SUPPLEMENTARY MATERIAL

Fig. S1 IR- Spectrum

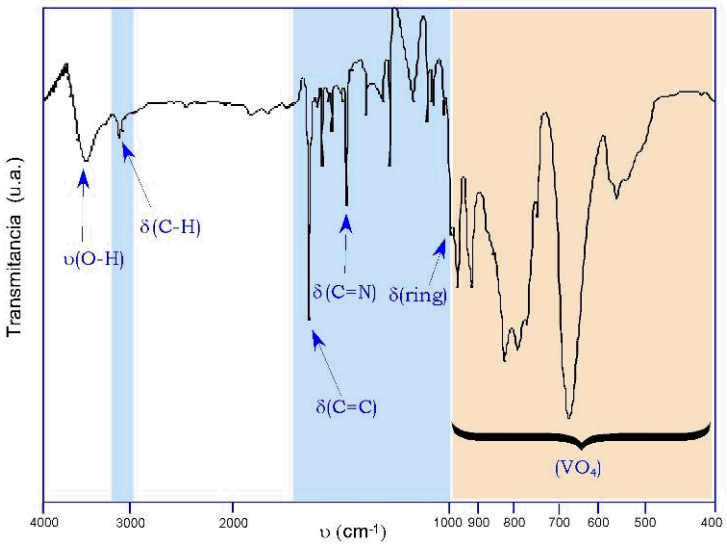
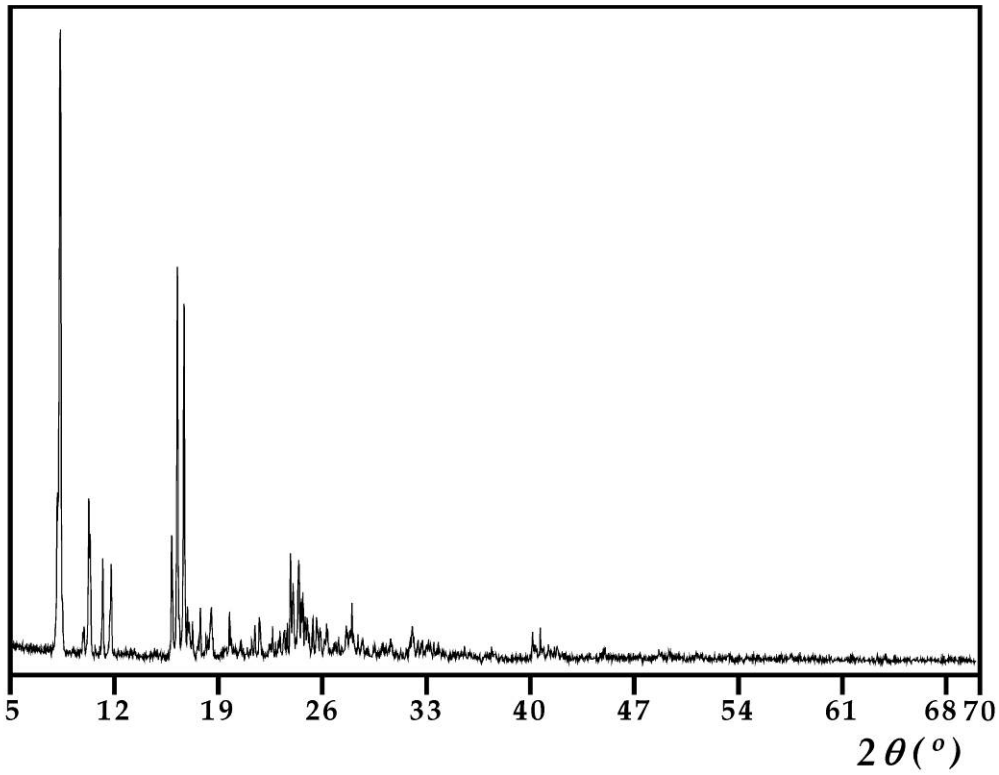
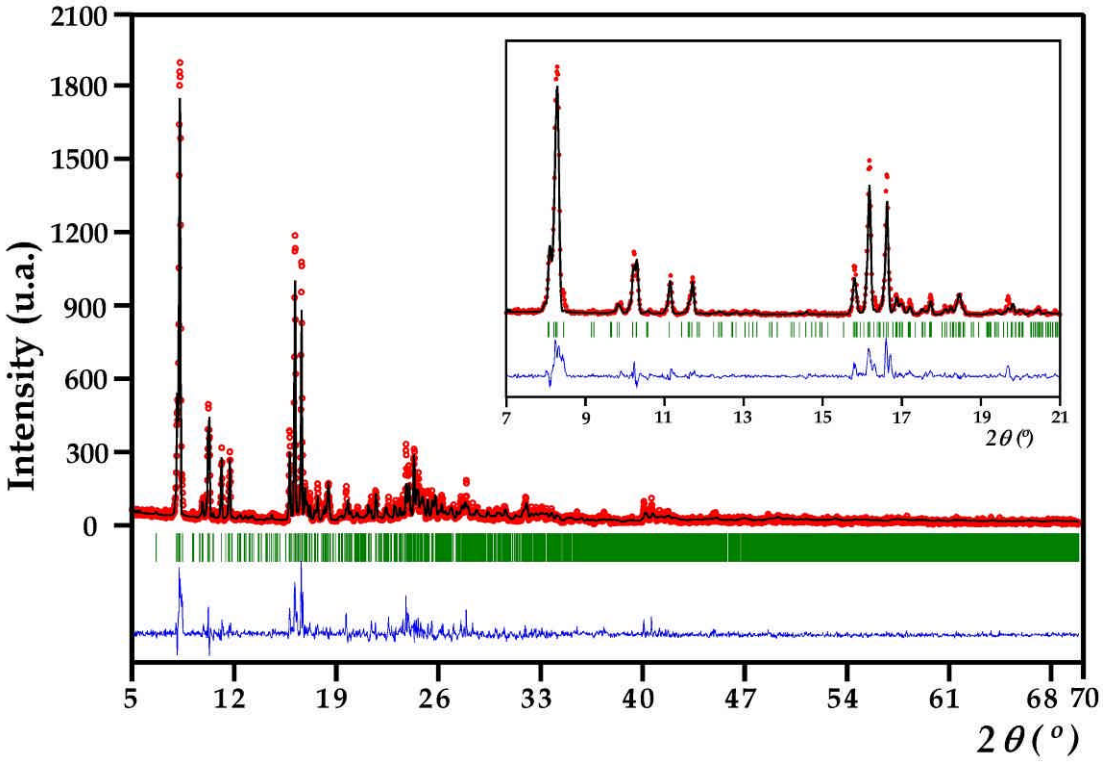


