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**Structural Characterization of the Nickel(II) Formate Complex,
Ni(py)₄(O₂CH)₂•2py, and Re-evaluation of the Nitrate Counterpart,
Ni(py)₄(ONO₂)₂•2py: Evidence for Non-Linear Nitrate Coordination[‡]**

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Abstract: The molecular structure of the nickel formate compound,
Ni(py)₄(O₂CH)₂•2py, has been determined by X-ray diffraction, thereby demonstrating
that the formate ligand coordinates in a unidentate manner. A similar investigation of
the nitrate compound, Ni(py)₄(ONO₂)₂•2py, indicates that the nitrate ligand also
coordinates in unidentate manner; however, the Ni–O–NO₂ bond angle is distinctly
bent, in contrast to the linear geometry that was previously reported.

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Keywords: Nickel, formate, nitrate, coordination mode.

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[‡] Dedicated with respect to Professor Malcolm L. H. Green on the occasion of his 80th
birthday. Happy birthday, Malcolm!

INTRODUCTION

While there is currently much interest in the use of hydrogen as a fuel, the inadequacy of current storage and transportation techniques¹ has prompted research to develop chemical methods to provide hydrogen on demand.² Formic acid, in particular, has attracted much attention as a chemical medium for storing H₂,^{3,4,5} but such implementation requires effective catalysts to release H₂ on demand. Therefore, we are currently interested in developing catalysts that utilize earth abundant nonprecious metals to achieve this transformation.⁶ In this regard, we have recently demonstrated that the zerovalent nickel compound, Ni(PMe₃)₄, can serve as a catalyst for the release of H₂ from formic acid.^{6c} As part of that study, we demonstrated that PMe₃ can induce the release of CO₂ and H₂ from the nickel formate complex, Ni(py)₄(O₂CH)₂, and thereby form Ni(PMe₃)₄. Prompted by this observation, we sought to determine the coordination mode of the formate ligand and so we describe here the molecular structure of Ni(py)₄(O₂CH)₂ as determined by X-ray diffraction; in addition, we also report the molecular structure of the nitrate counterpart, Ni(py)₄(ONO₂)₂, which differs considerably from that previously reported.

RESULTS AND DISCUSSION

A large variety of compounds of composition M(py)₄X₂•2py have been previously investigated with respect to their clathrate nature, the ability to maintain a structural similarity upon varying the M(py)₄X₂ host molecules, and the ability to introduce guest molecules other than pyridine.⁷⁻¹³ Our particular interest in this class of compounds, however, pertains to the nickel formate derivative, Ni(py)₄(O₂CH)₂•2py,⁸ due to the fact that the formate ligands in this complex are subject to facile decarboxylation in the presence of PMe₃.^{6c} Therefore, we have determined the molecular structure of Ni(py)₄(O₂CH)₂•2py by single crystal X-ray diffraction.

As observed for other $M(\text{py})_4\text{X}_2 \cdot 2\text{py}$ derivatives,⁷ the structure of $\text{Ni}(\text{py})_4(\text{O}_2\text{CH})_2 \cdot 2\text{py}$ (Figure 1) is comprised of well-defined octahedral $\text{Ni}(\text{py})_4(\text{O}_2\text{CH})_2$ units with pyridine occupying interstitial sites, rather than an alternative ionic formulation $[\text{Ni}(\text{py})_6][\text{O}_2\text{CH}]_2$.⁸ Also of note, the formate ligands of $\text{Ni}(\text{py})_4(\text{O}_2\text{CH})_2$ are clearly identified as coordinating in a unidentate manner according to the criteria listed in Table 1 and Figure 2.¹⁴ Specifically, the Ni–O distances of 2.075(2) Å and 3.784(3) Å of the two crystallographically equivalent formate ligands differ by 1.71 Å, while the Ni–O–C bond angles of 151.5(3)° and 53.1(2)° differ by 98.4°. For comparison, metrical data for other monomeric nickel formate compounds are listed in Table 2.^{15–27}

Figure 1. Molecular structure of $\text{Ni}(\text{py})_4(\text{O}_2\text{CH})_2 \cdot 2\text{py}$ (only the host is shown).

