Ln(III)-Ni(II) heteropolynuclear metal organic frameworks of oxydiacetate with promising proton-conductive properties

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Figure S1- Infrared spectra of obtained compounds.

Figure S2- Indexed x-ray powder diffraction patterns of **Nd-Ni** (a) and **Tm-Ni** (b) compounds showing the high crystallinity and the absence of significant impurity peaks in the samples.



Figure S3- Isostructural **Ce-Ni** compounds obtained by alternative synthetic procedures (DR = direct reaction, HT 7d = 7 days hydrothermal reaction and HT 3d = 3 days hydrothermal reaction); calculated pattern from the single-crystal structure is also included for comparison. Inset: zoom in the 28-35° window for a detailed comparison between different reaction times of hydrothermal production of **Ce-Ni**.



Figure S4- X-ray powder diffraction patterns of **Ln-Ni** compounds exposed to different stressing conditions. a) **Sm-Ni** sample after being exposed to water reflux for a week, compared to the simulated pattern obtained from the single-crystal structure. b) **Tm-Ni** sample after and before being exposed to 100% RH for more than 5 hours at room temperature during conductivity measurements, compared to the simulated pattern obtained from the single-crystal structure. Two marked peaks in the used sample correspond to metallic Ag (111) and (200) peaks.





Figure S5- Semi-logarithmic plot of conductivity variation with % RH at 25 $^\circ C.$

Table S1- Water content results of **Ln-Ni** compounds obtained in this work. ^aShannon's ionic radii for coordination number 9.¹ ^bChannel volume calculated from single-crystal data in PLATON software.² ^cChannel diameter calculated from modeling the empty volume as a cylinder of base radii ϕ_{ch} and height *c* (crystallographic edge). ^dWeight loss for crystallization/coordination water molecules determined from thermogravimetric analysis. ^eWeight loss for crystallization/coordination water molecules calculated using the number of water molecules in the next column. ^fMaximum number of crystallization water molecules per formula unit that can fit in the free voids by employing the nominal H₂O density (0.997 g·mL⁻¹).

Ln	Channel dimensions		Crystallization				Coordination			
	rª (Å)	$V_{ch}{}^{b}$	$\phi_{ch}{}^{c}$	H ₂ O we	eight %		λι Δι f	H ₂ O weight %		#110
		(Å ³)	(Å)	TGA ^d	calc. ^e	# п ₂ О	v _{ch} / v _{H2O} [·]	TGA ^d	calc. ^e	# П ₂ О
La	1.216	993	9.18	15.7	15.7	14	16.5	6.7	6.7	6
Ce	1.196	906	8.71	15.0	15.7	14	15.1	6.6	6.7	6
Pr	1.179	998	9.14	15.6	15.6	14	16.6	6.6	6.7	6
Nd	1.163	977	9.01	14.6	14.6	13	16.3	6.6	6.8	6
Sm	1.132	928	8.74	14.6	14.5	13	15.5	6.6	6.7	6
Eu	1.120	878	7.85	14.2	14.5	13	14.6	6.6	6.7	6
Tb	1.095	891	8.52	13.8	13.4	12	14.8	6.5	6.7	6
Dy	1.083	873	8.41	13.8	13.4	12	14.5	6.5	6.7	6
Y	1.075	728	7.35	14.3	14.7	12	12.1	7.2	7.3	6
Но	1.072	874	8.41	13.4	13.3	12	14.6	6.4	6.7	6
Er	1.062	830	8.14	13.0	13.3	12	13.8	6.5	6.6	6
Tm	1.052	799	7.55	12.8	12.3	11	13.3	6.5	6.7	6
Yb	1.042	723	7.98	12.5	12.2	11	12.0	6.5	6.7	6