Fig. S2 (a) Powder pattern (b) Rietveld refinement

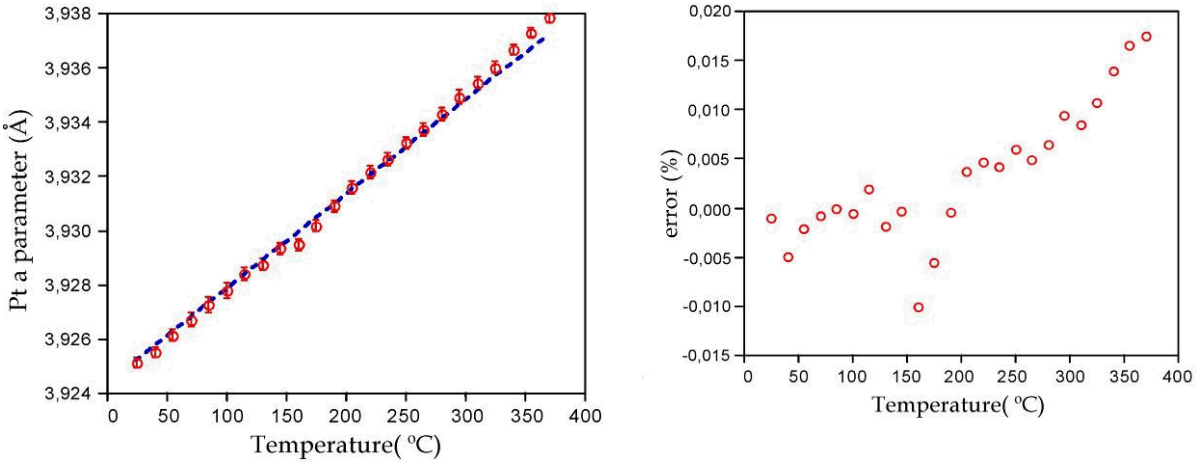


(a)