Selected bond lengths (Å) and angles (°): Ni–O1 = 2.0750(19), Ni–N11 = 2.099(2), Ni–N21 = 2.101(2), Ni–N31 = 2.1451(18), C1–O1 = 1.228(3), C1–O2 = 1.205(5), O1–Ni–O1' = 177.57(10), C1–O1–Ni = 151.5(3), O1–C1–O2 = 127.4(4), O1–Ni–N11 = 91.22(5), O1–Ni–N21 = 88.78(5), O1–Ni–N31 = 96.58(11), O1–Ni–N31 = 83.40(11), N11–Ni–N31 = 90.31(5), N21–Ni–N31 = 89.69(5).

Table 1. Criteria for assigning carboxylate coordination modes in which the secondary oxygen atom is proximal.^a

Coordination mode	$\Delta d/\text{\AA}$	$\Delta\theta/^\circ$
unidentate	> 0.6	> 28
anisobidentate	$0.3 - 0.6$	$14 - 28$
bidentate	< 0.3	< 14

(a) Adopted from the values for nitrate ligands. See reference 34a.

$$\Delta d = d_2 - d_1$$

$$\Delta\theta = \theta_1 - \theta_2$$

Figure 2. Classification of carboxylate coordination modes with a proximal conformation.

It is also pertinent to point out that the formate ligand adopts a proximal conformation in which the uncoordinated oxygen resides with a cis-like disposition relative to the metal, rather than a distal conformation in which the uncoordinated oxygen atom and metal adopt a trans-like disposition (Figure 3).

Figure 3. Proximal and distal conformations of unidentate formate ligands.

Proximal and distal conformations may be distinguished by M–O–C–O torsion angles of $|\tau| < 90^\circ$ and $|\tau| > 90^\circ$, respectively, and the value of 2.2° for $\text{Ni}(\text{py})_4(\text{O}_2\text{CH})_2$ is clearly in accord with the proximal classification. In this regard, examination of the Cambridge Structural Database (CSD) indicates that most terminal metal formate compounds (59 %) possess a proximal conformation (Figure 4). Moreover, the average torsion angle values for these two classes are 6.8° and 171.6° , which are close to the idealized values (0° and 180°) expected if the metal were to reside in the plane of the formate ligand.

Figure 4. Distribution of proximal and distal metal formate compounds as classified by the magnitude of the M–O–C–O torsion angle.

Examination of the CSD indicates that most other mononuclear nickel formate compounds are also unidentate with a proximal conformation (Table 2). Furthermore, those that adopt a distal conformation, namely (phen)Ni(O₂CH)₂(OH₂),¹⁵ (Im^{Me})₂Ni(O₂CH)₂(OH₂)₂,¹⁶ and (Im^{Me2})₂Ni(O₂CH)₂(OH₂)₂,¹⁶ exhibit hydrogen bonding interactions to the uncoordinated formate oxygen atom.²⁸ Mononuclear nickel formate compounds that exhibit bidentate coordination are not common, but one example is provided by (phen)Ni(O₂CH)₂(OH₂).¹⁵

Table 2. Metrical data for selected mononuclear nickel formate compounds.