Table S2.- Absorption Energy as a function of the number of water molecules, *n*, according to:

$$E_{abs}(eV) = E_{Tm-Ni}(eV) - n E_{H2O}(eV)$$

Equation 1

n	$E_{\rm absorption}$ (eV)
0	0.0
9	-10.2
18	-12.3
27	-15.4
36	-16.9

Table S3- Crystallographic data of Ln-Ni compounds

	La-Ni	Ce-Ni	Pr-Ni	Nd-Ni	Sm-Ni
Empirical formula	$C_{24}H_{36}La_2O_{39}Ni_3\\$	$C_{24}H_{36}Ce_{2}O_{42}Ni_{3}$	$C_{24}H_{36}Pr_{2}O_{39}Ni_{3}$	$C_{24}H_{36}Nd_2O_{39}Ni_3\\$	$C_{24}H_{36}Sm_2O_{40}Ni_3$
Formula weight	1402.48	1452.90	1406.53	1413.14	1441.41
Crystal system	Hexagonal	Hexagonal	Hexagonal	Hexagonal	Hexagonal
Space group	P6/mcc	P6/mcc	P6/mcc	P6/mcc	P6/mcc
a, b (Å)	15.3094(3)	15.0898(7)	15.0750(2)	14.9796(11)	14.7938(11)
<i>c</i> (Å)	15.0182(3)	15.1899(7)	15.2136(2)	15.3052(12)	15.4673(12)
α, β (°)	90	90	90	90	90
γ (°)	120	120	120	120	120
<i>V</i> (ų)	3048.35(13)	2995.4(3)	2994.17(9)	2974.2(5)	2931.6(5)
Ζ	2	2	2	2	2
ρ _{calc} (g cm ⁻³)	1.528	1.611	1.560	1.578	1.633
μ (mm ⁻¹)	2.367	2.509	2.610	2.735	3.009
F(000)	1380	1432.0	1388	1392	1416
Crystal dimensions (mm)	0.20×0.08×0.05	0.40×0.23×0.13	0.12×0.08×0.06	0.14×0.06×0.03	0.11×0.06×0.04
20 range for data collection (°)	5.322 to 56.562	6.204 to 50.04	5.356 to 56.558	6.182 to 60.146	5.508 to 55.862
	-20 ≤ h ≤ 20	-17 ≤ h ≤ 17	-19 ≤ h ≤ 19	-12 ≤ h ≤ 21	-13 ≤ h ≤ 18
Limiting indices	-17 ≤ k ≤ 20	-17 ≤ k ≤ 17	-11 ≤ k ≤ 20	-11 ≤ k ≤ 20	-19 ≤ k ≤ 10
	-15 ≤ l ≤ 20	-16 ≤ l ≤ 18	-20 ≤ l ≤ 16	-20 ≤ l ≤ 18	-19 ≤ l ≤ 18
Reflections (collected/unique/R _{int})	12016/1323/0.03 19	38785/923/0.0244	8953/1299/0.0201	9422/1434/0.0308	6642/1140/0.0458
Data/restraints/parameters	1323/0/62	923/83/83	1299/0/62	1434/0/62	1140/4/59
R_1^{a} , wR_2^{b} (all data)	0.0363, 0.1320	0.0267, 0.1116	0.0283, 0.1162	0.0308, 0.1101	0.0476, 0.1481
Goodness-of-fit on F ²	1.122	1.161	1.080	1.097	1.045
$\Delta ho_{max} / \Delta ho_{min}$	1.23/-0.80	0.62/-0.59	1.15/-0.53	1.11/-0.52	1.17/-1.95
	Eu-Ni	Tb-Ni	Dy-Ni	Ho-Ni	Er-Ni
Empirical formula	C ₂₄ H ₃₆ Eu ₂ O _{40.56} Ni ₃	$C_{24}H_{36}Tb_2O_{41}Ni_3$	C ₂₄ H ₃₆ Dy ₂ O ₃₉ Ni ₃	$C_{24}H_{36}Ho_2O_{39}Ni_3$	$C_{24}H_{36}Er_2O_{41}Ni_3$
Formula weight	1453.54	1474.55	1449.66	1454.52	1491.24
Crystal system	Hexagonal	Hexagonal	Hexagonal	Hexagonal	Hexagonal
Space group	P6/mcc	P6/mcc	P6/mcc	P6/mcc	P6/mcc
a, b (Å)	14.5288(9)	14.5401(16)	14.4438(6)	14.4055(6)	14.2113(13)
<i>c</i> (Å)	15.6072(12)	15.617(2)	15.7220(6)	15.7515(6)	15.9401(18)
α, β (°)	90	90	90	90	90
γ (°)	120	120	120	120	120
<i>V</i> (ų)	2853.1(4)	2859.2(7)	2840.5(3)	2830.8(3)	2788.0(6)
Ζ	2	2	2	2	2
ρ _{calc} (g cm ⁻³)	1.692	1.713	1.695	1.706	1.776
μ (mm ⁻¹)	17.440	3.507	3.667	3.835	4.070

