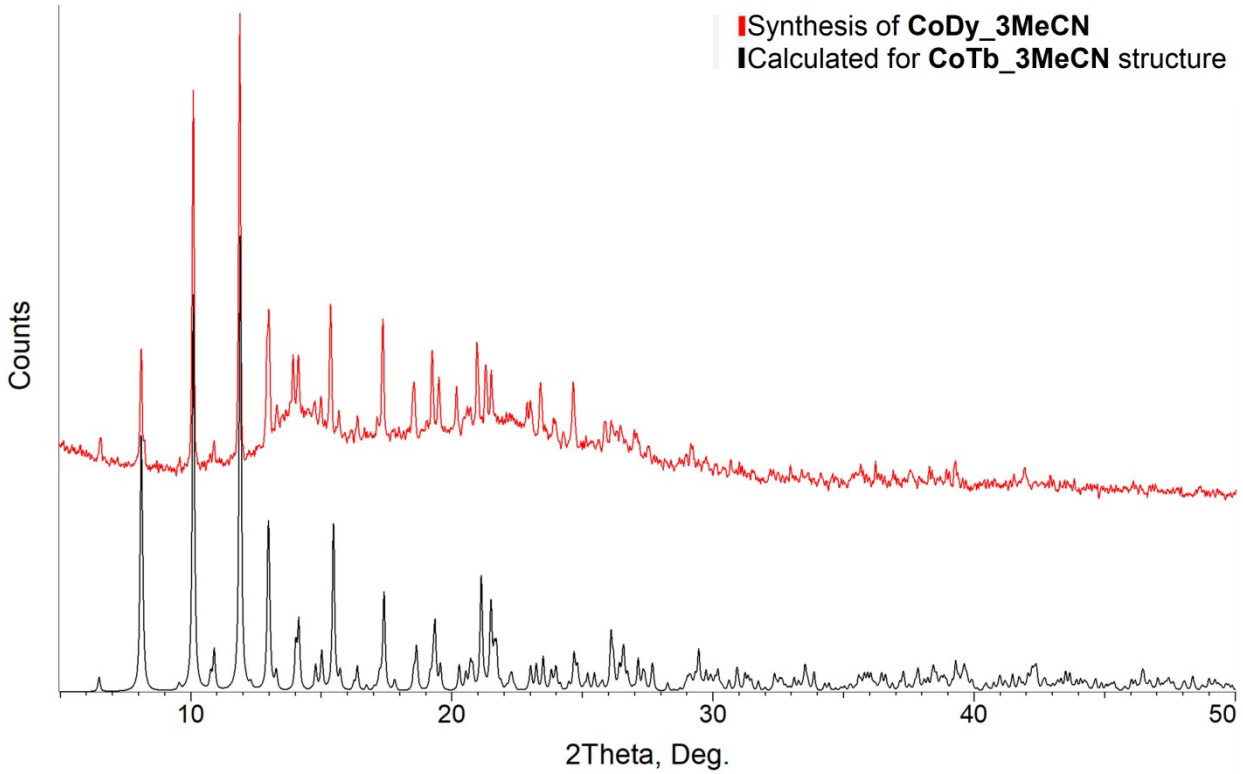



**Fig. S4.** Powder XRD patterns of the sample isolated from the synthesis of **CoDy_3MeCN**.

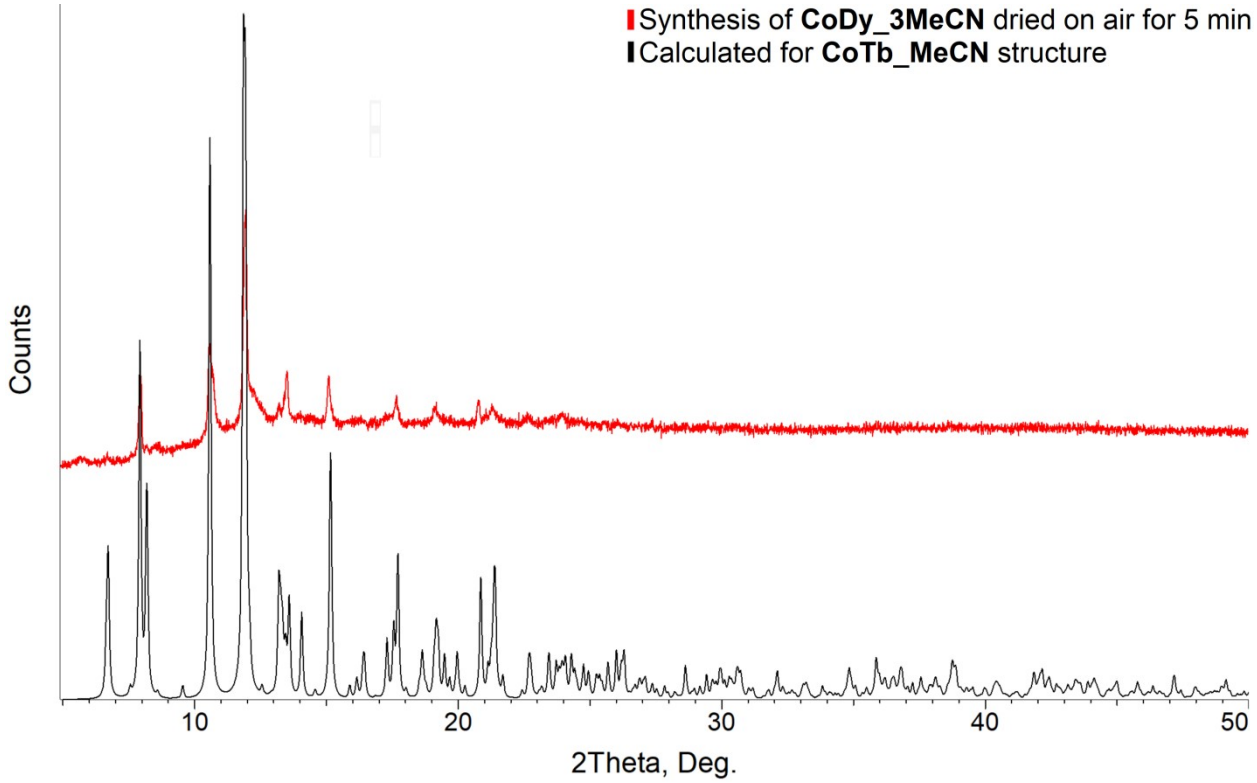



**Fig. S5.** Powder XRD patterns of the product of partial desolvation of **CoDy_3MeCN**.

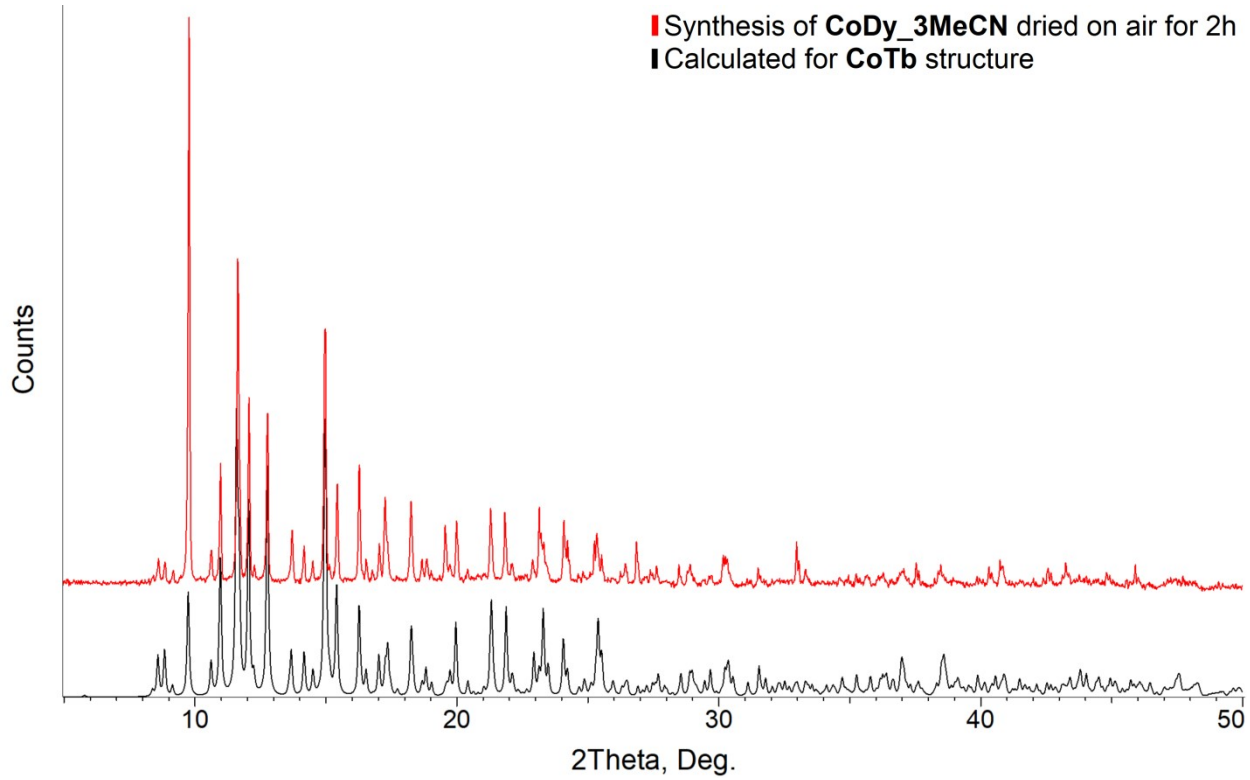



**Fig. S6.** Powder XRD patterns of the product of complete desolvation of **CoDy_3MeCN**.

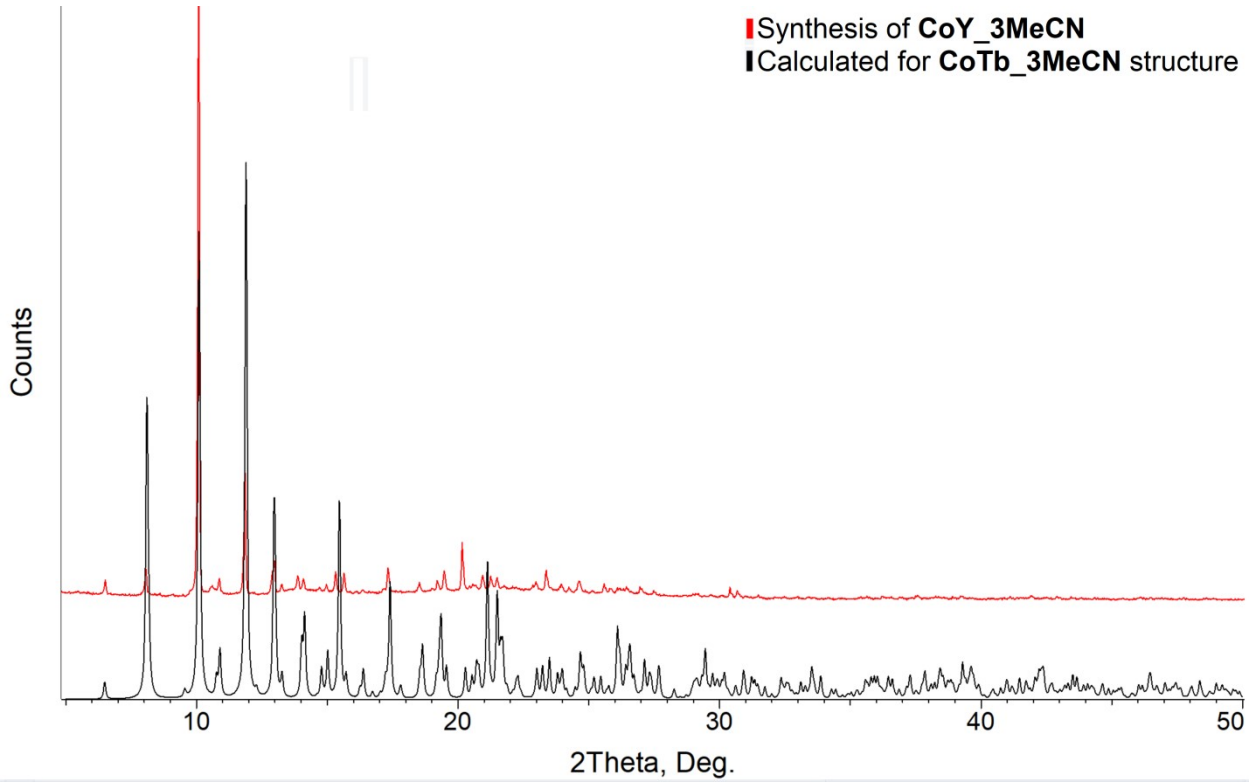



**Fig. S7.** Powder XRD patterns of the sample isolated from the synthesis of **CoY_3MeCN**.

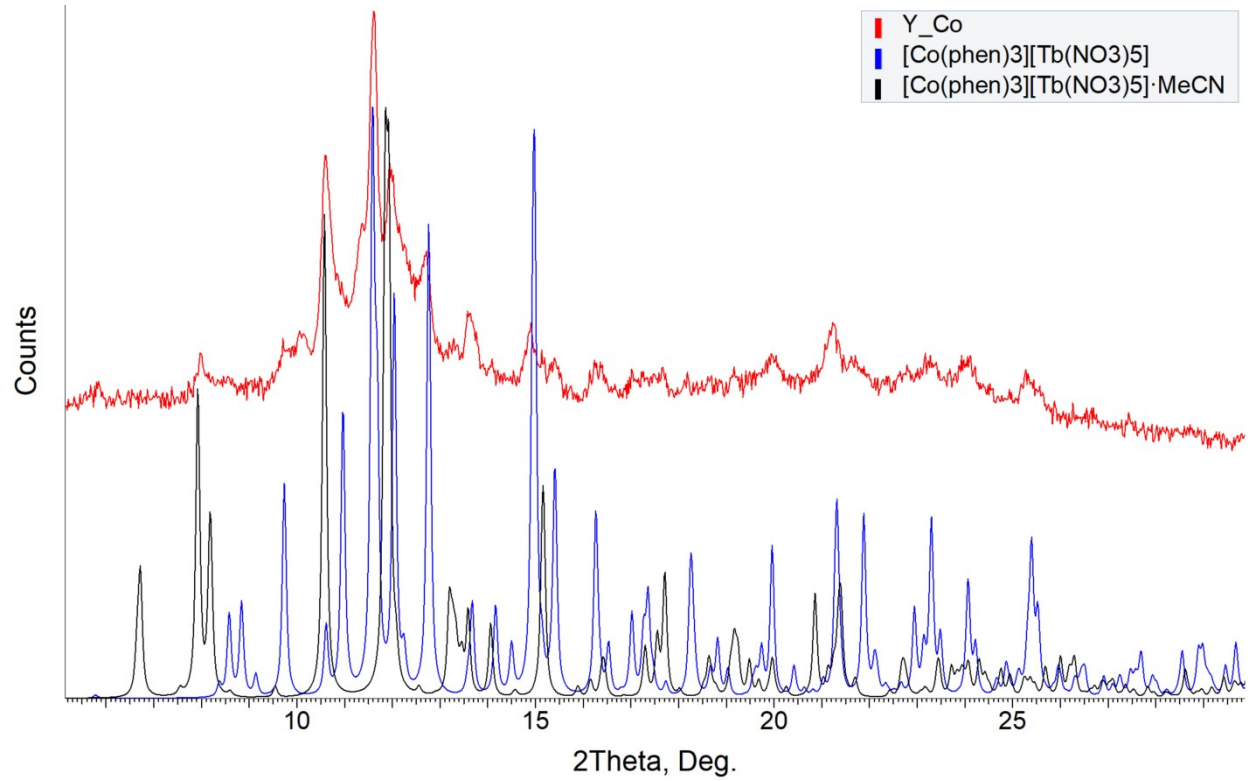



**Fig. S8.** Powder XRD patterns of the product of partial desolvation of **CoY_3MeCN**.

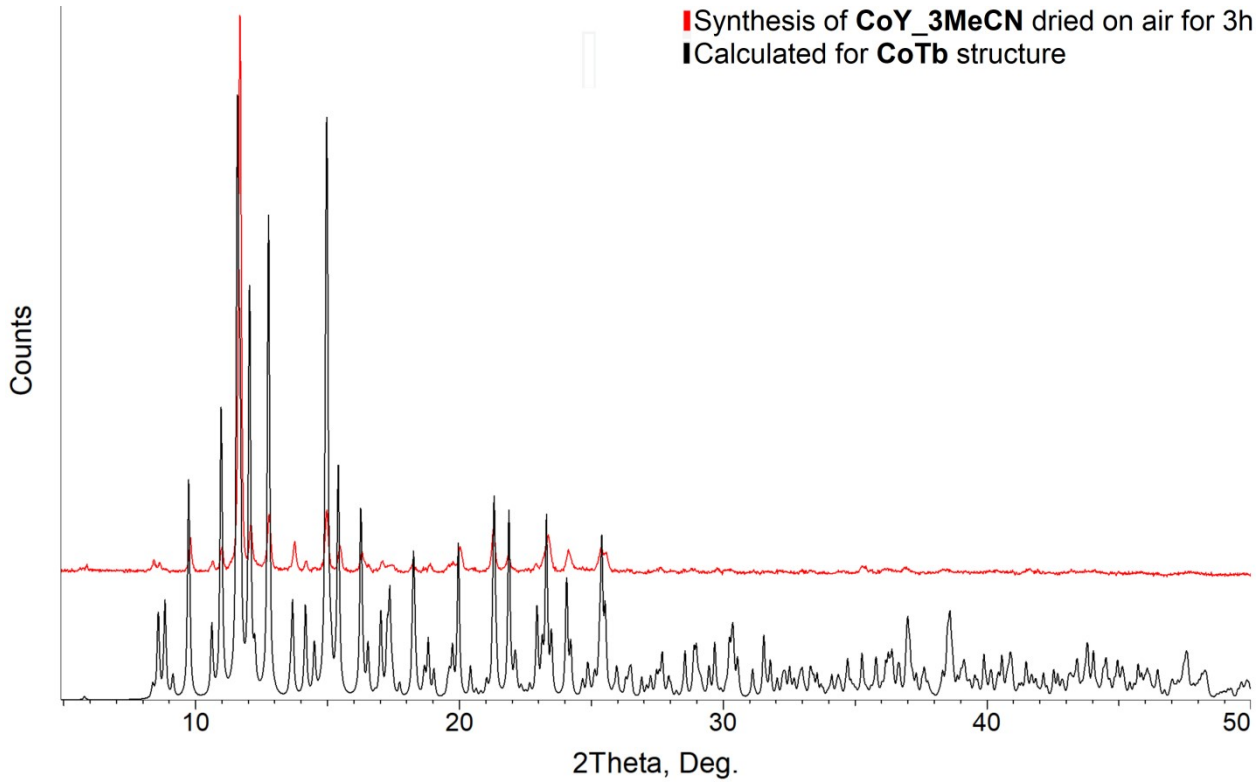



**Fig. S9.** Powder XRD patterns of the product of complete desolvation of **CoY_3MeCN**.

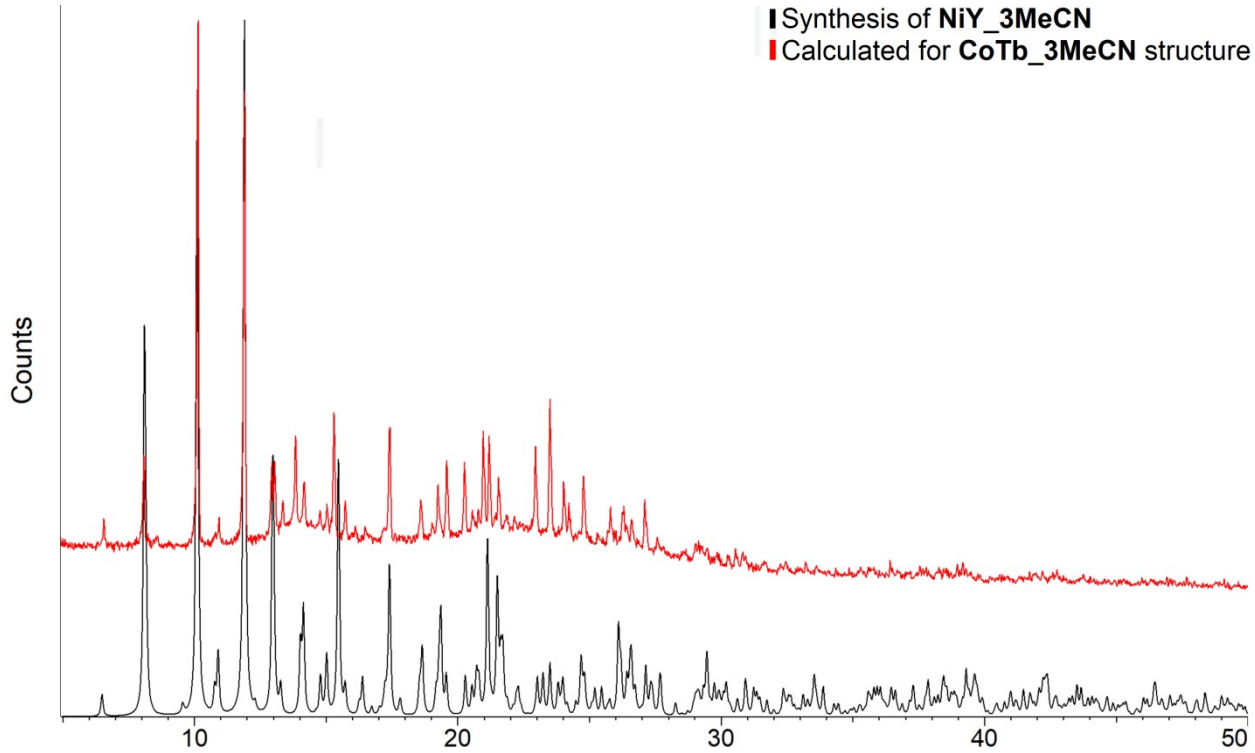