Compound	$d_1/\text{\AA}$	$d_2/\text{\AA}$	$\Delta d/\text{\AA}$	$\theta_1/^\circ$	$\theta_2/^\circ$	$\Delta\theta/^\circ$	$ \tau $	Reference
Ni(py) ₄ (O ₂ CH) ₂	2.075	3.784	1.709	151.5	53.1	98.4	2.2	this work
(phen)Ni(O ₂ CH) ₂ (OH ₂)	2.045	4.091	2.046	121.6	11.2	110.4	173.7	15
	2.148	2.150	0.002	88.6	88.4	0.2	0.4	
(Im ^{Me}) ₂ Ni(O ₂ CH) ₂ (OH ₂) ₂	2.082	4.189	2.107	129.4	16.5	112.9	170.5	16
(Im ^{Me2}) ₂ Ni(O ₂ CH) ₂ (OH ₂) ₂	2.071	4.165	2.094	126.2	15.4	110.8	162.5	16
[NEt ₄][(NNN ^{Mes})Ni(O ₂ CH)]	1.856	2.858	1.002	114.3	67.5	46.8	0.0	17
[(N ₄)Ni(O ₂ CH)(OH ₂)] [ClO ₄]	2.001	3.296	1.295	127.3	62.8	64.5	7.2	18
[N ^{Me2} CN ^{Me2}]Ni(O ₂ CH)	1.936	3.126	1.190	122.9	65.0	57.9	2.9	19,20
[P ^{Pr2} NP ^{Pr2}]Ni(O ₂ CH)	1.893	3.004	1.111	117.2	64.8	52.4	0.9	21
[P ^{Pr2} CP ^{Pr2}]Ni(O ₂ CH)	1.914	3.135	1.221	123.2	64.1	59.1	2.4	22
[P ^{Bu2} CP ^{Bu2}]Ni(O ₂ CH)	1.928	3.338	1.410	132.6	59.0	73.6	7.6	23
[P ^{Cy2} CP ^{Cy2}]Ni(O ₂ CH) ^a	1.923	3.225	1.302	129.8	61.4	68.4	12.5	24
[P ^{Pe2} CP ^{Pe2}]Ni(O ₂ CH)	1.910	3.126	1.216	122.8	64.2	58.6	1.9	22
	1.906	3.129	1.223	122.9	64.2	58.7	2.9	
[P ^{Bu2} OCOP ^{Bu2}]Ni(O ₂ CH)	1.920	3.270	1.350	129.4	61.0	68.44	1.2	25
[P ^{Bu2} OC _{sp3} OP ^{Bu2}]Ni(O ₂ CH)	1.945	3.195	1.250	125.0	63.6	61.4	1.5	26
[P ^{Cy2} SiP ^{Cy2}]Ni(O ₂ CH)	1.968	2.976	1.008	116.2	68.1	48.1	2.7	24
(Ox) ₂ Ni(O ₂ CH) ₂	2.070	3.464	1.394	132.6	61.0	71.6	9.1	27
	2.048	3.464	1.416	133.9	60.1	73.8	5.9	

(a) the formate ligand is disordered and data are only given for one component.

Another noteworthy feature of the structure of Ni(py)₄(O₂CH)₂•2py pertains to the fact that the unit cell β angle of 90.076(3)° is sufficiently close to 90° that the crystal could possibly correspond to the orthorhombic, rather than monoclinic, crystal system. Indeed, a previous unit cell determination identified Ni(py)₄(O₂CH)₂•2py as orthorhombic *Ccca*,²⁹ although this assignment was not confirmed by a complete

determination of the molecular structure. Therefore, to establish that the crystal of $\text{Ni}(\text{py})_4(\text{O}_2\text{CH})_2 \cdot 2\text{py}$ described here does not belong to the orthorhombic system, the molecular structure of $\text{Ni}(\text{py})_4(\text{O}_2\text{CH})_2 \cdot 2\text{py}$ was also evaluated in the previously assigned orthorhombic *Ccca* space group.⁸ Decisive evidence that the orthorhombic *Ccca* space group is not appropriate for this crystal of $\text{Ni}(\text{py})_4(\text{O}_2\text{CH})_2 \cdot 2\text{py}$, however, is provided by the observations that (i) whereas the formate ligands in the monoclinic *C2/c* version are ordered, they are disordered in the orthorhombic *Ccca* space group (Figure 5) and (ii) the *R* values are significantly higher (Table 3). Furthermore, there are a significant number of systematic absence violations for the *Ccca* space group.³⁰

In addition to refining the oxygen atom attached to nickel off the two-fold axis (Figure 5), the *Ccca* structure may also be refined with the oxygen residing on the axis (Figure 6), as has been reported for nitrate and nitrite derivatives (*vide infra*).^{8,31,32} However, this refinement is even less satisfactory than that in which the oxygen does not reside on the axis (Table 3). Thus, $\text{Ni}(\text{py})_4(\text{O}_2\text{CH})_2 \cdot 2\text{py}$ is an example of a monoclinic crystal where the β angle is very close to 90° . Albeit uncommon, examples of such compounds are, nevertheless, well precedented. For example, the CSD lists 3,276 monoclinic entries with a β angle in the range 90.0° to 90.1° .³³

Figure 5. Molecular structure of $\text{Ni}(\text{py})_4(\text{O}_2\text{CH})_2 \cdot 2\text{py}$ (only the host is shown) refined in the incorrect *Ccca* space group with the oxygen attached to nickel not being located on the two-fold axis.

