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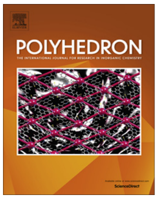

Structural characterization of the nickel(II) formate complex, $Ni(py)_4(O_2CH)_2{\cdot}2py$, and re-evaluation of the nitrate counterpart, $Ni(py)_4(ONO_2)_2{\cdot}2py$: Evidence for non-linear nitrate coordination ☆

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ABSTRACT

The molecular structure of the nickel formate compound, $Ni(py)_4(O_2CH)_2{\cdot}2py$, 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, $Ni(py)_4(ONO_2)_2{\cdot}2py$, indicates that the nitrate ligand also coordinates in a unidentate manner; however, the Ni–O–NO_2 bond angle is distinctly bent, in contrast to the linear geometry that was previously reported.

1. Introduction

While there is currently much interest in the use of hydrogen as a fuel, the inadequacy of current storage and transportation techniques [1] 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 H_2 [3–5], but such implementation requires effective catalysts to release H_2 on demand. Therefore, we are currently interested in developing catalysts that utilize earth abundant nonprecious metals to achieve this transformation [6]. As part of these studies, we have demonstrated that PMe_3 can induce the release of CO_2 and H_2 from the nickel formate complex, $Ni(py)_4(O_2CH)_2$, and thereby form $Ni(PMe_3)_4$ [6c]. Prompted by this observation, we sought to determine the coordination modes of the formate ligands of $Ni(py)_4(O_2CH)_2$ and so we describe here the molecular structure as determined by X-ray diffraction; in addition, we also report the molecular structure of the nitrate counterpart, $Ni(py)_4(ONO_2)_2$, which differs considerably from that previously reported.

2. Results and discussion

A large variety of compounds of composition $M(py)_4X_2{\cdot}2py$ have been previously investigated with respect to (*i*) their clathrate nature, (*ii*) the ability to maintain a structural similarity upon varying the $M(py)_4X_2$ host molecules, and (*iii*) 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, $Ni(py)_4(O_2CH)_2{\cdot}2py$ [8], due to the fact that the formate ligands in this complex are subject to facile decarboxylation in the presence of PMe_3 [6c]. Therefore, we have determined the molecular structure of $Ni(py)_4(O_2CH)_2{\cdot}2py$ by single crystal X-ray diffraction.

As observed for other $M(py)_4X_2{\cdot}2py$ derivatives [7], the structure of $Ni(py)_4(O_2CH)_2{\cdot}2py$ (Fig. 1) is comprised of well-defined octahedral $Ni(py)_4(O_2CH)_2$ units with pyridine occupying interstitial sites, rather than an alternative ionic formulation $[Ni(py)_6][O_2CH]_2$ [8]. Also of note, the formate ligands of $Ni(py)_4(O_2CH)_2$ are clearly identified as coordinating in a unidentate manner according to the criteria listed in Table 1 and Fig. 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].

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

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

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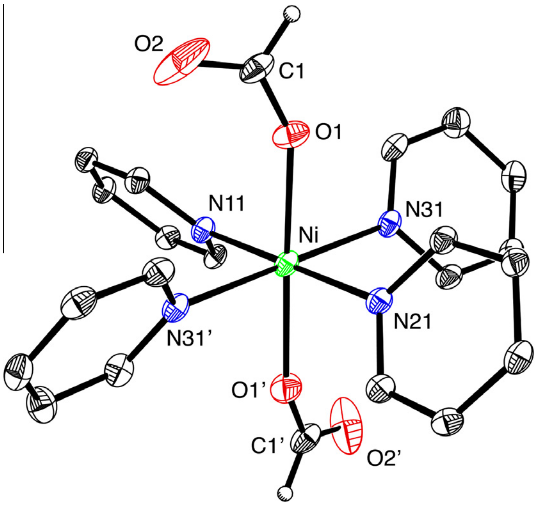

Fig. 1. Molecular structure of $Ni(py)_4(O_2CH)_2 \cdot 2py$ (only the host is shown). Selected bond lengths (Å) and angles (°): Ni–O1 = 2.0750(19), Ni–N11 = 2.099(2), Ni–N21 = 2.101(2), Ni–N31 = 2.1451(18), C1–O1 = 1.228(3), C1–O2 = 1.205(5), O1–Ni–O1′ = 177.57(10), C1–O1–Ni = 151.5(3), O1–C1–O2 = 127.4(4), 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	Δd (Å)	$\Delta\theta$ (°)
Unidentate	>0.6	>28
Anisobidentate	0.3–0.6	14–28
Bidentate	<0.3	<14

[a] Adopted from the values for nitrate ligands. See Ref. [31a].

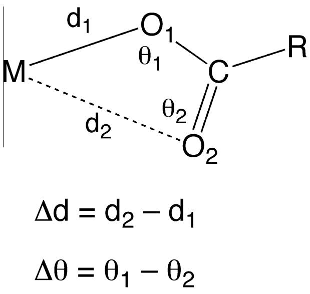

Fig. 2. Classification of carboxylate coordination modes with a proximal conformation.