**Fig. S10.** Powder XRD patterns of the sample isolated from the synthesis of **NiY_3MeCN**.

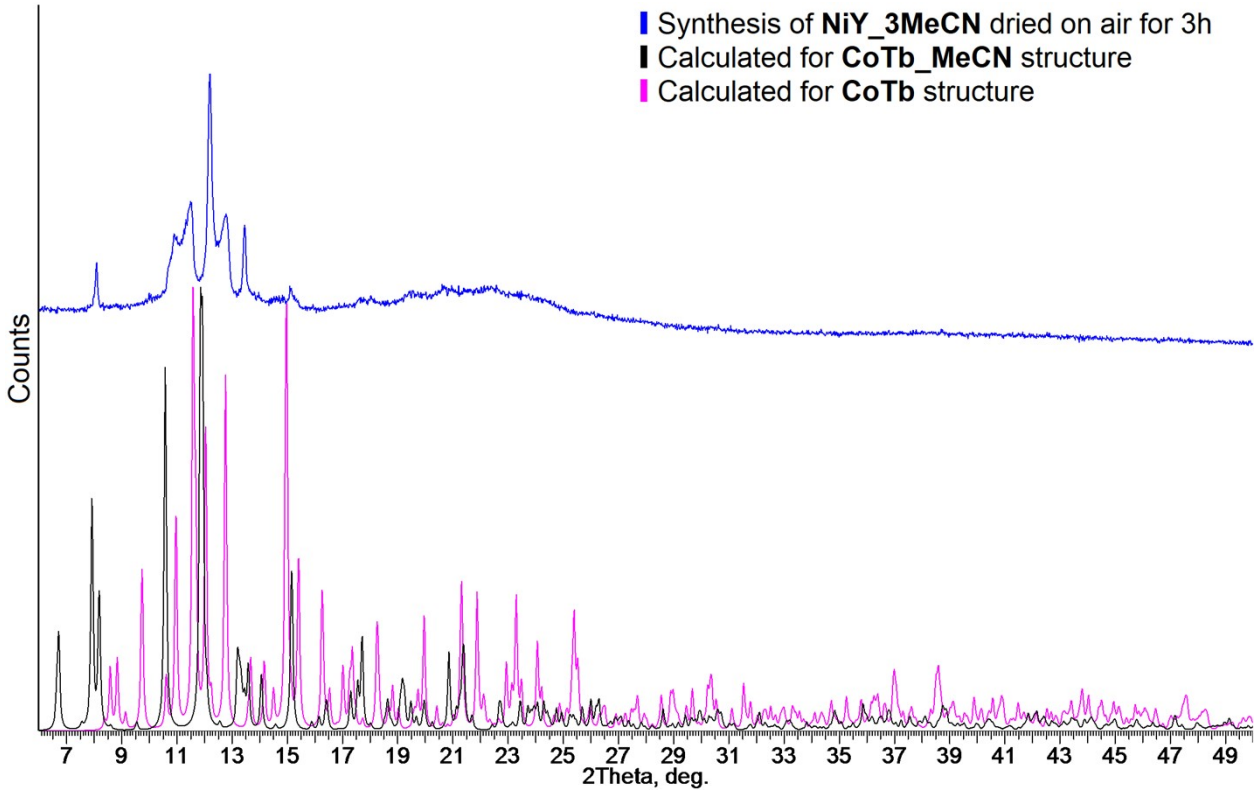



**Fig. S11.** Powder XRD patterns of the product of partial desolvation of **NiY_3MeCN**.

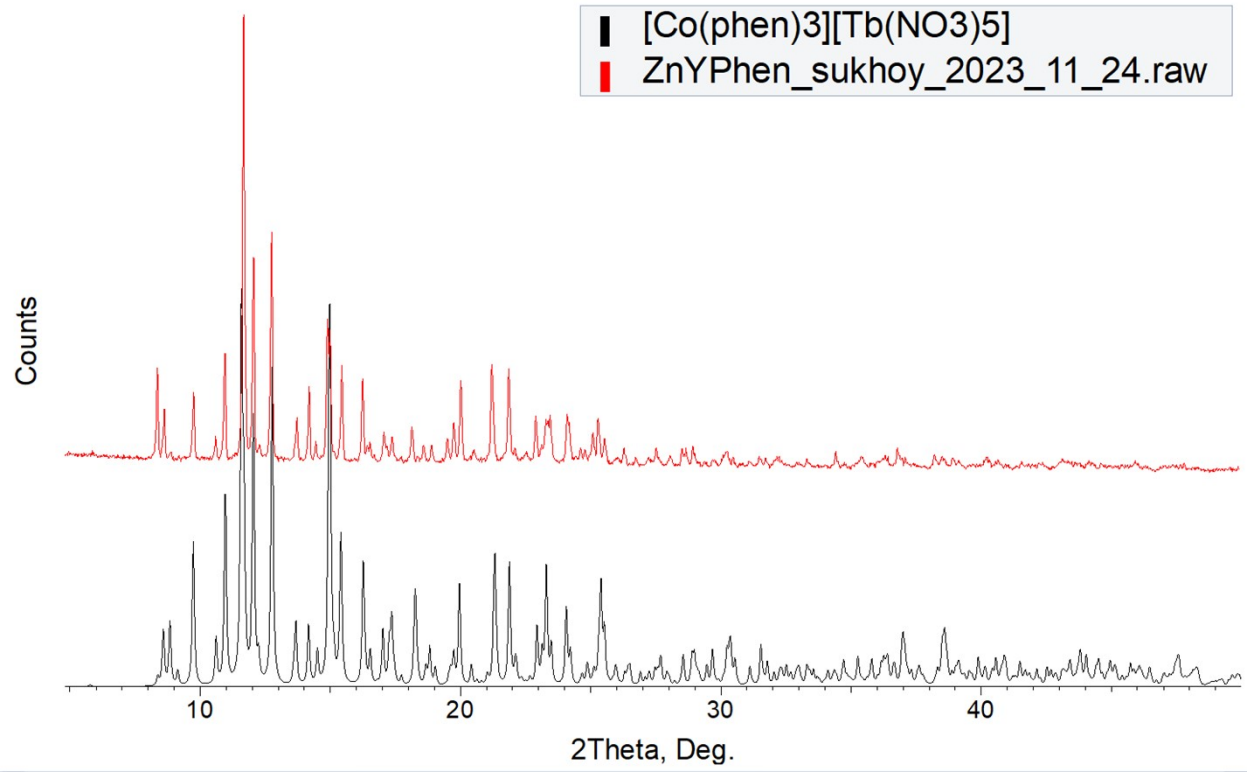



**Fig. S12.** Powder XRD patterns of the sample isolated from the synthesis of **ZnY_3MeCN**.

# checkCIF/PLATON report

Structure factors have been supplied for datablock(s) shelx

No syntax errors found. CIF dictionary Interpreting this report

# Datablock: shelx

Bond precision: C-C = 0.0057 A Wavelength=0.71073

Cell: a=12.4723(8) b=20.1964(10) c=22.0456(11)
alpha=90 beta=90 gamma=90

Temperature: **150 K**

| | Calculated | Reported |
|---|---|---|
| Volume | 5553.2(5) | 5553.2(5) |
| Space group | P212121 | P212121 |
| Hall group | P 2ac 2ab | P 2ac 2ab |
| Moiety formula | C36 H24 Co N6, C12 H8 La N7 O15, 3(C2 H3 N) | C36 H24 Co N6, C12 H8 La N7 O15, 3(C2 H3 N) |