Figure 6. Molecular structure of $\text{Ni}(\text{py})_4(\text{O}_2\text{CH})_2 \cdot 2\text{py}$ (only the host is shown) refined in the incorrect *Ccca* space group with the oxygen attached to nickel being located on the two-fold axis.

Table 3. Comparison of refinement values for $\text{Ni}(\text{py})_4(\text{O}_2\text{CH})_2 \cdot 2\text{py}$.

Space Group	R_1 [$I > 2\sigma(I)$]	wR_2 [$I > 2\sigma(I)$]	R_1 [all data]	wR_2 [all data]	GOOF
<i>C2/c</i>	0.0435	0.0974	0.0675	0.1081	1.026
<i>Ccca</i> ^a	0.0884	0.1981	0.1038	0.2042	1.231
<i>Ccca</i> ^b	0.0945	0.2048	0.1099	0.2114	1.209

(a) refinement in which the formate ligand is disordered and the oxygen attached to nickel does not reside on a crystallographic two-fold axis.

(b) refinement in which the formate ligand is disordered and the oxygen attached to nickel resides on a crystallographic two-fold axis.

A variety of other $\text{Ni}(\text{py})_4\text{X}_2 \cdot 2\text{py}$ compounds have been structurally characterized,^{8,9,10a-d,12} but it is particularly appropriate to compare the coordination geometry of $\text{Ni}(\text{py})_4(\text{O}_2\text{CH})_2$ with that of the nitrate derivative, $\text{Ni}(\text{py})_4(\text{ONO}_2)_2$, since both carboxylate¹⁴ and nitrate³⁴ ligands can coordinate *via* unidentate and bidentate modes. It is, therefore, interesting to note that whereas the Ni–O–C angle of $\text{Ni}(\text{py})_4(\text{O}_2\text{CH})_2$ is distinctly bent, the Ni–O–N angle for $\text{Ni}(\text{py})_4(\text{ONO}_2)_2$ was reported to be 180°.³¹ In addition to the difference between $\text{Ni}(\text{py})_4(\text{O}_2\text{CH})_2$ and $\text{Ni}(\text{py})_4(\text{ONO}_2)_2$ being unexpected, the linearity of the nitrate compound has little precedence. For example, analysis of structurally characterized metal nitrate compounds listed in the Cambridge Structural Database indicates that the mean M–O–N angle is 119.5°, with <0.2% having a bond angle of 180° (Figure 7).

Figure 7. Distribution of M–O–NO₂ bond angles for structurally characterized metal nitrate compounds listed in the Cambridge Structural Database.

In view of the unusual coordination mode of the nitrate ligand reported for $\text{Ni}(\text{py})_4(\text{ONO}_2)_2 \cdot 2\text{py}$ at 293 K,^{8,31} we considered it worthwhile to investigate the structure at a lower temperature, especially because the nitrate ligand was characterized by large atom displacement parameters.^{31,35} Significantly, data collected at 240 K resulted in a well defined structure that features a distinctly non-linear coordination of the nitrate ligand [$141.72(10)^\circ$], as illustrated in Figure 8.

Figure 8. Molecular structure of $\text{Ni}(\text{py})_4(\text{ONO}_2)_2 \cdot 2\text{py}$ (only the host is shown).

Selected bond lengths ($\text{\AA}$) and angles ($^\circ$): $\text{Ni}-\text{O1} = 2.1366(15)$, $\text{Ni}-\text{N11} = 2.1125(19)$, $\text{Ni}-\text{N21} = 2.0821(19)$, $\text{Ni}-\text{N31} = 2.1328(15)$, $\text{N1}-\text{O1} = 1.2759(17)$, $\text{N1}-\text{O2} = 1.2229(18)$, $\text{N1}-\text{O3} = 1.2185(17)$, $\text{O1}-\text{Ni}-\text{O1}' = 166.89(6)$, $\text{Ni}-\text{O1}-\text{N1} = 141.72(10)$, $\text{O1}-\text{N1}-\text{O2} = 118.77(13)$, $\text{O1}-\text{N1}-\text{O3} = 120.27(13)$, $\text{O2}-\text{N1}-\text{O3} = 120.87(15)$, $\text{N11}-\text{Ni}-\text{O1} = 83.44(3)$, $\text{N21}-\text{Ni}-\text{O1} = 96.56(3)$, $\text{N31}-\text{Ni}-\text{O1} = 91.56(4)$, $\text{N11}-\text{Ni}-\text{N31} = 91.53(3)$, $\text{N21}-\text{Ni}-\text{N31} = 88.47(3)$.