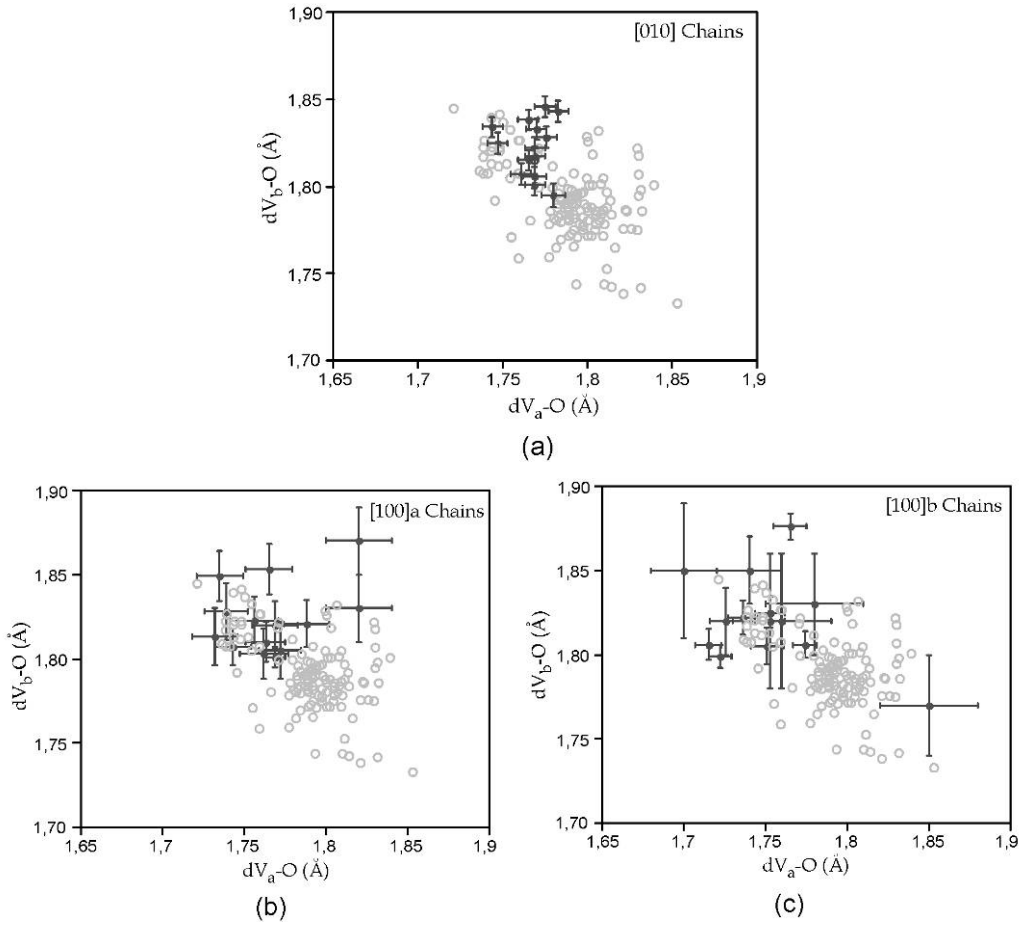
(b)

Fig. S3 (a) Thermal expansion of the platinum sample holder. (b) Error in the obtained parameters in comparison with the expected ones calculated in function of the thermal expansion coefficient of the Pt (right).



(a) **(b)**

Fig. S4. Va-O *vs.* Vb-O bond distances. Circles: data retrieved from the CSD database. (a) V-O bond distances in [010] vanadate chains. (b) V-O bond distances in [100]a chains and (c) V-O bond distances in [100]b chains.



(a)

(b) (c)

Fig. S5. (a) Distortion of the metal organic framework due to the relative displacement of the nodes due to the value of the node-node-node angle. (b) Distortion of the [010] channels. (c) Distortion of the [100] channels.