| Sum formula | C54 H41 Co La N16 O15 | C54 H41 Co La N16 O15 |
| Mr | 1351.87 | 1351.87 |
| Dx,g cm-3 | 1.617 | 1.617 |
| Z | 4 | 4 |
| Mu (mm-1) | 1.142 | 1.142 |
| F000 | 2724.0 | 2724.0 |
| F000' | 2725.36 | |
| h,k,lmax | 17,28,31 | 17,28,31 |
| Nref | 16976[ 9246] | 16863 |
| Tmin,Tmax | 0.734,0.796 | 0.666,0.746 |
| Tmin' | 0.719 | |

Correction method= # Reported T Limits: Tmin=0.666 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 1.82/0.99 Theta(max)= 30.528

R(reflections)= 0.0347( 14609) wR2(reflections)= 0.0629( 16863)

S = 1.022 Npar= 787

**Alert level C**

| | | | | |
|---|---|---|---|---|
| PLAT244_ALERT_4_C | Low 'Solvent' Ueq as Compared to Neighbors of | | C51 | Check |
| PLAT244_ALERT_4_C | Low 'Solvent' Ueq as Compared to Neighbors of | | C53 | Check |
| PLAT260_ALERT_2_C | Large Average Ueq of Residue Including | N16 | 0.102 | Check |
| PLAT910_ALERT_3_C | Missing # of FCF Reflection(s) Below Theta(Min). | | 5 | Note |
| PLAT977_ALERT_2_C | Check Negative Difference Density on H44A | . | -0.38 | eA-3 |

**Alert level G**

| | | | | |
|---|---|---|---|---|
| PLAT232_ALERT_2_G | Hirshfeld Test Diff (M-X) La1 | --O1 | 5.3 | s.u. |
| PLAT232_ALERT_2_G | Hirshfeld Test Diff (M-X) La1 | --O2 | 6.0 | s.u. |
| PLAT232_ALERT_2_G | Hirshfeld Test Diff (M-X) La1 | --O5 | 5.3 | s.u. |
| PLAT232_ALERT_2_G | Hirshfeld Test Diff (M-X) La1 | --O7 | 6.1 | s.u. |
| PLAT232_ALERT_2_G | Hirshfeld Test Diff (M-X) La1 | --O13 | 5.8 | s.u. |
| PLAT794_ALERT_5_G | Tentative Bond Valency for La1 | (III) | 3.93 | Info |

```
PLAT794_ALERT_5_G Tentative Bond Valency for Co1       (II)       .      1.98 Info
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=   0.600        29 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          4 Info
```