An interesting feature of the structure of $\text{Ni}(\text{py})_4(\text{ONO}_2)_2 \cdot 2\text{py}$ is the displacement of the metal from the nitrate plane, as indicated by the Ni–O–N–O torsion angles of 79.5° and 103.9° . Examination of the CSD indicates that most torsion angles for metal nitrate compounds are close to either 0° or 180° (Figure 9), thereby indicating that the metal commonly resides in the plane of the nitrate ligand. Precedent for the type of nitrate coordination mode observed in $\text{Ni}(\text{py})_4(\text{ONO}_2)_2 \cdot 2\text{py}$ is, nevertheless, provided by the copper counterpart, $\text{Cu}(\text{py})_4(\text{ONO}_2)_2 \cdot 2\text{py}$, which has been reported several times and is isomorphous (*Pnna*) with $\text{Ni}(\text{py})_4(\text{ONO}_2)_2 \cdot 2\text{py}$.^{7,36,37,38} Furthermore, the cadmium complex, $\text{Cd}(\text{py})_4(\text{ONO}_2)_2 \cdot 2\text{py}$, also displays the same coordination modes for the nitrate ligands in two different crystalline modifications (*Pcca* and *Ccca*).^{39,40,41} With respect to the existence of these other crystalline forms, it is pertinent to note that compounds of the class $\text{M}(\text{py})_4(\text{ONO}_2)_2 \cdot 2\text{py}$ undergo temperature dependent phase changes in the solid state,^{9b,39,40} and a variety of different crystalline forms have been identified, as illustrated in Table 4.⁴²

Figure 9. Distribution of M–O–N–O torsion angles for metal nitrate compounds.

Table 4. Unit cell data for different crystalline forms of $M(\text{py})_4(\text{ONO}_2)_2 \cdot 2\text{py}$.

M	<i>a</i> /Å	<i>b</i> /Å	<i>c</i> /Å	β /°	Space Group	Reference
Mg	12.081	15.146	17.222	90	<i>Ccca</i>	12
Mn	12.097	15.197	17.213	90	<i>Ccca</i>	44
Co	12.012	15.120	17.169	90	<i>Ccca</i>	8
Ni	14.809	11.866	17.193	90	<i>Pnna</i>	this work
Ni	12.148	15.019	16.960	90	<i>Ccca</i>	31
Ni	12.127	14.985	16.920	90	<i>Ccca</i>	8
Cu	14.601	12.420	16.838	90	<i>Pnna</i>	36
Cu	14.446	12.154	16.881	90	<i>Pnna</i>	37
Cu	12.708	14.792	16.670	90	<i>Ccca</i>	7
Cu	12.523	14.792	16.894	90	<i>Ccca</i>	8
Zn	12.108	14.996	17.113	90	<i>Ccca</i>	43
Zn	12.111	15.110	17.200	90	<i>Ccca</i>	8,11
Cd	11.953	15.129	17.234	90	<i>Pcca</i>	39
Cd	12.360	15.456	16.931	90	<i>Ccca</i>	39
Cd	12.330	15.470	17.050	90	<i>Ccca</i>	8,11
Hg	12.189	34.295	29.934	90.02	<i>P2₁/n</i>	13

