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2-Mercapto-1-t-butylimidazolyl as a Bridging Ligand: Synthesis and Structural Characterization of Nickel and Palladium Paddlewheel Complexes[‡]

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Abstract

Nickel and palladium paddlewheel complexes that feature 2-mercapto-1-t-butylimidazolyl (mim^{Bu^t}) bridging ligands, namely $\text{Ni}_2[\text{mim}^{\text{Bu}^t}]_4$ and $\text{Pd}_2[\text{mim}^{\text{Bu}^t}]_4$, have been synthesized and structurally characterized by X-ray diffraction. Since the mim^{Bu^t} ligand bridges in an asymmetric manner *via* a sulfur and nitrogen donor, paddlewheel compounds of the type $\text{M}_2[\text{mim}^{\text{Bu}^t}]_4$ may exist as isomers that are distinguished by the relative orientations of the ligands. In this regard, the (4,0)- $\text{Ni}_2[\text{mim}^{\text{Bu}^t}]_4$ and *trans*-(2,2)- $\text{Ni}_2[\text{mim}^{\text{Bu}^t}]_4$ isomers have been isolated for the nickel system, while the (4,0)- $\text{Pd}_2[\text{mim}^{\text{Bu}^t}]_4$ and (3,1)- $\text{Pd}_2[\text{mim}^{\text{Bu}^t}]_4$ isomers have been isolated for the palladium system.

INTRODUCTION

Metal-thiolate complexes are of considerable interest due to the significance of M–S bonds in biological systems.¹ For example, there is presently interest in nickel-thiolate chemistry due to its relevance to hydrogenase chemistry.² In many cases, biological thiols are derived from cysteine. However, there is also a class that is related to histidine, as illustrated by ergothioneine,³ a derivative of 2-mercaptoimidazole that exists primarily as the resonance stabilized thione tautomer (Figure 1). Since the coordination chemistry of ergothioneine is not well established, useful information may be obtained by investigating simpler 1-R-2-mercaptoimidazole/1-R-imidazole-2-thione systems (Figure 2), $[\text{Hmim}^{\text{R}}]_4^{1+}$ that are also of interest due to the discovery that the methyl derivative, methimazole, is an antithyroid drug.⁵ In this paper, we report the synthesis of nickel complexes derived from 2-mercapto-1-t-butylimidazole [$\text{Hmim}^{\text{Bu}^t}$], including dinuclear paddlewheel complexes.

RESULTS AND DISCUSSION

The *tetrakis*(1-Bu^t-imidazole-2-thione) nickel complex $\{\text{Ni}[\text{Hmim}^{\text{Bu}^t}]_4\}\text{I}_2$ is readily obtained by the reaction of $\text{Hmim}^{\text{Bu}^t}$ with NiI_2 in acetonitrile (Scheme 1). The molecular structure of $\{\text{Ni}[\text{Hmim}^{\text{Bu}^t}]_4\}\text{I}_2$ has been determined by X-ray diffraction, thereby demonstrating that it possesses a square-planar geometry (Figure 3), with each iodide counterion bridging two $\text{Hmim}^{\text{Bu}^t}$ ligands *via* hydrogen bonding interactions.^[2]⁶ Interestingly, the coordinated

[‡]Dedicated to the memory of Swiatoslaw (“Jerry”) Trofimenko.

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¹For representative 2-mercaptoimidazole/imidazole–2-thione compounds, see reference ⁴.

²For $\{\text{Ni}[(\text{mim}^{\text{Me}})\text{H}]_4\}\text{X}_2$ derivatives, see reference ⁶.

Hmim^{Bu^t} groups may be deprotonated by treatment with KH to generate incipient {Ni[mim^{Bu^t}]₄}²⁻ which, in the presence of NiI₂, yields dinuclear Ni₂[mim^{Bu^t}]₄ (Scheme 1). The latter compound may also be isolated from the reaction of [κ⁴-B(mim^{Bu^t})₃]NiCl⁷ with KOH (Scheme 1).