# checkCIF/PLATON report

Structure factors have been supplied for datablock(s) shelx

No syntax errors found. CIF dictionary Interpreting this report

# Datablock: shelx

Bond precision: C-C = 0.0064 A Wavelength=0.71073

Cell: a=12.5205(4) b=20.2855(5) c=22.2201(6)
alpha=90 beta=90 gamma=90

Temperature: **250 K**

| | Calculated | Reported |
|---|---|---|
| Volume | 5643.6(3) | 5643.6(3) |
| Space group | P212121 | P212121 |
| Hall group | P 2ac 2ab | P 2ac 2ab |
| Moiety formula | C36 H24 Co N6, C12 H8 La N7 O15, 3(C2 H3 N) | C36 H24 Co N6, C12 H8 La N7 O15, 3(C2 H3 N) |
| Sum formula | C54 H41 Co La N16 O15 | C54 H41 Co La N16 O15 |
| Mr | 1351.87 | 1351.87 |
| Dx,g cm-3 | 1.591 | 1.591 |
| Z | 4 | 4 |
| Mu (mm-1) | 1.124 | 1.124 |
| F000 | 2724.0 | 2724.0 |
| F000’ | 2725.36 | |
| h,k,lmax | 16,26,28 | 16,26,28 |
| Nref | 12464[ 6849] | 12440 |
| Tmin,Tmax | 0.737,0.799 | 0.682,0.746 |
| Tmin’ | 0.723 | |

Correction method= # Reported T Limits: Tmin=0.682 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 1.82/1.00 Theta(max)= 27.114

R(reflections)= 0.0281( 11268) wR2(reflections)= 0.0527( 12440)

S = 1.000 Npar= 787

**Alert level C**

```
PLAT234_ALERT_4_C Large Hirshfeld Difference C19      --C20       .      0.16 Ang.
PLAT244_ALERT_4_C Low    ’Solvent’ Ueq as Compared  to Neighbors of       C49 Check
PLAT244_ALERT_4_C Low    ’Solvent’ Ueq as Compared  to Neighbors of       C51 Check
PLAT244_ALERT_4_C Low    ’Solvent’ Ueq as Compared to Neighbors of       C53 Check
PLAT260_ALERT_2_C Large Average Ueq of Residue Including       N14     0.109 Check
PLAT260_ALERT_2_C Large Average Ueq of Residue Including       N16     0.162 Check
PLAT910_ALERT_3_C Missing # of FCF Reflection(s) Below Theta(Min).         5 Note
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600         3 Report
```

**Alert level G**

```
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  La1      --O1        .        5.4 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  La1      --O2        .        7.1 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  La1      --O4        .        5.0 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  La1      --O5        .        6.1 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  La1      --O7        .        7.2 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  La1      --O8        .        5.3 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  La1      --O10       .        5.8 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  La1      --O11       .        5.7 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  La1      --O13       .        6.7 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X)  La1      --O14       .        8.9 s.u.
PLAT794_ALERT_5_G Tentative Bond Valency for La1       (III)      .       3.88 Info
PLAT794_ALERT_5_G Tentative Bond Valency for Co1       (II)       .       1.97 Info
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600          7 Note
PLAT913_ALERT_3_G Missing # of Very Strong Reflections in FCF ....          3 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.         2 Info
```

# checkCIF/PLATON report

Structure factors have been supplied for datablock(s) shelx

No syntax errors found. CIF dictionary Interpreting this report

# Datablock: shelx

```
Bond precision:   C-C = 0.0373 A          Wavelength=0.71073

Cell:             a=12.5614(18)      b=20.372(3)      c=22.451(3)
                  alpha=90           beta=90          gamma=90
Temperature:      350 K
```

| | Calculated | Reported |
|---|---|---|
| Volume | 5745.2(14) | 5745.1(13) |
| Space group | P212121 | P212121 |
| Hall group | P 2ac 2ab | P 2ac 2ab |
| Moiety formula | C36 H24 Co N6, C12 H8 La N7 O15, 3(C2 H3 N) | C36 H24 Co N6, C12 H8 La N7 O15, 3(C2 H3 N) |
| Sum formula | C54 H41 Co La N16 O15 | C54 H41 Co La N16 O15 |
| Mr | 1351.87 | 1351.87 |
| Dx,g cm-3 | 1.563 | 1.563 |
| Z | 4 | 4 |
| Mu (mm-1) | 1.104 | 1.104 |
| F000 | 2724.0 | 2724.0 |
| F000′ | 2725.36 | |
| h,k,lmax | 15,25,28 | 15,25,28 |
| Nref | 11871[ 6532] | 11750 |
| Tmin,Tmax | 0.741,0.802 | 0.596,0.745 |
| Tmin′ | 0.727 | |

```
Correction method= # Reported T Limits: Tmin=0.596 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 1.80/0.99        Theta(max)= 26.470
```

R(reflections)= 0.0972( 8515)  wR2(reflections)= 0.2720( 11750)

S = 1.201  Npar= 788

## Alert level A

PLAT971_ALERT_2_A Check Calcd Resid. Dens. 1.55Ang From O11 3.61 eA-3

## Alert level B

PLAT342_ALERT_3_B Low Bond Precision on C-C Bonds ..... 0.03725 Ang.

## Alert level C

PLAT084_ALERT_3_C High wR2 Value (i.e. > 0.25) ..... 0.27 Report
PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density .... 2.55 Report
PLAT234_ALERT_4_C Large Hirshfeld Difference Co1 --N6 . 0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N5 --C25 . 0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference La1 --O7 . 0.17 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference La1 --O10 . 0.18 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference O10 --N12 . 0.23 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C41 --C42 . 0.22 Ang.
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C3 Check
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C6 Check
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C13 Check
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C17 Check
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C27 Check
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of O4 Check
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of O5 Check
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of O8 Check
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of O14 Check
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C41 Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of C7 Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of La1 Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of N10 Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of N11 Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of C40 Check
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of C49 Check
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of C51 Check
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of C53 Check
PLAT260_ALERT_2_C Large Average Ueq of Residue Including N14 0.139 Check
PLAT260_ALERT_2_C Large Average Ueq of Residue Including N15 0.155 Check
PLAT260_ALERT_2_C Large Average Ueq of Residue Including N16 0.290 Check
PLAT364_ALERT_2_C Short C(sp3)-C(sp) Bond C49 - C50 . 1.35 Ang.
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ..... 2.593 Check
PLAT910_ALERT_3_C Missing # of FCF Reflection(s) Below Theta(Min). 5 Note
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.600 15 Report
PLAT934_ALERT_3_C Number of (Iobs-Icalc)/Sigma(W) > 10 Outliers .. 1 Check
PLAT971_ALERT_2_C Check Calcd Resid. Dens. 1.46Ang From O1 1.69 eA-3
PLAT972_ALERT_2_C Check Calcd Resid. Dens. 1.26Ang From O2 -1.60 eA-3
PLAT977_ALERT_2_C Check Negative Difference Density on H9A . -0.33 eA-3
PLAT977_ALERT_2_C Check Negative Difference Density on H13A . -0.32 eA-3
PLAT977_ALERT_2_C Check Negative Difference Density on H44A . -1.05 eA-3