In view of the existence of these different crystalline forms for $M(\text{py})_4(\text{ONO}_2)_2 \cdot 2\text{py}$, we considered it appropriate to evaluate the data for $\text{Ni}(\text{py})_4(\text{ONO}_2)_2 \cdot 2\text{py}$ by assuming that the crystal belonged to the previously reported C-centered polymorph (*Ccca*)³¹ that has similar cell dimensions to that reported here (Table 4). Interestingly, a solution that corresponds closely to the previously reported *Ccca* structure³¹ can be obtained (Figure 10), with specific similarities being that (i) both nitrate ligands are linear and (ii) the atoms of the nitrate ligand are characterized by

abnormal displacement parameters. Both of these features are a consequence of the fact that the molecule in *Ccca* resides on a site with 222 symmetry, whereas in *Pnna* the molecule resides on a site with only 2.. symmetry. Thus, whereas the asymmetric unit of $\text{Ni}(\text{py})_4(\text{ONO}_2)_2$ in *Pnna* corresponds to half of a molecule on a two-fold axis, that in *Ccca* corresponds to a quarter of a molecule on three two-fold axes. Since the disposition of the nitrate ligands in the correct *Pnna* structure are such that they are only related by a single two-fold axis, the presence of additional two-fold axes in the *Ccca* structure forces the nitrate ligands to *appear* to adopt positions that are consistent with the additional symmetry. As such, the Ni–O–N bonds are required to reside on a two-fold axis, thereby giving the appearance of a linearly coordinated nitrate ligand. Since the atoms of the nitrate ligands are not actually located in these positions, the atoms are associated with large atom displacement parameters.

Figure 10. Molecular structure of $\text{Ni}(\text{py})_4(\text{ONO}_2)_2 \cdot 2\text{py}$ (only the host is shown) refined in the incorrect *Ccca* space group with the oxygen attached to nickel being located on the two-fold axis.

Since the nitrate ligands do not reside on a two-fold axis, a more appropriate model in the *Ccca* space group is one in which the nitrate ligands are modeled as disordered groups. The result of this refinement is illustrated in Figure 11, but is also characterized by a larger *R* value and abnormal atom displacement parameters.

Figure 11. Molecular structure of $\text{Ni}(\text{py})_4(\text{ONO}_2)_2 \cdot 2\text{py}$ (only the host is shown) refined in the incorrect *Ccca* space group with the oxygen attached to nickel not being located on the two-fold axis.

Comparison of the *Ccca* molecular structures in Figure 10 and Figure 11 with that of the *Pnna* structure of Figure 8 clearly indicates that the latter corresponds to the best solution. Furthermore, the *R* values and goodness-of-fits (Table 5) support this assessment, as do the number of systematic absence violations for the *Ccca* refinements, which is a clear indication the crystal is *not* C-centered, but primitive.

Table 5. Comparison of refinement values for Ni(py)₄(ONO₂)₂•2py.

Space Group	R_1 [$I > 2\sigma(I)$]	wR_2 [$I > 2\sigma(I)$]	R_1 [all data]	wR_2 [all data]	GOOF
<i>Pnna</i>	0.0387	0.1018	0.0623	0.1170	1.022
<i>Ccca</i> ^a	0.1208	0.2671	0.1493	0.2832	1.094
<i>Ccca</i> ^b	0.0985	0.1935	0.1253	0.2046	1.266

(a) refinement in which the nitrate ligand is disordered and the oxygen attached to nickel resides on a crystallographic two-fold axis.

(b) refinement in which the nitrate ligand is disordered and the oxygen attached to nickel does not reside on a crystallographic two-fold axis.

Returning to the issue of the feasibility of linear coordination of terminal nitrate ligands, examination of the CSD indicates that only 10 compounds have been reported to possess M–O–N bond angles of 180°, corresponding to only 0.2 % of listed compounds. Of these, 3 correspond to M(py)₄(ONO₂)₂•2py derivatives, namely Ni(py)₄(ONO₂)₂•2py,³¹ Zn(py)₄(ONO₂)₂•2py,⁴³ and Mn(py)₄(ONO₂)₂•2py,^{44,45} which, as discussed above, are unlikely to represent an accurate description of the coordination mode.⁴⁶ Other examples also exhibit large atom displacement parameters for the nitrate ligand;^{47,48,49,50} as such, the nitrate is unlikely to correspond to a truly linear geometry. Only one of the compounds listed in the CSD with a linear M–O–NO₂ unit, namely a calcium compound, exhibits well-behaved atom displacement parameters for the nitrate ligand; however, the uncoordinated oxygen atoms are involved in hydrogen bonding interactions that serve to enforce linear coordination.⁵¹ Thus, in the absence of other overriding factors, it is evident that caution should be exercised in proposing metal nitrate compounds that feature a linear M–O–NO₂ moiety.