F(000)	1429	1444	1416	1420	1456
Crystal dime	0.19×0.097×0.056	0.22×0.05×0.04	0.13×0.05×0.03	0.13×0.04×0.03	0.12×0.05×0.03
nsions (mm)					
20 range for data collection (°)	7.026 to 152.544	5.216 to 56.564	5.182 to 56.562	5.172 to 56.56	5.73 to 56.614
	-18 < h < 18	-18 < h < 19	-19 < h < 17	-17 < h < 12	-15 < h < 19
Limiting indices	-18 < k < 17	-19 < k < 14	-15 < k < 19	-19 < k < 15	-14 < k < 19
	-19 ≤ I ≤ 19	-19 ≤ I ≤ 20	-20 ≤ I ≤ 19	-13≤ ≤21	-22 ≤ l ≤ 16
Reflections	28180/1043/0.14				
(collected/unique/R _{int})	78	8418/1241/0.0500	9545/1232/0.0379	8788/1225/0.0341	8417/1310/0.0894
Data/restraints/parameters	1043/6/72	1241/0/62	1232/0/62	1225/0/62	1310/0/62
$R_{1^{a}}, wR_{2^{b}}$ (all data)	0.0553, 0.1576	0.0522, 0.1742	0.0360, 0.1217	0.0343, 0.01165	0.0466, 0.0959
Goodness-of-fit on F ²	1.133	1.152	1.141	1.129	0.913
$\Delta \rho_{max} / \Delta \rho_{min}$	1.20/-0.50	2.62/-1.50	1.21/-1.03	1.22/-0.71	0.85/-0.68
	Yb-Ni	Tm-Ni	Lu-Ni	Y-Ni	
Empirical formula	Ca4HacYbaOaoNia	CatHacTmaOaoNia	CatHacl UpOpe caNia	CatHacYaQ40 aNia	
Formula weight	1470.79	1462.52	1466.90	1321.68	
Crystal system	Hexagonal	Hexagonal	Cubic	Hexagonal	
Snace group	P6/mcc	P6/mcc	P6/mcc	P6/mcc	
$a h (\Lambda)$	13 9032(4)	14 1712(9)	25 296(5)	13 9318(10)	
c (Å)	15.5052(4)	14.1712(5) 15 0715(17)	25.290(5)	15.5518(10)	
α β (°)	10.471(4)	13.3713(17)	23.230(3)	10.1001(13)	
u, 0 ()	120	120	90	120	
γ() \/(Å3)	120	120	90	120	
V (A ³)	2703.05(17)	2///./(5)	10180(10)	2707.3(4)	
Z (3)	2	2	16	2	
ρ_{calc} (g cm ⁻³)	1.807	1.749	2.408	1.621	
μ (mm ⁻¹)	4.549	4.254	6.332	4.823	
F(000)	1432	1428	11426	1327	
Crystal dimensions (mm)	0.08×0.04×0.04	0.08×0.06×0.05	0.21×0.21×0.20	0.18×0.094×0.05	
20 range for data collection (°)	3.382 to 56.564	3.318 to 56.55	5.578 to 58.242	7.326 to 172.83	
	-13 ≤ h ≤ 17	-18 ≤ h ≤ 12	-34 ≤ h ≤ 34	-9 ≤ h ≤ 0	
Limiting indices	-7 ≤ k ≤ 18	-17 ≤ k ≤ 18	-34 ≤ k ≤ 34	$0 \le k \le 18$	
	-21 ≤ l ≤ 16	-19 ≤ l ≤ 21	-34 ≤ l ≤ 34	$0 \le I \le 20$	
Reflections (collected/unique/R _{int})	6981/1170/0.0270	10406/1205/0.0304	217123/922/0.0674	2712/2712/*	
Data/restraints/ parameters	1170/0/62	1205/4/67	992/5/66	2712/6/75	
R_1^a , wR_2^b (all data)	0.0331, 0.1187	0.0344, 0.1182	0.0279, 0.0853	0.0653, 0.2050	
Goodness-of-fit on F ²	1.109	1.115	1.290	1.084	
$\Delta ho_{max} / \Delta ho_{min}$	1.58/-0.79	1.22/-0.55	0.37/-1.22	0.82/-0.87	
$a_{R_1} = \Delta [P_1 + P_1 + P_1 + P_1] + \Delta P_1$	$ _{bWR_{2}} = \bigcup_{w \in V} _{bWR_{2}}$				

