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$Ni[(EP^iPr_2)_2N]_2$ Complexes: Stereoisomers (E = Se) and Square-Planar Coordination (E = Te)

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The reaction of $(^iPr_2PE)_2NM\cdot TMEDA$ (M = Li, E = Se; M = Na, E = Te) with $NiBr_2\cdot DME$ in THF affords $Ni[(SeP^iPr_2)_2N]_2$ as either square-planar (green) or tetrahedral (red) stereoisomers, depending on the recrystallization solvent; the Te analogue is obtained as the square-planar complex $Ni[(TeP^iPr_2)_2N]_2$.

It is well established that Ni^{II} complexes exhibit a range of coordination spheres of various geometries, including octahedral, tetrahedral (T_d), and square planar (SP).[1] This structural flexibility is also manifested in the active sites of Ni-containing metalloenzymes, which adopt structures that will provide the electronic properties needed for a specific biological reactivity. However, the geometries of the metalloenzyme active sites are usually distorted from the ideal geometries.[2–5]

A common feature in structural bioinorganic chemistry is the presence of sulfur-containing ligands in the active site of metalloenzymes for various metal ions, including Ni^{II}, most usually in the form of cysteine thiolate or sulfide, S^{2-}. Selenocysteine (SeCys) selenolate is also known to coordinate either Mo or W in the active site of formate dehydrogenase[6] or Ni in the so-called Ni−Fe−Se hydrogenases.[7] Several coordination compounds that reproduce the structural features of Ni−Se−enzyme active sites have been characterized.[8–11] Te has not been found to form metal−Te bonds in biological systems.

The majority of $Ni^{II}S_4$-containing complexes exhibit SP structural cores, although a few T_d arrangements have also been established.[12] Conversely, among the $Ni^{II}Se_4$-containing complexes, only one (considerably distorted) tetrahedral motif has been reported to date, i.e., $[Ni(SePh)_4]^{2-}$,[11] whereas numerous SP structures are known.[13] A T_d structure has very recently been described for a mixed chalcogen complex with a disordered $Ni^{II}S_2Se_2$ core.[14] To the best of our knowledge, there are as yet no structurally characterized mononuclear $Ni^{II}Te_4$ complexes.

In this context, it would be highly desirable to synthesize and structurally characterize a series of $Ni^{II}E_4$-containing compounds (E = S, Se, Te) by using the same type of ligand in order to thoroughly appraise the effects of the chalcogen atom E on the core structure. For that purpose, the well-established chalcogenidoimidodiphosphinato ligands, $[(EPR_2)_2N]^-$ (E = S, Se),[12,15–17] and the more recently discovered Te analogues[18] would be appropriate because they exhibit many desirable features. For example, their large E···E bite would accommodate a range of coordination sphere geometries. Such ligands

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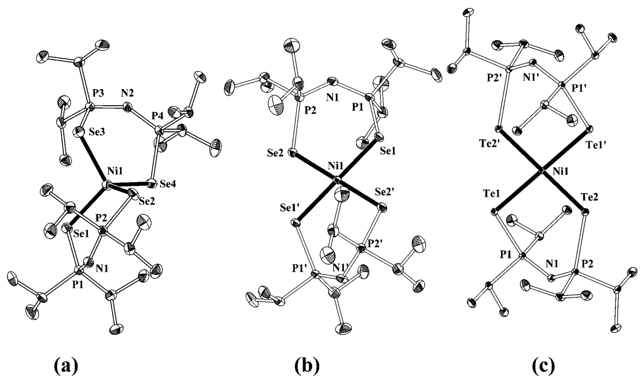

Figure 1. Thermal ellipsoid plot (30% probability) of the X-ray structure of (a) red ($\mathbf{2_{Td}}$) and (b) green ($\mathbf{2_{SP}}$) crystals of Ni[(SeP^{i}Pr$_2$)$_2$N]$_2$, as well as of (c) Ni[(TeP^{i}Pr$_2$)$_2$N]$_2$ (**3**).