X-ray diffraction studies demonstrate that Ni₂[mim^{Bu^t}]₄ exists as two crystalline modifications, each of which adopts a paddlewheel (or lantern) structure with two square-planar nickel centers (Figures 4 and 5). The two square planar metal centers are not, however, eclipsed, as illustrated by the view down the Ni...Ni vector shown in Figure 6. For example, the N–Ni–Ni–S torsion angle for the *P4/n* modification is 25°.

While paddlewheel compounds that feature four bridging bidentate ligands are a common feature in coordination chemistry, the bridging ligands are frequently symmetric with respect to the interaction, such that only one isomer is possible.⁸ However, if the bridging ligand (A–B–C) is asymmetric with respect to its coordination to the two metals, as with [mim^{Bu^t}], four different isomeric arrangements are possible (Figure 7).⁸ The different isomers may be designated by the prefixes (*4,0*), (*3,1*), *cis*-(*2,2*) and *trans*-(*2,2*), in which the (*x,y*) values indicate the number of ligands with each orientation relative to the metal...metal vector.

With respect to this classification, the structures shown in Figures 4 and 5 may be described as (*4,0*)-Ni₂[mim^{Bu^t}]₄. In this regard, while paddlewheel complexes of nickel are known,^[3]⁹ we are only aware of two that possess the (*4,0*) motif, and both of these also possess axial ligands.¹⁰ Thus, (*4,0*)-Ni₂[mim^{Bu^t}]₄ is unique by being devoid of axial ligation.

The two nickel centers of (*4,0*)-Ni₂[mim^{Bu^t}]₄ are electronically distinct, with one nickel center having a {Ni[N₄]} coordination environment while the other has a {Ni[S₄]} coordination environment. The formation of this (*4,0*)-isomer, rather than a more symmetric (*2,2*) variant with a {Ni[N₂S₂]}Ni[N₂S₂]} core and equivalent nickel centers, is presumably a consequence of the method of synthesis. Specifically, if the four sulfur atoms attached to {Ni[Hmim^{Bu^t}]₄}²⁺ remain coordinated following deprotonation, then only the nitrogen atoms are available for coordinating the second nickel, thereby resulting in a polar isomer of Ni₂[mim^{Bu^t}]₄.^[4]

In this regard, a nonpolar isomer that features two identical nickel centers, namely *trans*-(*2,2*)-Ni₂[mim^{Bu^t}]₄ with a {Ni[N₂S₂]}Ni[N₂S₂]} core, has been isolated *via* degradation of *trans*-Ni(PMe₃)₂[κ¹-*N*-mim^{Bu^t}]₂¹¹ by [PhC(O)O]₂ (Scheme 2) and has been structurally characterized by X-ray diffraction (Figure 8). The formation of a more symmetric isomer may be conceptually rationalized by considering that dissociation of PMe₃ would generate incipient *trans*-{Ni[κ¹-*N*-mim^{Bu^t}]₂} and subsequent dimerization of this species would generate a dinuclear {Ni[N₂S₂]}Ni[N₂S₂]} core (Scheme 2).^[4]

The Ni–S and Ni–N bond lengths in the two isomers of Ni₂[mim^{Bu^t}]₄ are very similar, as are the Ni...Ni separations (Table 1). A variety of paddlewheel complexes of the type Ni₂[(LX)]₄, where LX is a bidentate bridging ligand with a three-atom linker (*e.g.* RNCHNR, RNNNR, RC(O)S, and RCS₂) have been structurally characterized^{10,12} and have Ni...Ni distances that are in the range 2.38 Å^{12b} – 2.65 Å.^{10b} Since these distances are comparable to the Ni–Ni bond length in the elemental form (2.49 Å),¹³ a degree of Ni–Ni bonding was originally proposed,^{12b,c} but calculations on hypothetical Ni₂(HNNH)₄ indicate that the bond order is formally zero.^{12a} Specifically, with a configuration of σ²π⁴δ²σ*²π*⁴σ*² for the

³For a review of Pt, Pd and Ni paddlewheel compounds, see reference ⁹.