## Alert level G

PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ... 5 Report
PLAT072_ALERT_2_G SHELXL First Parameter in WGHT Unusually Large 0.12 Report
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large 20.00 Why ?
PLAT177_ALERT_4_G The CIF-Embedded .res File Contains DELU Records 3 Report
PLAT333_ALERT_2_G Large Aver C6-Ring C-C Dist C40 -C48 . 1.43 Ang.
PLAT335_ALERT_2_G Check Large C6 Ring C-C Range C16 -C24 0.16 Ang.
PLAT335_ALERT_2_G Check Large C6 Ring C-C Range C40 -C48 0.16 Ang.
PLAT721_ALERT_1_G Bond Calc 0.97000, Rep 0.96000 Dev... 0.01 Ang.
C54 -H54B 1_555 1_555 ..... # 143 Check
PLAT721_ALERT_1_G Bond Calc 0.97000, Rep 0.96000 Dev... 0.01 Ang.
C54 -H54C 1_555 1_555 ..... # 144 Check
PLAT794_ALERT_5_G Tentative Bond Valency for La1 (III) . 3.91 Info

| | | | | |
|---|---|---|---|---|
| PLAT794_ALERT_5_G | Tentative Bond Valency for Co1 (II) | . | 1.93 | Info |
| PLAT860_ALERT_3_G | Number of Least-Squares Restraints ..... | | 3 | Note |
| PLAT883_ALERT_1_G | No Info/Value for _atom_sites_solution_primary . | | Please | Do ! |
| PLAT912_ALERT_4_G | Missing # of FCF Reflections Above STh/L= 0.600 | | 37 | Note |
| PLAT913_ALERT_3_G | Missing # of Very Strong Reflections in FCF .... | | 1 | Note |
| PLAT933_ALERT_2_G | Number of HKL-OMIT Records in Embedded .res File | | 12 | Note |
| PLAT978_ALERT_2_G | Number C-C Bonds with Positive Residual Density. | | 0 | Info |

# checkCIF/PLATON report

Structure factors have been supplied for datablock(s) shelx

No syntax errors found. CIF dictionary Interpreting this report

# Datablock: shelx

Bond precision: C-C = 0.0191 A Wavelength=0.71073

Cell: a=12.6555(6) b=17.9417(8) c=22.6477(10)
alpha=90 beta=90 gamma=90

Temperature: **400 K**

| | Calculated | Reported |
|---|---|---|
| Volume | 5142.4(4) | 5142.4(4) |
| Space group | P212121 | P212121 |
| Hall group | P 2ac 2ab | P 2ac 2ab |
| Moiety formula | C36 H24 Co N6, C12 H8 La N7 O15 | C36 H24 Co N6, C12 H8 La N7 O15 |
| Sum formula | C48 H32 Co La N13 O15 | C48 H32 Co La N13 O15 |
| Mr | 1228.71 | 1228.70 |
| Dx,g cm-3 | 1.587 | 1.587 |
| Z | 4 | 4 |
| Mu (mm-1) | 1.223 | 1.223 |
| F000 | 2460.0 | 2460.0 |
| F000' | 2461.29 | |
| h,k,lmax | 15,22,28 | 15,22,28 |
| Nref | 10581[ 5840] | 10561 |
| Tmin,Tmax | 0.717,0.783 | 0.625,0.745 |
| Tmin' | 0.703 | |

Correction method= # Reported T Limits: Tmin=0.625 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 1.81/1.00 Theta(max)= 26.422

R(reflections)= 0.0499( 6188) wR2(reflections)= 0.0791( 10561)

S = 1.044 Npar= 703

**Alert level C**

| | | | | |
|---|---|---|---|---|
| PLAT234_ALERT_4_C | Large Hirshfeld Difference N3 --C13 | . | 0.16 | Ang. |
| PLAT234_ALERT_4_C | Large Hirshfeld Difference C9 --C10 | . | 0.16 | Ang. |
| PLAT234_ALERT_4_C | Large Hirshfeld Difference C11 --C12 | . | 0.17 | Ang. |
| PLAT234_ALERT_4_C | Large Hirshfeld Difference C15 --C16 | . | 0.21 | Ang. |
| PLAT234_ALERT_4_C | Large Hirshfeld Difference C27 --C28 | . | 0.18 | Ang. |

```
PLAT234_ALERT_4_C Large Hirshfeld Difference La1      --O8       .       0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference O1       --N9       .       0.18 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference O14      --N13      .       0.18 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C38      --C39      .       0.20 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C40      --C41      .       0.22 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C40      --C48      .       0.18 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C42      --C43      .       0.24 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C43      --C44      .       0.21 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C43      --C47      .       0.20 Ang.
PLAT241_ALERT_2_C High    'MainMol' Ueq as Compared to Neighbors of         C2 Check
PLAT241_ALERT_2_C High    'MainMol' Ueq as Compared to Neighbors of         C3 Check
PLAT241_ALERT_2_C High    'MainMol' Ueq as Compared to Neighbors of         C5 Check
PLAT241_ALERT_2_C High    'MainMol' Ueq as Compared to Neighbors of         C6 Check
PLAT241_ALERT_2_C High    'MainMol' Ueq as Compared to Neighbors of         C8 Check
PLAT241_ALERT_2_C High    'MainMol' Ueq as Compared to Neighbors of        C14 Check
PLAT241_ALERT_2_C High    'MainMol' Ueq as Compared to Neighbors of        C15 Check
PLAT241_ALERT_2_C High    'MainMol' Ueq as Compared to Neighbors of        C17 Check
PLAT241_ALERT_2_C High    'MainMol' Ueq as Compared to Neighbors of        C18 Check
PLAT241_ALERT_2_C High    'MainMol' Ueq as Compared to Neighbors of        C29 Check
PLAT241_ALERT_2_C High    'MainMol' Ueq as Compared to Neighbors of         O2 Check
PLAT241_ALERT_2_C High    'MainMol' Ueq as Compared to Neighbors of         O7 Check
PLAT241_ALERT_2_C High    'MainMol' Ueq as Compared to Neighbors of         O8 Check
PLAT241_ALERT_2_C High    'MainMol' Ueq as Compared to Neighbors of        O10 Check
PLAT241_ALERT_2_C High    'MainMol' Ueq as Compared to Neighbors of        O11 Check
PLAT241_ALERT_2_C High    'MainMol' Ueq as Compared to Neighbors of        O13 Check
PLAT241_ALERT_2_C High    'MainMol' Ueq as Compared to Neighbors of        C39 Check
PLAT241_ALERT_2_C High    'MainMol' Ueq as Compared to Neighbors of        C41 Check
PLAT242_ALERT_2_C Low     'MainMol' Ueq as Compared to Neighbors of        C19 Check
PLAT242_ALERT_2_C Low     'MainMol' Ueq as Compared to Neighbors of        C31 Check
PLAT242_ALERT_2_C Low     'MainMol' Ueq as Compared to Neighbors of        La1 Check
PLAT242_ALERT_2_C Low     'MainMol' Ueq as Compared to Neighbors of         N9 Check
PLAT242_ALERT_2_C Low     'MainMol' Ueq as Compared to Neighbors of        N10 Check
PLAT242_ALERT_2_C Low     'MainMol' Ueq as Compared to Neighbors of        N11 Check
PLAT242_ALERT_2_C Low     'MainMol' Ueq as Compared to Neighbors of        N12 Check
PLAT242_ALERT_2_C Low     'MainMol' Ueq as Compared to Neighbors of        N13 Check
PLAT242_ALERT_2_C Low     'MainMol' Ueq as Compared to Neighbors of        C40 Check
PLAT242_ALERT_2_C Low     'MainMol' Ueq as Compared to Neighbors of        C47 Check
PLAT260_ALERT_2_C Large Average Ueq of Residue Including       Co1      0.104 Check
PLAT260_ALERT_2_C Large Average Ueq of Residue Including       La1      0.115 Check
PLAT342_ALERT_3_C Low Bond Precision on  C-C Bonds ..............     0.0191 Ang.
PLAT601_ALERT_2_C Unit Cell Contains Solvent Accessible VOIDS of .         34 Ang**3
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**Alert level G**

```
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) La1 --O10                    6.3 s.u.
PLAT432_ALERT_2_G Short Inter X...Y Contact  O6        ..C34      .      3.01  Ang.
                                          1/2-x,1-y,-1/2+z  =      2_564 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact  O7        ..C21      .      2.98  Ang.
                                            x,y,z  =      1_555 Check
PLAT794_ALERT_5_G Tentative Bond Valency for La1       (III)     .      3.69  Info
PLAT794_ALERT_5_G Tentative Bond Valency for Co1       (II)      .      2.00  Info
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).         4  Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600         7  Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.         0  Info
```

# checkCIF/PLATON report

Structure factors have been supplied for datablock(s) shelx