have previously displayed great versatility, producing both monomeric and oligomeric metal complexes with a variety of bonding modes.[19–21]

In this Communication, the synthesis and characterization of the Ni^{II} complexes Ni[(EP^{i}Pr$_2$)$_2$N]$_2$ (**2**, E = Se; **3**, E = Te) are reported, and their structures and solution behavior are compared with those of Ni[(SP^{i}Pr$_2$)$_2$N]$_2$ (**1**).[22] The new complexes **2** and **3** reveal two structural features of wider implications. First, complex **2** is formed as a mixture of stereoisomers in the form of discrete red and green crystals containing tetrahedral ($\mathbf{2_{Td}}$) or square-planar ($\mathbf{2_{SP}}$) Ni^{II}Se$_4$ cores, respectively. Second, complex **3** represents the first structurally characterized mononuclear Ni^{II}Te$_4$ complex.

Complexes **2** and **3** were prepared in good yields by the reaction of the TMEDA-solvated alkali-metal salts of the anion [(EPR$_2$)$_2$N]$^-$ with NiBr$_2$·DME in THF at room temperature.[23,24] In contrast to complex **1**, which has crystallographically imposed S_4 symmetry,[22] complex **2** is obtained as a mixture of stereoisomers.[25] When the red-brown powder of **2** was slowly crystallized at −18 °C from CH$_2$Cl$_2$/MeOH, discrete red (relative yield 57%) and green (43%) crystals were formed, corresponding to T$_d$ and SP Ni^{II}Se$_4$ cores, respectively (Figure 1). These crystals could be produced selectively by varying the recrystallization solvent. A large excess of MeOH was added to a saturated solution of **2** in warm CH$_2$Cl$_2$, which was quickly cooled to −35 °C, precipitating red crystals ($\mathbf{2_{Td}}$; yield 82%). Similarly, the addition of a large excess of hexane to a saturated solution of **2** in hot THF followed by cooling to −35 °C deposited green crystals ($\mathbf{2_{SP}}$; yield 59%). These two isomers can be continually interconverted by recrystallization from the appropriate solvent system. Selected bond lengths and angles of the isomers $\mathbf{2_{Td}}$ and $\mathbf{2_{SP}}$ are compared in Table 1.

Table 1. Selected Interatomic Distances (Å) and Angles (deg) for Complexes Ni[(EP^{i}Pr$_2$)$_2$N]$_2$ Where E = Se ($\mathbf{2_{Td}}$ and $\mathbf{2_{SP}}$), Te (**3**)

	$\mathbf{2_{Td}}$	$\mathbf{2_{SP}}$[a]	**3**[b]
Ni1−E1	2.401(1)	2.3579(8)	2.5154(7)
Ni1−E2	2.398(1)	2.3496(8)	2.5083(7)
Ni1−E3	2.398(1)		
Ni1−E4	2.403(1)		
E1−P1	2.182(1)	2.201(2)	2.436(1)
E2−P2	2.184(1)	2.196(2)	2.474(1)
E3−P3	2.180(1)		
E4−P4	2.181(1)		
P1−N1	1.591(4)	1.601(6)	1.598(2)
P2−N1	1.594(4)	1.610(5)	1.599(2)
P3−N2	1.592(4)		
P4−N2	1.595(4)		
E1−Ni1−E2	110.67(3)	100.95(3)	99.02(3)
E1−Ni1−E3	107.69(3)		
E1−Ni1−E4	112.90(4)		
E2−Ni1−E3	108.95(4)		
E2−Ni1−E4	106.61(3)		
E3−Ni1−E4	109.98(3)		
E1−Ni1−E1A		179.76(6)	180
E1−Ni1−E2A		79.05(3)	80.98(3)
E2−Ni1−E2A		179.58(6)	180
P1−E1−Ni1	106.35(4)	113.57(5)	103.34(3)
P2−E2−Ni1	107.31(4)	108.92(5)	113.24(3)
P3−E3−Ni1	106.84(4)		
P4−E4−Ni1	107.12(4)		
E1−P1−N1	118.7(1)	117.2(2)	117.5(1)
E2−P2−N1	117.9(1)	116.2(2)	118.8(1)
E3−P3−N2	118.0(1)		
E4−P4−N2	118.5(1)		
P1−N1−P2	137.0(2)	125.8(3)	132.8(2)
P3−N2−P4	136.3(2)		