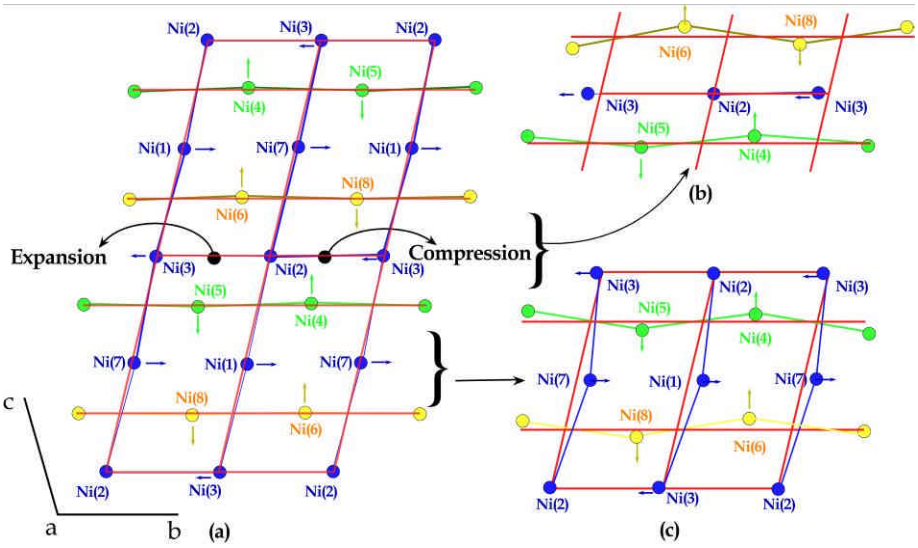


Fig. S6. VDP polyhedra for the crystallization water molecules

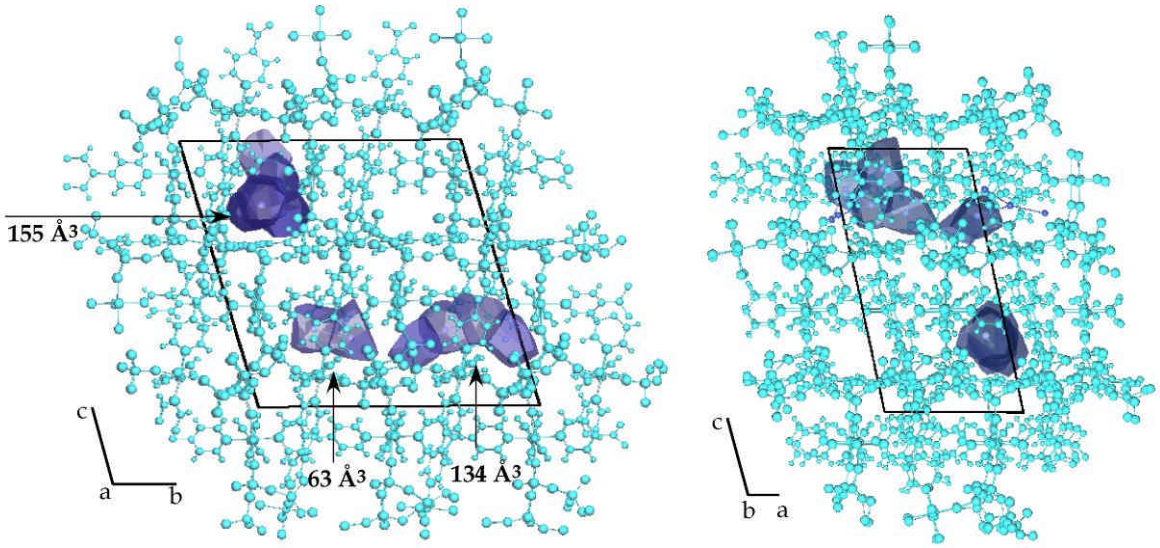


Fig. S7. Geometry of the channels in the crystal structure of the title compound calculated with the Scan method.