⁴It is, of course, possible that other isomers could be present in the reaction mixture.

interaction between the two d^8 metal centers, all Ni–Ni bonding and antibonding orbitals are filled and so there is no net bonding interaction.^[5]¹⁴

Paddlewheel complexes of palladium are not as common as those of nickel,^{[3],[5],15} and so it is noteworthy that we have also structurally characterized two palladium derivatives in which [mim^{Bu^t}] serves as the bridging ligand. For example, (4,0)-Pd₂[mim^{Bu^t}]₄ has been isolated from the reaction of $\{[\mu-\kappa^1, \kappa^3-B(mim^{Bu^t})_3]Pd\}_2$ ¹⁶ with 1-methylimidazole (Him^{Me}) in acetonitrile in the presence of air (Scheme 3).^[6]¹⁷ Furthermore, isomeric (3,1)-Pd₂[mim^{Bu^t}]₄ has been isolated from the reaction of {Ni[Hmim^{Bu^t}]₄}I₂ with KH and Pd(OAc)₂; in the absence of KH, the simple substitution product {Pd[Hmim^{Bu^t}]₄}I₂ is obtained (Scheme 4). The molecular structures of (4,0)-Pd₂[mim^{Bu^t}]₄, (3,1)-Pd₂[mim^{Bu^t}]₄ and {Pd[Hmim^{Bu^t}]₄}I₂ have been determined by X-ray diffraction, as illustrated in Figures 9–11. Of particular note, the Pd...Pd distances in (4,0)-Pd₂[mim^{Bu^t}]₄ [2.728(1) Å] and (3,1)-Pd₂[mim^{Bu^t}]₄ [2.734(2) Å] are considerably shorter than that in $[(\mu-N,S-mim^{Me})PdCl(PMe_3)]_2$ [3.104(2) Å], which possesses only two bridging ligands.¹⁸

CONCLUSIONS

In summary, a series of nickel and palladium paddlewheel complexes that feature 2-mercapto-1-t-butylimidazolyl bridging ligands has been synthesized. As a result of the fact that the 2-mercapto-1-t-butylimidazolyl ligand bridges asymmetrically, coordinating to each metal *via* either a nitrogen or a sulfur donor, the M₂[mim^{Bu^t}]₄ paddlewheel complexes may exist as isomers that are differentiated by the relative orientations of the bridging [mim^{Bu^t}] ligands. X-ray diffraction studies demonstrate that Ni₂[mim^{Bu^t}]₄ exists as both (4,0)-Ni₂[mim^{Bu^t}]₄ and *trans*-(2,2)-Ni₂[mim^{Bu^t}]₄ isomers. The two nickel centers of the former isomer are inequivalent, with one nickel having a {Ni[S₄]} coordination environment, while the other has a {Ni[N₄]} coordination environment. In contrast, the two nickel centers of the latter isomer are equivalent, with both having a {Ni[N₂S₂]} coordination environment. For the palladium system, (4,0)-Pd₂[mim^{Bu^t}]₄ and (3,1)-Pd₂[mim^{Bu^t}]₄ isomers, have been isolated, with the latter being characterized by palladium centers that have {Pd[NS₃]} and {Pd[N₃S]} coordination environments.

EXPERIMENTAL SECTION

General Considerations

All manipulations were performed using a combination of glovebox, high vacuum, and Schlenk techniques under a nitrogen atmosphere unless otherwise specified.¹⁹ Solvents were purified and degassed by standard procedures. ¹H NMR spectra were measured on Bruker 300 DRX and Bruker 400 DRX spectrometers. ¹H chemical shifts are reported in ppm relative to SiMe₄ ($\delta = 0$) and were referenced internally with respect to the protio solvent impurity ($\delta 1.94$ for CD₃CN).²⁰ Coupling constants are given in hertz. Infrared spectra were recorded on Nicolet Avatar 370 DTGS spectrometer and are reported in cm⁻¹. Hmim^{Bu^t},²¹ $\{[\mu-\kappa^1, \kappa^3-B(mim^{Bu^t})_3]Pd\}_2$,¹⁶ $[\kappa^4-B(mim^{Bu^t})_3]NiCl$ ⁷ were prepared by the literature methods.