*R_{int} was not determined because the crystal was a twin and data integration required merging of equivalent reflections.

	La-Ni	Ce-Ni	Pr-Ni	Nd-Ni
Ln1-O1 (x6)	2.499(3)	2.480(2)	2.469(2)	2.457(3)
Ln1-O3 (x3)	2.593(4)	2.573(4)	2.552(4)	2.534(4)
Ni1-01W (x2)	2.087(4)	2.094(3)	2.095(3)	2.093(4)
Ni1-O2 (x3)	2.039(3)	2.038(9)	2.036(2)	2.033(3)
01-Ln1-03	60.79(7)	61.13(5)	61.60(6)	62.03(6)
01–Ln1-03 ⁱ	138.30(8)	137.72(6)	137.62(6)	137.37(7)
01-Ln1-01 ⁱ	80.90(10)	81.17(8)	80.86(9)	80.36(10)
01-Ln1-01"	82.09(12)	84.56(11)	84.76(13)	85.26(14)
01-Ln1-01 ⁱⁱⁱ	121.59(14)	122.26(10)	123.20(11)	124.06(12)
O1-Ln1-O3 ^{iv}	75.01(8)	75.10(6)	74.75(6)	74.53(7)
02-Ni1-02 ^v	88.8(2)	78.1(6)	88.84(19)	88.9(2)
O2-Ni1-O2 ^{vi}	91.2(2)	101.9(6)	91.16(19)	91.1(2)
O2 ^{vi} -Ni1-O1W ^{vi}	85.80(12)	86.6(3)	85.84(10)	86.11(11)
O2 ^v -Ni1-O1W ^{vi}	94.20(12)	93.4(3)	94.16(10)	93.89(11)
	Eu-Ni	Sm-Ni	Tb-Ni	Dy-Ni
Ln1-O1 (x6)	2.416(4)	2.432(4)	2.397(4)	2.392(3)
Ln1-O3 (x3)	2.498(7)	2.486(6)	2.470(7)	2.458(5)
Ni1-01W (x2)	2.092(6)	2.098(6)	2.089(5)	2.093(4)
Ni1-O2 (x3)	2.028(5)	2.027(5)	2.022(4)	2.020(4)
01-Ln1-03	63.07(10)	62.70(10)	63.37(10)	63.56(8)
01–Ln1-03 ⁱ	136.55(12)	136.88(11)	136.34(11)	136.13(9)
01-Ln1-01 ⁱ	78.86(18)	79.43(17)	78.47(17)	78.12(14)
01-Ln1-01"	86.9(2)	86.2(2)	87.3(2)	87.74(18)
01-Ln1-01 ⁱⁱⁱ	126.1(2)	125.40(19)	126.7(2)	127.11(16)
01-Ln1-03 ^{iv}	74.15(11)	74.26(10)	74.02(11)	74.00(8)
02-Ni1-02 ^v	88.6(3)	89.0(3)	88.6(3)	88.6(3)
O2-Ni1-O2 ^{vi}	91.4(3)	91.0(3)	91.4(3)	91.4(3)
O2 ^{vi} -Ni1-O1W ^{vi}	86.44(18)	86.2(2)	86.48(16)	86.58(14)
O2 ^v -Ni1-O1W ^{vi}	93.56(18)	93.8(2)	93.52(16)	93.42(14)
	Ho-Ni	Er-Ni	Yb-Ni	Tm-Ni
Ln1-O1 (x6)	2.382(3)	2.368(7)	2.353(3)	2.369(3)
Ln1-O3 (x3)	2.447(5)	2.440(10)	2.418(5)	2.433(5)
Ni1-O1W (x2)	2.092(4)	2.094(10)	2.098(4)	2.108(5)
Ni1-O2 (x3)	2.019(3)	2.024(8)	2.026(4)	2.024(4)
01-Ln1-03	63.80(8)	64.07(19)	64.39(8)	64.22(8)
01–Ln1-03 ⁱ	135.99(9)	135.77(19)	135.24(10)	135.60(9)
01-Ln1-01 ⁱ	77.84(13)	77.4(3)	76.60(15)	77.15(14)
01-Ln1-01"	88.01(18)	88.5(4)	89.5(2)	88.81(19)
01-Ln1-01 ⁱⁱⁱ	127.60(16)	128.1(4)	128.78(16)	128.45(16)
01-Ln1-03 ^{iv}	73.87(8)	73.78(19)	73.87(9)	73.76(9)
02-Ni1-02 ^v	88.3(3)	88.5(6)	87.8(2)	88.0(3)
02-Ni1-02 ^{vi}	91.7(3)	91.5(6)	92.2(2)	92.0(3)
O2 ^{vi} -Ni1-O1W ^{vi}	86.84(14)	86.7(3)	86.95(14)	87.06(14)
02 ^v -Ni1-01W ^{vi}	93.16(14)	93.3(3)	93.05(14)	92.94(14)
ⁱ y,1-x+y,1-z; ⁱⁱ 1-x,1-x+y,-1/2+	z; ⁱⁱⁱ x-y,1-y,-1/2+z; ^{iv} y,x,-1/2	2+z; ^v x,y,1-z; ^{vi} x-y,x,1-z		