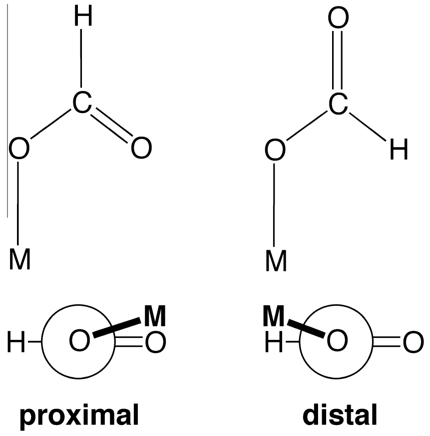

Fig. 3. Proximal and distal conformations of unidentate formate ligands.

conformation in which the uncoordinated oxygen atom and metal adopt a trans-like disposition (Fig. 3).

Proximal and distal conformations may be distinguished by M–O–C–O torsion angles of $|\tau| < 90°$ and $|\tau| > 90°$, respectively, and the value of 2.2° for $Ni(py)_4(O_2CH)_2$ is clearly in accord with the proximal classification. In this regard, examination of the Cambridge Structural Database (CSD) indicates that most (59%) unidentate metal formate compounds possess a proximal conformation (Fig. 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.

Further examination of the CSD also indicates that, in accord with the distribution for all metal formate compounds, most mononuclear unidentate nickel formate compounds likewise have a proximal conformation with $|\tau| < 90°$ (Table 2). In addition, those that adopt a distal conformation, namely $(phen)Ni(O_2CH)_2(OH_2)$ [15], $(Im^{Me})_2Ni(O_2CH)_2(OH_2)_2$ [16] and $(Im^{Me_2})_2Ni(O_2CH)_2(OH_2)_2$ [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 $(phen)Ni(O_2CH)_2(OH_2)$ [15].

Another noteworthy feature of the structure of $Ni(py)_4(O_2CH)_2 \cdot 2py$ pertains to the fact that the unit cell β angle of 90.076(3)° is sufficiently close to 90° that the crystal could

Table 2
Metrical data for selected mononuclear nickel formate compounds.

Compound	d_1 (Å)	d_2 (Å)	Δd (Å)	θ_1 (°)	θ_2 (°)	$\Delta\theta$ (°)	$\lvert\tau\rvert$ (°)	References
$Ni(py)_4(O_2CH)_2$	2.075	3.784	1.709	151.5	53.1	98.4	2.2	This work
$(phen)Ni(O_2CH)_2(OH_2)$	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	
$(Im^{Me})_2Ni(O_2CH)_2(OH_2)_2$	2.082	4.189	2.107	129.4	16.5	112.9	170.5	[16]
$(Im^{Me_2})_2Ni(O_2CH)_2(OH_2)_2$	2.071	4.165	2.094	126.2	15.4	110.8	162.5	[16]
$[NEt_4][(NNN^{Mes})Ni(O_2CH)]$	1.856	2.858	1.002	114.3	67.5	46.8	0.0	[17]
$[(N_4)Ni(O_2CH)(OH_2)][ClO_4]$	2.001	3.296	1.295	127.3	62.8	64.5	7.2	[18]
$[N^{Me_2}CN^{Me_2}]Ni(O_2CH)$	1.936	3.126	1.190	122.9	65.0	57.9	2.9	[19,20]
$[P^{Pr^i_2}NP^{Pr^i_2}]Ni(O_2CH)$	1.893	3.004	1.111	117.2	64.8	52.4	0.9	[21]
$[P^{Pr^i_2}CP^{Pr^i_2}]Ni(O_2CH)$	1.914	3.135	1.221	123.2	64.1	59.1	2.4	[22]
$[P^{Bu^t_2}CP^{Bu^t_2}]Ni(O_2CH)$	1.928	3.338	1.410	132.6	59.0	73.6	7.6	[23]
$[P^{Cy_2}CP^{Cy_2}]Ni(O_2CH)$[a]	1.923	3.225	1.302	129.8	61.4	68.4	12.5	[24]
$[P^{cPe_2}CP^{cPe_2}]Ni(O_2CH)$	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	
$[P^{Bu^t_2}OCOP^{Bu^t_2}]Ni(O_2CH)$	1.920	3.270	1.350	129.4	61.0	68.4	1.2	[25]
$[P^{Bu^t_2}OC_{sp3}OP^{Bu^t_2}]Ni(O_2CH)$	1.945	3.195	1.250	125.0	63.6	61.4	1.5	[26]
$[P^{Cy_2}SiP^{Cy_2}]Ni(O_2CH)$	1.968	2.976	1.008	116.2	68.1	48.1	2.7	[24]
$(Ox)_2Ni(O_2CH)_2$	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.