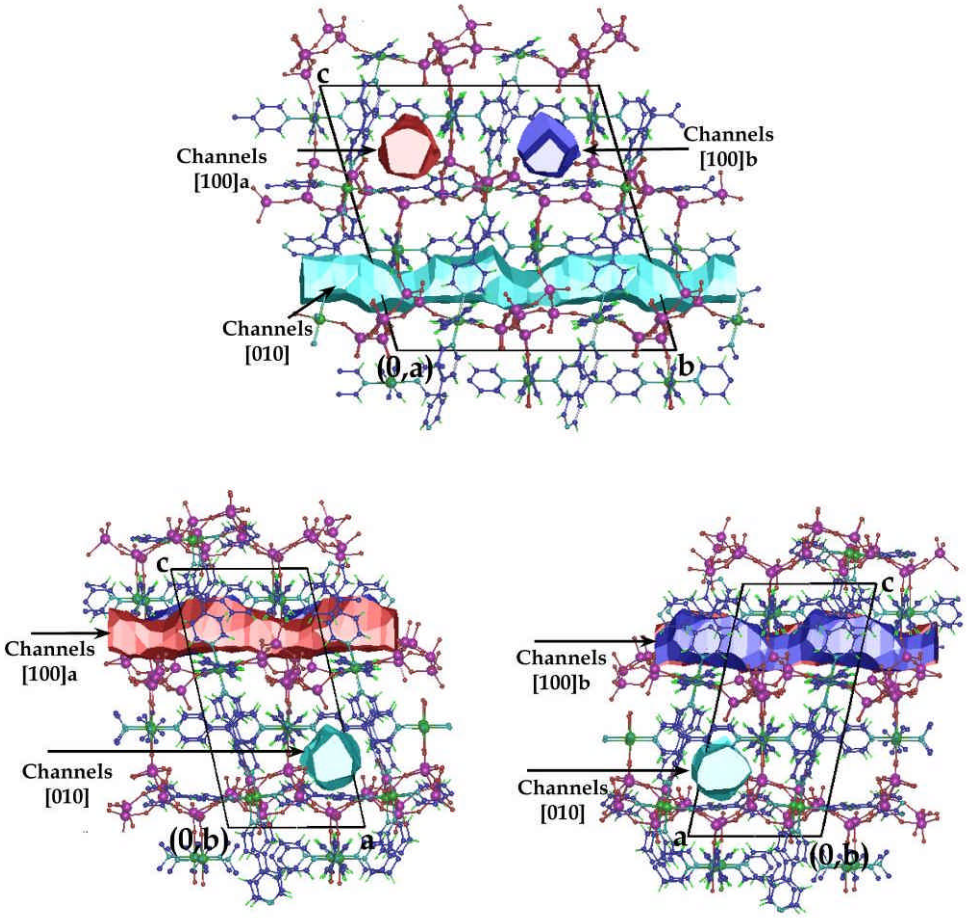


Fig. S8. Thermogravimetic curve. Heating ratio 5ºCmin^{-1}.

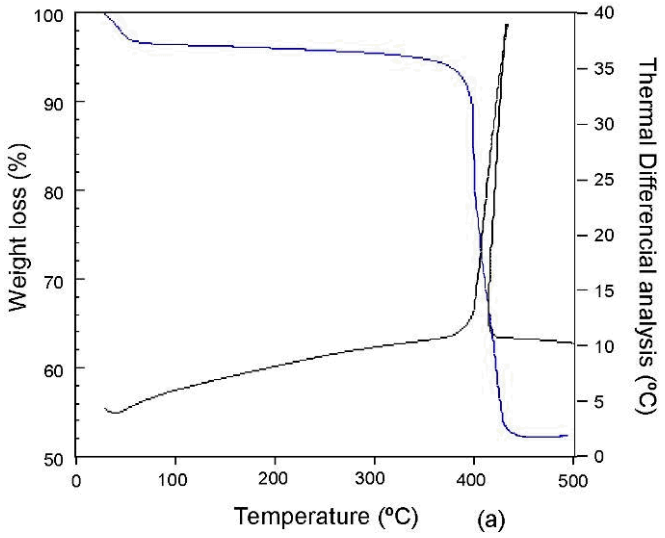


Fig. S9. (a)-(d) Relative thermal expansion of the crystal parameters and cell volume. (e)-(g) Thermal evolution of the cell angles.