Table S4- Selected structural parameters for hexagonal Ln-Ni compounds

	Y-Ni	
Ln1-O1 (x6)	2.368(3)	
Ln1-O3 (x3)	2.417(5)	
Ni1-O1W (x2)	2.073(4)	
Ni1-O2 (x3)	2.021(3)	
01-Ln1-03	64.13(7)	
01–Ln1-03 ⁱ	134.99(9)	
01-Ln1-01 ⁱ	76.32(13)	
01-Ln1-01"	90.02(18)	
01-Ln1-01 ^{III}	128.25(15)	
01-Ln1-03 ^{iv}	74.30(8)	
02-Ni1-02 ^v	89.4(2)	
02-Ni1-02 ^{vi}	90.6(2)	
02 ^{vi} -Ni1-01W ^{vi}	86.53(12)	
O2 ^v -Ni1-O1W ^{vi}	93.47(12)	
ⁱ y,1-x+y,1-z; ⁱⁱ 1-x,1-x+y,-1/2+	z; ⁱⁱⁱ x-y,1-y,-1/2+z; ^{iv} y,x,-1/2+z; ^v x,y,1-z; ^{vi} x-y,x,1-z	

Table S5- Selected structural parameters for Lu-Ni.

	Lu-Ni	
Lu1-O3 (x3)	2.399(3)	
Lu1-O1 (x6)	2.324(2)	
Ni1-O2 (x6)	2.068(2)	
Ni2-O1W (x6)	2.035(4)	
01-Lu1-O3	65.00(6)	
01-Lu1-03 ⁱ	72.18(6)	
02-Ni-02 ⁱⁱ	94.01(9)	
O2-Ni-O2 ⁱⁱⁱ	85.99(9)	
ⁱ -1/4+z,1-y,1/4+x; ⁱⁱ -1/4+y	,3/2-z,1/4+x; ⁱⁱⁱ z,5/4-x,5/4-y	

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