X-ray structure determinations

X-ray diffraction data were collected on either a Bruker Apex II diffractometer or a Bruker P4 diffractometer equipped with a SMART CCD detector. Crystal data, data collection and refinement parameters are summarized in Table 2. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares

⁵For calculations on related dipalladium compounds, see reference 14.

⁶For a heterobimetallic counterpart that features 6-coordinate Pd, see reference 17.

procedures on F^2 with SHELXTL (Version 6.10).²² The crystallographic data for (4,0)-Ni₂[mim^{Bu^t}]₄ (CCDC #724098 and #724100), *trans*-(2,2)-Ni₂[mim^{Bu^t}]₄ (CCDC #724097), (4,0)-Pd₂[mim^{Bu^t}]₄ (CCDC #724101), (3,1)-Pd₂[mim^{Bu^t}]₄ (CCDC #724102), {Ni[Hmim^{Bu^t}]₄}I₂ (CCDC #724096), and {Pd[Hmim^{Bu^t}]₄}I₂ (CCDC #724099) have been deposited with the Cambridge Crystallographic Data Centre.

Synthesis of {Ni[Hmim^{Bu^t}]₄}I₂

A mixture of Hmim^{Bu^t} (1.0 g, 6.4 mmol) and NiI₂ (0.50 g, 1.6 mmol) in CH₃CN (30 mL) was stirred for 14 hours. The resulting brown precipitate was isolated by filtration, washed with pentane (20 mL) and then dried *in vacuo* (1.32 g, 88%). Crystals of composition [Ni[Hmim^{Bu^t}]₄]I₂·CH₂Cl₂ suitable for X-ray diffraction were grown by slow evaporation of a dichloromethane solution. ¹H NMR (CD₃CN): 2.24 (s, 36H of Bu^t), 6.42 (s, 4H of CH₂ mim^{Bu^t}), 8.94 (s, 4H of CH mim^{Bu^t}). Anal. calcd. for C₂₈H₄₈I₂N₈NiS₄: C, 35.9%; H, 5.2%; N, 12.0%. Found: C, 35.6%; H, 5.6%; N, 12.1%. IR Data (KBr pellet, cm⁻¹): 3176 (m), 3130 (m), 2980 (m), 2882 (w), 1569 (m), 1450 (s), 1418 (w), 1363 (w), 1325 (w), 1315 (w), 1247 (w), 1235 (s), 1219 (m), 1132 (w), 1117 (w), 1099 (w), 735 (m), 692 (w), 683 (w).

Synthesis of Ni₂[mim^{Bu^t}]₄

- A suspension of [κ⁴-B(mim^{Bu^t})₃]NiCl (100 mg, 0.18 mmol) in MeOH (7 mL) was treated with a solution of KOH (10 mg, 0.18 mmol) in CH₃OH (3 mL). The resulting mixture was stirred for 10 hours and filtered. The green filtrate was allowed to stand at room temperature for 1 week, thereby depositing dark green needle-shaped crystals of (4,0)-Ni₂[mim^{Bu^t}]₄ suitable for X-ray diffraction analysis. The crystals were isolated, washed with acetone (2 × 2 mL) and hexanes (2 × 2 mL) and then dried *in vacuo* (37 mg, 57%). ¹H NMR (CD₃CN): 1.33 (s, 36H of Bu^t), 6.67 (s, 4H of CH₂ mim^{Bu^t}), 7.06 (s, 4H of CH mim^{Bu^t}). Anal. calcd. for C₂₈H₄₄N₈Ni₂S₄: C, 45.6%; H, 6.0%; N, 15.2%. Found: C, 45.3%; H, 5.8%; N, 15.0%. IR Data (KBr pellet, cm⁻¹): 3113 (w), 2979 (m), 2930 (w), 1414 (m), 1394 (m), 1367 (m), 1348 (s), 1253 (s), 1187 (w), 1150 (m), 1134 (m), 1050 (w), 1021 (w), 712 (w), 685 (s).
- A mixture of {Ni[Hmim^{Bu^t}]₄}I₂ (25 mg, 0.027 mmol) and KH (5 mg, 0.13 mmol) in CH₃CN (0.5 mL) was stirred for 5 minutes, after which period NiI₂ (8 mg, 0.026 mmol) was added. The resulting mixture was stirred for 5 hours and filtered. The filtrate was allowed to stand at room temperature, thereby depositing dark green needle-shaped crystals within 2 weeks, along with some colorless blocks (presumably KI). The green crystals were identified as (4,0)-Ni₂[mim^{Bu^t}]₄ by X-ray diffraction.
- Trans*-(2,2)-Ni₂[mim^{Bu^t}]₄ was obtained by treating a solution of *trans*-Ni(PMe₃)₂[κ¹-N-mim^{Bu^t}]₂ (15 mg) in benzene (*ca.* 0.7 mL) with [PhC(O)O]₂ (7 mg) and crystals were obtained by slow evaporation.