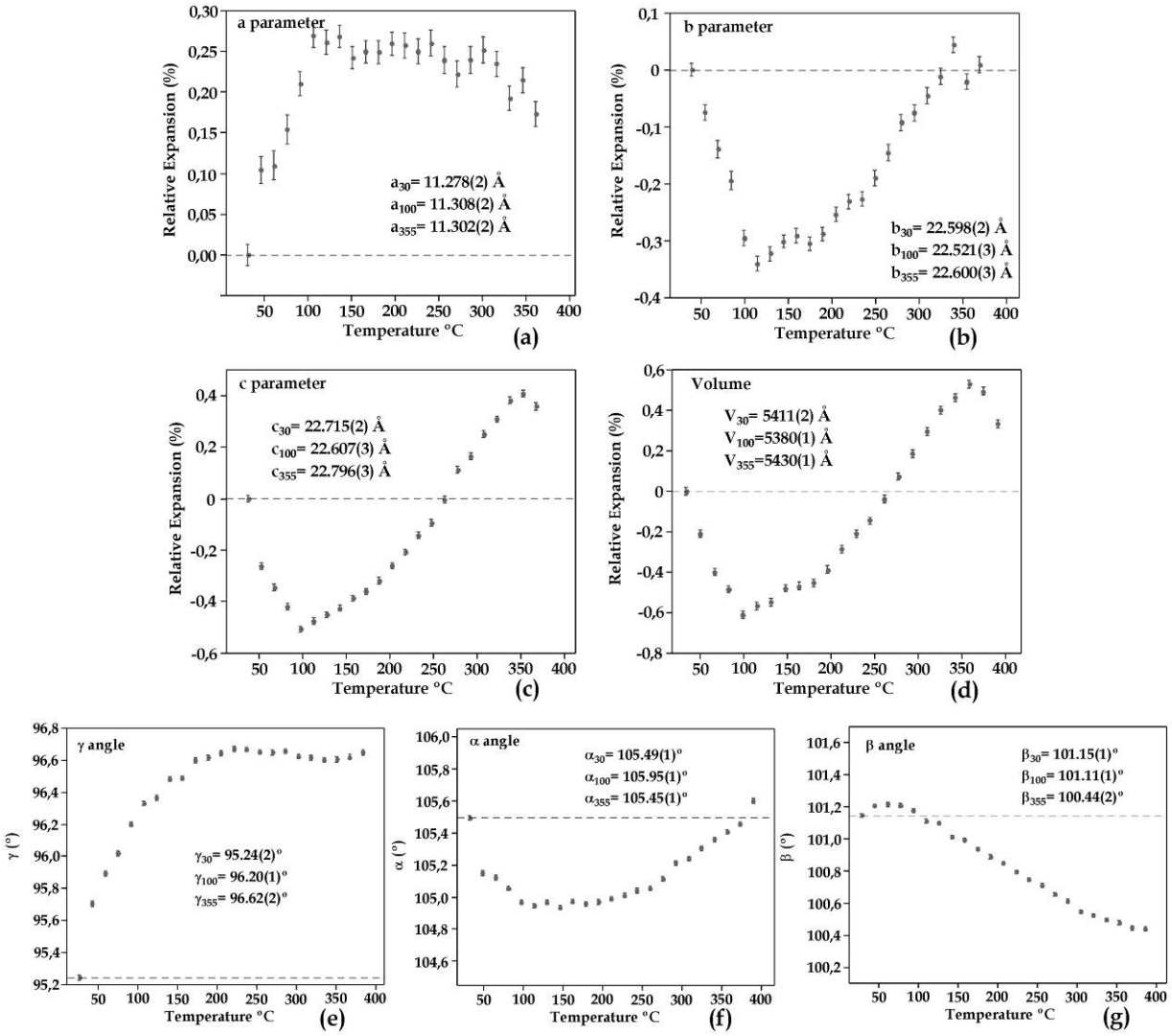


Fig. S10. UV-vis spectrum.

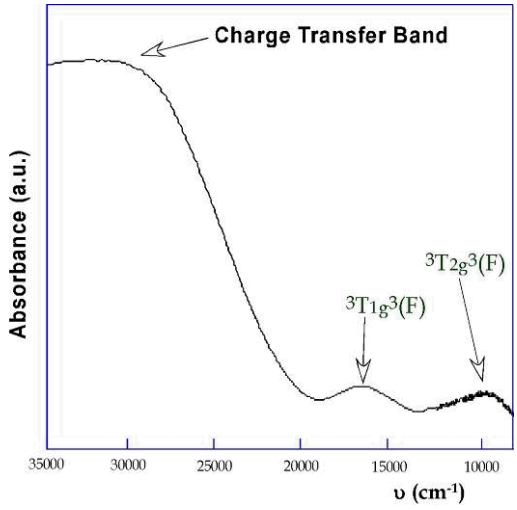


Table S1.- (a) Node-Node-Node angles of the "cds" metal organic net and "sql" metal organic layers. (b) Tilting angles in the metal organic framework of the title compound.