SUMMARY

In conclusion, the molecular structure of the clathrate compound, $\text{Ni}(\text{py})_4(\text{O}_2\text{CH})_2 \cdot 2\text{py}$, has been determined by X-ray diffraction, thereby demonstrating that the formate ligands coordinate in a unidentate manner. Interestingly, $\text{Ni}(\text{py})_4(\text{O}_2\text{CH})_2 \cdot 2\text{py}$ provides an example of a monoclinic cell in which the β angle of $90.076(3)^\circ$ is very close to 90° , such that the unit cell dimensions could suggest an orthorhombic, rather than monoclinic, crystal system; however, the refinement indicates that it is better represented as monoclinic. The molecular structure of the nitrate counterpart has also been determined, and the nitrate ligand is observed to coordinate in a unidentate manner with a distinctly bent coordination mode [$\text{Ni}-\text{O}-\text{NO}_2 = 141.72(10)^\circ$], rather than the linear coordination mode that has been previously reported.

EXPERIMENTAL SECTION

General considerations

$\text{Ni}(\text{py})_4(\text{O}_2\text{CH})_2 \cdot 2\text{py}$ and $\text{Ni}(\text{py})_4(\text{ONO}_2)_2 \cdot 2\text{py}$ were obtained by the literature methods⁸ and crystals suitable for X-ray diffraction were obtained from pyridine.

X-ray Structure Determination

X-ray diffraction data were collected on a Bruker Apex II diffractometer. Crystal data, data collection and refinement parameters are summarized in Table 6. The structures were solved by using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 2014/7).⁵² As with other monoclinic structures with a β angle close to 90° , the structure of $\text{Ni}(\text{py})_4(\text{O}_2\text{CH})_2 \cdot 2\text{py}$ was refined as a pseudo-merohedral twin.⁵³

Table 6. Crystal, intensity collection, and refinement data.

	Ni(py)₄(O₂CH)₂•2py	Ni(py)₄(ONO₂)₂•2py
lattice	Monoclinic	Orthorhombic
formula	C ₃₂ H ₃₂ N ₆ NiO ₄	C ₃₀ H ₃₀ N ₈ NiO ₆
formula weight	623.34	657.33
space group	<i>C2/c</i>	<i>Pnna</i>
<i>a</i> /Å	11.641(3)	14.809(7)
<i>b</i> /Å	15.035(3)	11.866(5)
<i>c</i> /Å	17.165(4)	17.193(8)
α /°	90	90
β /°	90.076(3)	90
γ /°	90	90
<i>V</i> /Å ³	3004.4(11)	3021(2)
<i>Z</i>	4	4
temperature (K)	130(2)	240(2)
radiation (λ , Å)	0.71073	0.71073
ρ (calcd.) g cm ⁻³	1.378	1.445
μ (Mo K α), mm ⁻¹	0.693	0.700
θ max, deg.	30.755	33.162
no. of data collected	24144	52033
no. of data	4675	5626
no. of parameters	198	208
R_1 [$I > 2\sigma(I)$]	0.0435	0.0387
wR_2 [$I > 2\sigma(I)$]	0.0974	0.1018
R_1 [all data]	0.0675	0.0623
wR_2 [all data]	0.1081	0.1170
GOF	1.026	1.022
R_{int}	0.0566	0.0329

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APPENDIX A. Supplementary Data

Crystallographic data in CIF format (CCDC # 1470548-1470549). These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.poly.xxxxxx>.

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Graphical Pictogram

Graphical Abstract

The molecular structures of the nickel formate and nitrate compounds, $\text{Ni}(\text{py})_4(\text{O}_2\text{CH})_2 \cdot 2\text{py}$ and $\text{Ni}(\text{py})_4(\text{ONO}_2)_2 \cdot 2\text{py}$, have been determined by X-ray diffraction, thereby demonstrating that both ligands coordinate in a unidentate manner. Of note, the $\text{Ni}-\text{O}-\text{NO}_2$ bond angle is distinctly bent, in contrast to the linear geometry that was previously reported.