Synthesis of Pd₂[mim^{Bu^t}]₄

- A mixture of {[μ-κ¹, κ³-B(mim^{Bu^t})₃]Pd}₂ (20 mg, 0.017 mmol) and Him^{Me} (10 μL, 0.13 mmol) in CD₃CN (1 mL) in an NMR tube equipped with a J-Young valve was exposed to air then heated at 100°C for 2 days. The resulting solution was allowed to cool down to room temperature and stand overnight, thereby depositing orange needle-shaped crystals of (4,0)-Pd₂[mim^{Bu^t}]₄ suitable for X-ray diffraction analysis. An additional crop of orange crystals were obtained by adding EtOH (95%, *ca.* 10 mL) to the mother solution. The crystals were separated by decanting, washed with EtOH (0.5 mL) and Et₂O, and then dried *in vacuo* (8 mg). ¹H NMR (CD₃CN): 1.75 (s, 36H of Bu^t), 6.69 (d, ²J_{H-H} = 2, 4H of CH₂ mim^{Bu^t}), 6.94 (d, ²J_{H-H} = 2, 4H of CH mim^{Bu^t}). Anal. calcd. for C₂₈H₄₄N₈Pd₂S₄·CH₃CN: C, 41.2%; H, 5.4%; N,

14.4%. Found: C, 41.5%; H, 5.3%; N, 13.6%. IR Data (KBr pellet, cm^{-1}): 2978 (m), 2910 (w), 1418 (w), 1396 (m), 1384 (s), 1367 (m), 1347 (s), 1266 (m), 1252 (m), 1190 (m), 1163 (m), 1155 (m), 1060 (w), 823 (w), 794 (m), 771 (w), 745 (w), 712 (w), 706 (w), 670 (w).

- b. A suspension of $\{\text{Ni}[\text{Hmim}^{\text{Bu}^t}]_4\}\text{I}_2$ (50 mg, 0.053 mmol) in CD_3CN (0.5 mL) was treated with KH (9 mg, 0.22 mmol) in small portions. The resulting mixture was stirred for 15 minutes, after which period $\text{Pd}(\text{OAc})_2$ (12 mg, 0.053 mmol) was added. The mixture was stirred for 2 hours and filtered. The red filtrate was placed at room temperature, thereby depositing red crystals over a period of 2 weeks. The crystals were isolated and demonstrated to be $(3,I)\text{-Pd}_2[\text{mim}^{\text{Bu}^t}]_4\cdot\text{CH}_3\text{CN}$ by X-ray diffraction.