Node-Node-Node	Angle(º)
3D "cds" net	
Ni2-Ni1-Ni3	177.21
Ni1-Ni3-Ni7	174.99
Ni3-Ni7-Ni2	175.15
Ni7-Ni2-Ni1	177.21
Ni1-Ni1-Ni1	180
Ni2-Ni2_Ni2	180
Ni3-Ni3-Ni3	180
Ni7-Ni7-Ni7	180
2D- "sql" layers	
Ni5-Ni4-Ni5	177.02
Ni5-Ni5-Ni5	180
Ni4-Ni4-Ni4	180
Ni8-Ni6-Ni8	173.11
Ni8-Ni8-Ni8	180
Ni6-Ni6-Ni6	180
(a)	

3D "cds" net		**2D- "sql" layers**	
Ni-Bpy-Ni	**Tilting angle(º)**	**Ni-Bpy-Ni**	**Tilting angle(º)**
N11-N9---N10	171.2	N15-N8---N7	176.3
N10-N12---N9	167.1	N16-N7---N8	175.9
N10-N12---N11	168.1	N7-N16---N15	174.2
N11-N9---N12	172.1	N18-N15---N16	171.8
N24-N31---N32	170.8	N1-N13---N1	177.3
N32-N22---N31	170.2	N13-N1---N13	177.3
N32-N22---N21	173.6	N18-N17---N18	170.6
N20-N21---N22	174.2	N17-N18---N17	170.6
N21-N20---N19	175.8	N5-N29---N30	176.2
N23-N19---N20	167.0	N30-N6---N5	176.5
N19-N23---N24	175.1	N6-N30---N29	176.4
N31-N24---N23	170.1	N29-N5---N6	174.3
N25-N26---N25	175.1	N3-N4---N3	176.7
N26-N25---N26	175.1	N4-N3---N4	176.7
N29-N27---N29	171.5	N1-N2---N1	174.4
N27-N29---N27	171.5	N2-N1---N2	174.4
(b)			

Table S2.- Geometry of the channels in the crystal structure of the title compound. (R_{sd}=Radius of the channel in the selected point, and S= Section of the channel)

Point Coordinates			**R_{sd}(Å)**	**S(Å^2)**	**Point Coordinates**			**R_{sd}(Å)**	**S(Å^2)**
X	**y**	**Z**			**x**	**y**	**z**		
Channels [100]a					**Channels [100]b**				
0.0	0.25	0.75	**1.52**	**35.0**	0.0	0.75	0.75	**1.47**	**34.9**
0.1	0.25	0.75	**1.44**	**34.0**	0.1	0.75	0.75	**1.48**	**35.5**
0.2	0.25	0.75	**1.39**	**34.4**	0.2	0.75	0.75	**1.50**	**35.7**
0.3	0.25	0.75	**1.40**	**34.1**	0.3	0.75	0.75	**1.51**	**35.3**
0.4	0.25	0.75	**1.36**	**33.4**	0.4	0.75	0.75	**1.43**	**31.8**
0.5	0.25	0.75	**1.39**	**34.5**	0.5	0.75	0.75	**1.17**	**27.2**
0.6	0.25	0.75	**1.40**	**33.5**	0.6	0.75	0.75	**1.17**	**29.7**
0.7	0.25	0.75	**1.31**	**30.8**	0.7	0.75	0.75	**1.33**	**34.3**
0.8	0.25	0.75	**1.27**	**31.5**	0.8	0.75	0.75	**1.40**	**34.7**
0.9	0.25	0.75	**1.40**	**35.4**	0.9	0.75	0.75	**1.44**	**35.0**
Channels [010]									
0.85	0.00	0.25	**1.36**	**31.0**	0.85	0.50	0.25	**1.26**	**32.5**
0.85	0.05	0.25	**1.23**	**28.0**	0.85	0.55	0.25	**1.36**	**33.4**
0.85	0.10	0.25	**1.18**	**30.5**	0.85	0.60	0.25	**1.37**	**31.3**
0.85	0.15	0.25	**1.28**	**32.7**	0.85	0.65	0.25	**1.31**	**30.6**
0.85	0.20	0.25	**1.32**	**32.5**	0.85	0.70	0.25	**1.29**	**30.7**
0.85	0.25	0.25	**1.36**	**34.4**	0.85	0.75	0.25	**1.34**	**33.9**
0.85	0.30	0.25	**1.47**	**36.4**	0.85	0.80	0.25	**1.46**	**35.6**
0.85	0.35	0.25	**1.54**	**36.0**	0.85	0.85	0.25	**1.48**	**35.1**
0.85	0.40	0.25	**1.39**	**31.5**	0.85	0.90	0.25	**1.43**	**33.8**
0.85	0.45	0.25	**1.23**	**28.9**	0.85	0.95	0.25	**1.38**	**34.4**