```
Bond precision:   C-C = 0.0089 A          Wavelength=0.71073

Cell:             a=12.4652(6)      b=17.7628(8)      c=22.4407(10)
```

alpha=90 beta=90 gamma=90

Temperature: **150 K**

| | Calculated | Reported |
|---|---|---|
| Volume | 4968.8(4) | 4968.7(4) |
| Space group | P212121 | P212121 |
| Hall group | P 2ac 2ab | P 2ac 2ab |
| Moiety formula | C36 H24 Co N6, C12 H8 La N7 O15 | C36 H24 Co N6, C12 H8 La N7 O15, 3(C2 H3 N) |
| Sum formula | C48 H32 Co La N13 O15 | C48 H32 Co La N13 O15 |
| Mr | 1228.71 | 1228.70 |
| Dx,g cm-3 | 1.643 | 1.643 |
| Z | 4 | 4 |
| Mu (mm-1) | 1.266 | 1.266 |
| F000 | 2460.0 | 2460.0 |
| F000' | 2461.29 | |
| h,k,lmax | 15,22,28 | 15,22,28 |
| Nref | 10184[ 5630] | 10164 |
| Tmin,Tmax | 0.709,0.776 | 0.639,0.745 |
| Tmin' | 0.695 | |

Correction method= # Reported T Limits: Tmin=0.639 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 1.81/1.00 Theta(max)= 26.398

R(reflections)= 0.0348( 9151) wR2(reflections)= 0.0715( 10164)

S = 1.038 Npar= 703

**Alert level C**

PLAT090_ALERT_3_C Poor Data / Parameter Ratio (Zmax > 18) ..... 7.99 Note
PLAT342_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.00885 Ang.
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.600 2 Report

**Alert level G**

FORMU01_ALERT_1_G There is a discrepancy between the atom counts in the _chemical_formula_sum and _chemical_formula_moiety. This is usually due to the moiety formula being in the wrong format.
Atom count from _chemical_formula_sum: C48 H32 Co1 La1 N13 O15
Atom count from _chemical_formula_moiety:C54 H41 Co1 La1 N16 O15

PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) La1 --O7 . 5.9 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) La1 --O8 . 6.0 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) La1 --O13 . 5.5 s.u.
PLAT432_ALERT_2_G Short Inter X...Y Contact O6 ..C34 . 2.91 Ang.
1/2-x,1-y,-1/2+z = 2_564 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact O7 ..C21 . 2.91 Ang.
x,y,z = 1_555 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact O7 ..C22 . 2.96 Ang.
x,y,z = 1_555 Check
PLAT794_ALERT_5_G Tentative Bond Valency for La1 (III) . 3.93 Info
PLAT794_ALERT_5_G Tentative Bond Valency for Co1 (II) . 1.99 Info
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary . Please Do !
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min). 4 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 5 Note
PLAT913_ALERT_3_G Missing # of Very Strong Reflections in FCF .... 1 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. 0 Info

**Fig.S13.** CheckCIF/PLATON report for **CoLaPhen_3MeCN** and **CoLaPhen** structures.

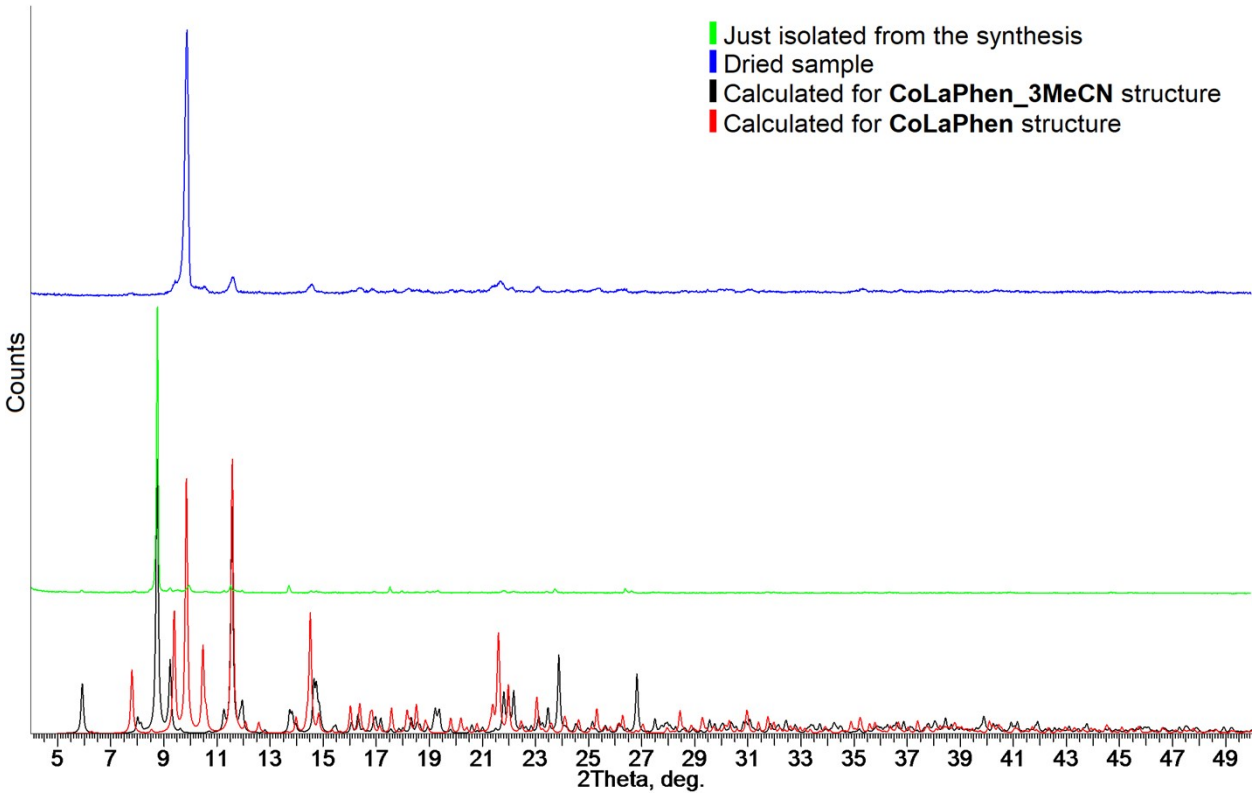


**Fig. S14.** Powder XRD patterns of the products isolated from the syntheses of **CoNdPhen_3MeCN**.

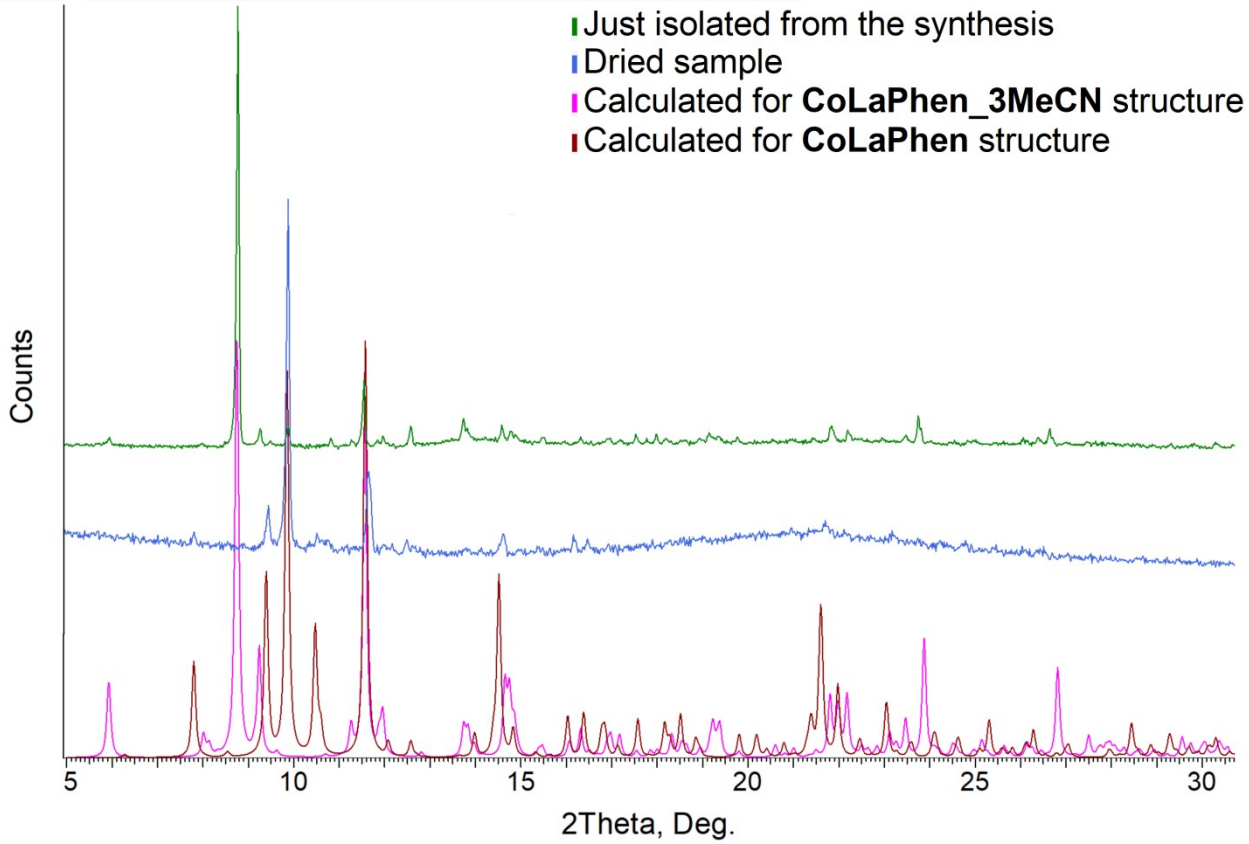


**Fig. S15.** Powder XRD patterns of the product isolated from the synthesis of **CoSmPhen_3MeCN**.

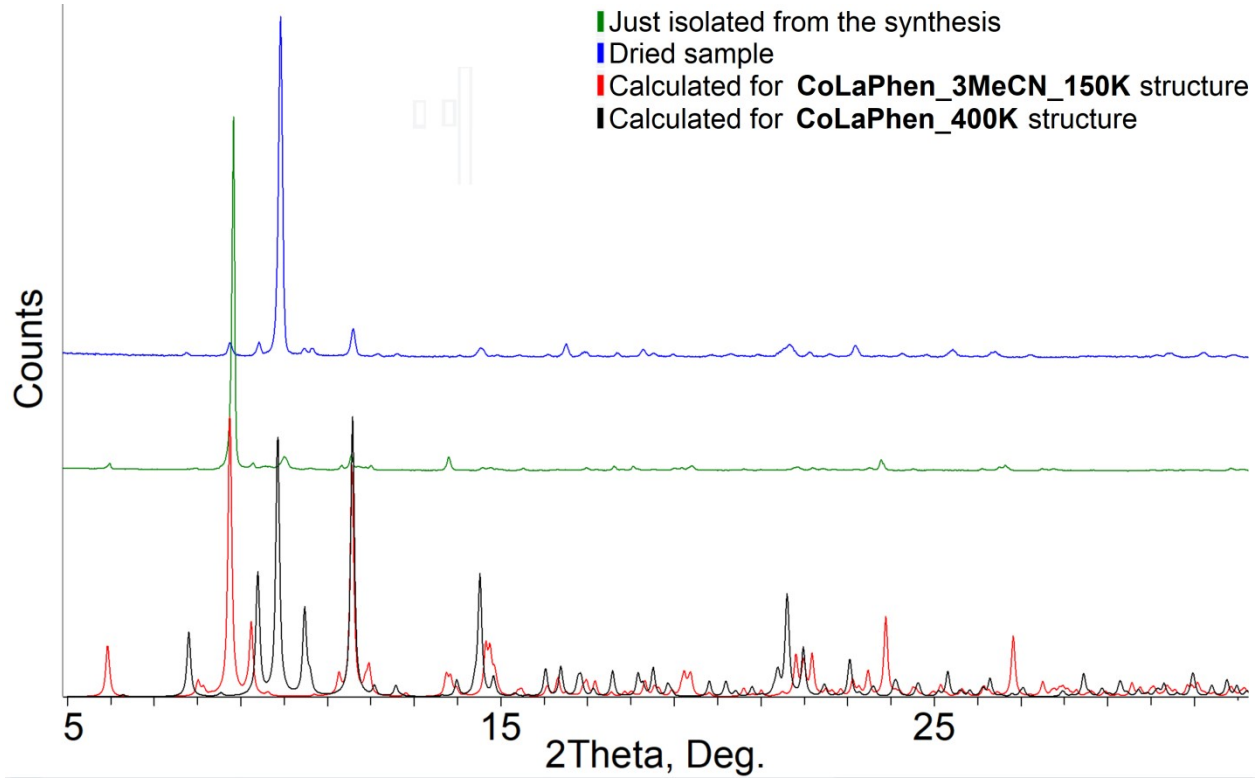


**Fig. S16.** Powder XRD patterns of the product isolated from the synthesis of **NiLaPhen_3MeCN**.

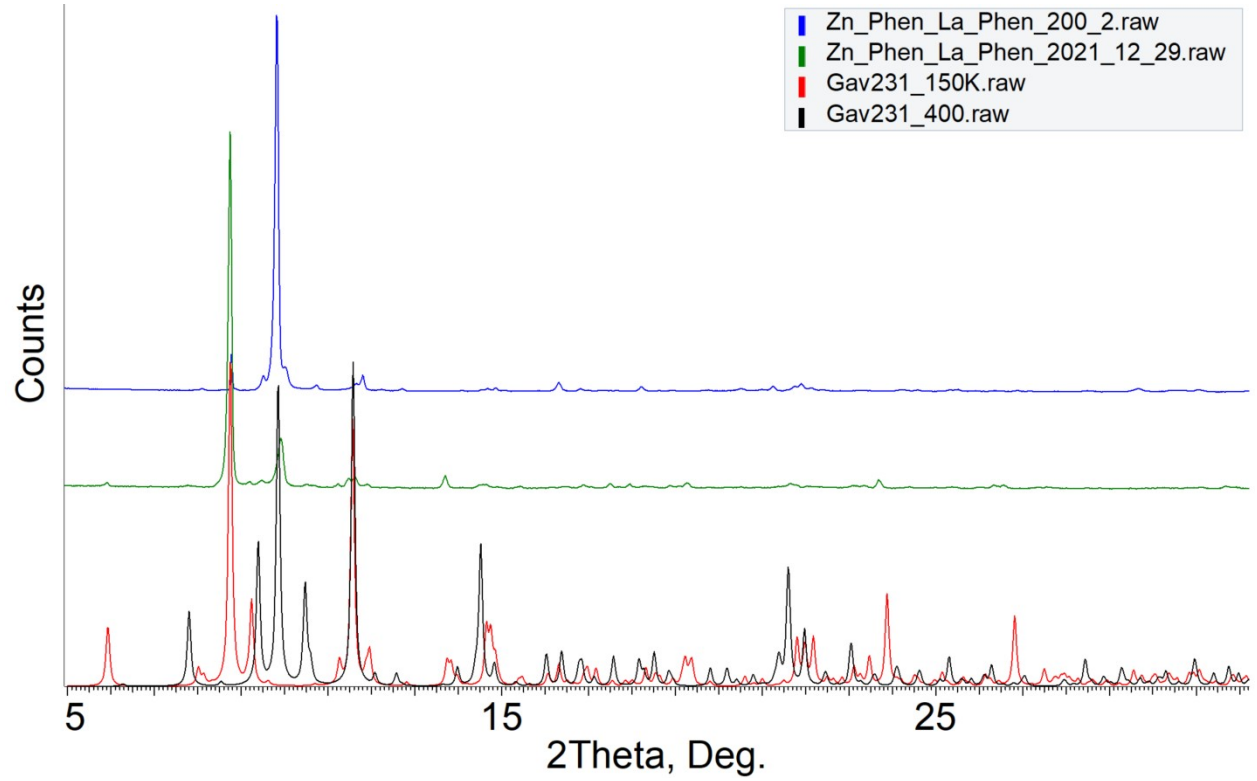


**Fig. S17.** Powder XRD pattern of the product isolated from the synthesis of **ZnLaPhen_3MeCN**.