Synthesis of $\{\text{Pd}[\text{Hmim}^{\text{Bu}^t}]_4\}\text{I}_2$

A suspension of $\{\text{Ni}[\text{Hmim}^{\text{Bu}^t}]_4\}\text{I}_2$ (30 mg, 0.032 mmol) in CH_3CN was treated with a solution of $\text{Pd}(\text{OAc})_2$ (7 mg, 0.031 mmol) in CH_3CN . The resulting mixture was stirred for 1 hour and filtered. The red filtrate was placed at room temperature, thereby depositing crystals over a period of 2 weeks. The crystals were isolated and demonstrated to be $\{\text{Pd}[\text{Hmim}^{\text{Bu}^t}]_4\}\text{I}_2\cdot\text{CH}_3\text{CN}$ by X-ray diffraction.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
Structure of ergothioneine.

Figure 2.
Thiol/thione tautomerism for 1-R-2-mercaptoimidazoles.

Figure 3.
Molecular structure of $\{\text{Ni}[\text{Hmim}^{\text{Bu}^t}]_4\}\text{I}_2$.

Figure 4.
Molecular structure of $(4,0)\text{-Ni}_2[\text{mim}^{\text{Bu}^t}]_4$ ($P4/n$).

Figure 5.
Molecular structure of $(4,0)\text{-Ni}_2[\text{mim}^{\text{Bu}^t}]_4$ ($C2/c$).

Figure 6.
View of $(4,0)\text{-Ni}_2[\text{mim Bu}^t]_4$ ($C2/c$) down $\text{Ni}\cdots\text{Ni}$ axis.

Figure 7.
Classification of isomers of paddlewheel complexes with asymmetric bridging ligands.

Figure 8.
Molecular structure of *trans*-(2,2)-Ni₂[mim^{Bu^t}]₄.

Figure 9.
Molecular structure of $(4,0)\text{-Pd}_2[\text{mim}^{\text{Bu}^t}]_4$.

Figure 10.
Molecular structure of $(3,1)\text{-Pd}_2[\text{mim}^{\text{Bu}^t}]_4$.

Figure 11.
Molecular structure of $\{\text{Pd}[\text{Hmim}^{\text{Bu}^t}]\}_4\text{I}_2$.

Scheme 1.

Scheme 2.

Scheme 3.

Scheme 4.

Table 1

M...M distances in paddlewheel complexes.

	$d(\text{M}\cdots\text{M})/\text{\AA}$
$(4,0)\text{-Ni}_2[\text{mim}^{\text{Bu}^t}]_4$ ($P4/n$)	2.574(2)
$(4,0)\text{-Ni}_2[\text{mim}^{\text{Bu}^t}]_4$ ($C2/c$)	2.581(1)
$\text{trans-}(2,2)\text{-Ni}_2[\text{mim}^{\text{Bu}^t}]_4$	2.563(1)
$(4,0)\text{-Pd}_2[\text{mim}^{\text{Bu}^t}]_4$	2.728(1)
$(3,1)\text{-Pd}_2[\text{mim}^{\text{Bu}^t}]_4$	2.734(2)

Table 2

Crystal, intensity collection and refinement data.

	$(4,0)$ -Ni ₂ [mim ^{Bu^t}] ₄ ·2CH ₃ CN	$(4,0)$ -Ni ₂ [mim ^{Bu^t}] ₄
lattice	monoclinic	tetragonal
formula	C ₃₂ H ₅₀ N ₁₀ Ni ₂ S ₄	C ₂₈ H ₄₄ N ₈ Ni ₂ S ₄
formula weight	820.48	738.37
space group	<i>C2/c</i>	<i>P4/n</i>
<i>a</i> /Å	30.045(11)	15.042(3)
<i>b</i> /Å	7.086(2)	15.042(3)
<i>c</i> /Å	21.133(7)	7.178(3)
α /°	90	90
β /°	116.990(5)	90
γ /°	90	90
<i>V</i> /Å ³	4009(2)	1624.1(9)
<i>Z</i>	4	2
temperature (K)	243	125
radiation (λ , Å)	0.71073	0.71073
ρ (calcd.), g cm ⁻³	1.359	1.510
μ (Mo K α), mm ⁻¹	1.184	1.450
θ max, deg.	28.31	25.51
no. of data	4582	1527
no. of parameters	225	100
<i>R</i> _{<i>I</i>}	0.0481	0.0499
<i>wR</i> ₂	0.1148	0.0920
GOF	1.001	1.014