[a] Symmetry transformation used to generate equivalent atoms: $-x + 1$, y, $-z + {}^1/_2$. [b] Symmetry transformation used to generate equivalent atoms: $1 - x$, $1 - y$, $1 - z$.

The mean Ni−Se bond length of 2.400 Å in $\mathbf{2_{Td}}$ is identical with the mean Ni−Se bond length (2.401 Å) in the tetrahedral [Ni(SePh)$_4$]$^{2-}$ complex.[11] Similarly, the mean Ni−Se bond length (2.354 Å) in the square-planar isomer $\mathbf{2_{SP}}$ is comparable to the value of 2.350 Å found for the phenyl-substituted analogue Ni[(SePPh$_2$)$_2$N]$_2$.[13] The six-membered NiSe$_2$P$_2$N ring in $\mathbf{2_{SP}}$ causes a widening of the endocyclic Se−Ni−Se angle by 10° with respect to the ideal square-planar angle, a value similar to that seen in the phenyl derivative. The exocyclic Se−Ni−Se angles are consequently tightened by 10° to compensate. However, $\mathbf{2_{Td}}$ displays much less deviation, with all of the Se−Ni−Se angles within 3.5° of the ideal tetrahedral angle of 109.5°. This structure is considerably less distorted than the only other reported tetrahedral Ni^{II}Se$_4$ complex whose analogous bond angles range from 90.66 to 125.87°.[11] The existence of both T$_d$ and SP geometries for **2** provides an opportunity to compare the effects of this change in geometry in the same molecule. As expected from a basic analysis of a four-coordinate d^8 configuration[26,27] in the framework of the angular overlap model,[28] the Ni−Se bond lengths are shorter

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(23) A solution of (^{i}Pr$_2$PTe)$_2$NNa·TMEDA (0.417 g, 0.648 mmol) in THF (10 mL) was added via cannula to a solution of NiBr$_2$·DME (0.100 g, 0.324 mmol) in THF (20 mL) at 23 °C. A color change from pink to brown occurred immediately upon the addition. The solution was allowed to stir for 1 h before the solvent was removed in vacuo. Fresh THF (10 mL) was added and, after filtration, hexane (25mL) was added, and this was left overnight to recrystallize. Complex **3** was obtained as brown crystals (0.259 g, 75%) after 16 h at −35 °C. Anal. Found (calcd) for C$_{24}$H$_{56}$N$_2$NiP$_4$Te$_4$ (%): C, 27.34 (27.05); H, 5.38 (5.30); N, 2.68 (2.63). ^{31}P{^{1}H} NMR: δ 32.1 (s, ^1J(P,Te) = 1365 Hz, ^3J(P,Te) = 142 Hz), −873.2(s). ^{125}Te{^{1}H} NMR: δ −466 (dt, ^1J(P,Te) = 1362 Hz, ^3J(P,Te) = 146 Hz). Complex **2** (0.225 g, 80%) was prepared in a similar manner by using (^{i}Pr$_2$PSe)$_2$NLi·TMEDA.[24] Anal. Found (calcd) for C$_{24}$H$_{56}$N$_2$NiP$_4$Se$_4$ (%): C, 32.52 (33.09); H, 6.38 (6.48); N, 2.68 (3.21). ^{31}P{^{1}H} NMR: δ −621.6 (s).