	<i>trans</i> -(2,2)-Ni ₂ [mim ^{Bu^t}] ₄	$(4,0)$ -Pd ₂ [mim ^{Bu^t}] ₄
lattice	monoclinic	tetragonal
formula	C ₃₀ H ₄₈ Cl ₄ N ₈ Ni ₂ S ₄	C ₂₈ H ₄₄ N ₈ Pd ₂ S ₄
formula weight	908.22	833.75
space group	<i>C2/c</i>	<i>P4/n</i>
<i>a</i> /Å	24.755(12)	15.1978(6)
<i>b</i> /Å	11.187(5)	15.1978(6)
<i>c</i> /Å	14.878(7)	7.1914(5)
α /°	90	90
β /°	91.708(9)	90
γ /°	90	90
<i>V</i> /Å ³	4118(3)	1661.02(15)
<i>Z</i>	4	2
temperature (K)	238(2)	125
radiation (λ , Å)	0.71073	0.71073
ρ (calcd.), g cm ⁻³	1.465	1.667

	<i>trans</i> -(2,2)-Ni ₂ [mim ^{Bu^t}] ₄	(4,0)-Pd ₂ [mim ^{Bu^t}] ₄
μ (Mo Kα), mm ⁻¹	1.409	1.367
θ max, deg.	24.71	32.38
no. of data	3433	2879
no. of parameters	218	100
<i>R</i> ₁	0.0395	0.0273
<i>wR</i> ₂	0.1018	0.0534
GOF	1.059	1.140

	(3, <i>I</i>)-Pd ₂ [mim ^{Bu^t}] ₄ ·CH ₃ CN	{Ni[Hmim ^{Bu^t}] ₄ }I ₂ ·2CH ₂ Cl ₂
lattice	orthorhombic	orthorhombic
formula	C ₃₀ H ₄₇ N ₉ Pd ₂ S ₄	C ₃₀ H ₅₂ Cl ₄ I ₂ N ₈ NiS ₄
formula weight	874.81	1107.35
space group	<i>Pna</i> 2 ₁	<i>Pbca</i>
<i>a</i> /Å	19.309(8)	11.3053(5)
<i>b</i> /Å	7.308(3)	17.2323(7)
<i>c</i> /Å	26.644(12)	23.3028(9)
α/°	90	90
β/°	90	90
γ/°	90	90
<i>V</i> /Å ³	3760(3)	4539.8(3)
<i>Z</i>	4	4
temperature (K)	125	243
radiation (λ, Å)	0.71073	0.71073
ρ (calcd.), g cm ⁻³	1.545	1.620
μ (Mo Kα), mm ⁻¹	1.213	2.238
θ max, deg.	25.03	28.30
no. of data	6629	5329
no. of parameters	420	230
<i>R</i> ₁	0.0849	0.0262
<i>wR</i> ₂	0.1867	0.0636
GOF	1.044	1.025

	{Pd[Hmim ^{Bu^t}] ₄ }I ₂ ·2CH ₃ CN
lattice	orthorhombic
formula	C ₃₂ H ₅₄ I ₂ N ₁₀ PdS ₄
formula weight	1067.29
space group	<i>Pbca</i>
<i>a</i> /Å	11.4809(4)
<i>b</i> /Å	17.1434(6)
<i>c</i> /Å	23.1983(9)
α/°	90
β/°	90

{Pd[Hmim ^{Bu}] ₄ }I ₂ ·2CH ₃ CN	
$\gamma/^\circ$	90
$V/\text{\AA}^3$	4565.9(3)
Z	4
temperature (K)	243
radiation (λ , $\text{\AA}$)	0.71073
ρ (calcd.), g cm^{-3}	1.553
μ (Mo $K\alpha$), mm^{-1}	1.975
θ max, deg.	28.35
no. of data	5547
no. of parameters	239
R_1	0.0246
wR_2	0.0586
GOF	1.022