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(by 0.05Å) in the SP isomer (Table 1). This results in a slight lengthening of the Se−P bonds in $\mathbf{2_{SP}}$. The square-planar isomer displays a considerable asymmetry in the six-membered $NiSe_2P_2N$ ring, as evidenced by the disparity in the two Ni−Se−P angles (113.57 and 108.92°). Such asymmetry is not as pronounced in $\mathbf{2_{Td}}$, with the difference in such angles being only 1°. As expected, $\mathbf{2_{Td}}$ has a larger Se−Ni−Se angle than $\mathbf{2_{SP}}$ and, consequently, a wider Se···Se bite. This has a subsequent effect, tightening the P−N−P angle in the SP isomer (125.8°) with respect to the protonated free ligand $HN(SeP^iPr_2)_2$ (131.2°)[29] and expanding this angle in the $\mathrm{T_d}$ isomer (136.7°).

It is well-known that Ni^{II} complexes of the type NiX_2L_2 (X = halide, L = PR_3) exist in solution as an equilibrium mixture of $\mathrm{T_d}$ and SP isomers. In the solid state, $\mathrm{T_d}$ structures are preferred for R = Ph, whereas SP structures are generally found for R = alkyl.[1] However, examples of the presence of both isomers in the solid state for the same complex are rare. In the complex $[NiBr_2(PBzPh_2)_2]$, two independent molecules *in the same unit cell* show SP and $\mathrm{T_d}$ geometry.[30] The unique feature of complex **2** is the isolation of both the $\mathrm{T_d}$ and SP isomers as separable red and green crystals, respectively, from one reaction. Although the related complex $Ni[(SPPh_2)_2N]_2$ has been characterized in both a $\mathrm{T_d}$[31,32] and a SP[33] geometry, the crystal of the SP isomer contains solvation molecules (THF).

The four Te atoms of **3** lie in the same plane (Figure 1 and Table 1). However, similarly to $\mathbf{2_{SP}}$ (vide supra), the $Ni^{II}Te_4$ site is distorted from a regular SP geometry as a result of the constraint imposed by the chelate ring endocyclic and exocyclic Te−Ni−Te angles of 99.02° and 80.98°, respectively. The six-membered $NiTe_2P_2N$ ring shows asymmetry at the Ni−Te−P angles, which in **3** is even more pronounced (103.34° and 113.24°) than in $\mathbf{2_{SP}}$. This increased asymmetry forces the P−N−P angle (132.8°) of **3** to increase by ca. 7° with respect to that in $\mathbf{2_{SP}}$. Despite this structural asymmetry, other structural features, such as the Ni−Te bond lengths (2.515 Å and 2.508 Å), are close in value. For comparison, the recently reported trinuclear complex $[(Cp^*{}_2Nb)_2NiTe_4]$, which contains a highly distorted square-planar $Ni^{II}Te_4$ core, has a mean Ni−Te bond length of 2.475 Å.[34] Both the $Ni^{II}Te_4$- and $Ni^{II}Te_4Nb_2$-containing systems incorporate weak intramolecular Te···Te interactions (3.26 and 3.16 Å, respectively), which might stabilize the observed distorted square-planar structures. In this context, we note the suggestion that complexes containing NiN_2E_2 cores are trans when E = S or Se, but cis when E = Te because of the stabilizing intramolecular Te···Te interactions of 3.45 Å.[35]

The solution behavior of complexes **1**–**3** has been probed by ^{31}P NMR spectroscopy in THF-d_8. The tetrahedral geometry of **1** is maintained in solution as revealed by a broad resonance at −758.4 ppm. Interestingly, crystals of $\mathbf{2_{SP}}$ and $\mathbf{2_{Td}}$ give identical ^{31}P NMR spectra, which show a broad resonance at −621.6 ppm. The appearance of this paramagnetically shifted peak indicates that **2** exists only as the $\mathrm{T_d}$ isomer in solution.[36] This conclusion is supported by the observations that green crystals of $\mathbf{2_{SP}}$ give a deep-red solution when dissolved in THF-d_8. Such a structural transformation has previously been observed for SP crystals of $Ni[(SPPh_2)_2N]_2$, which show a ^{31}P NMR chemical shift at −459 ppm.[33] The large width of its ^{31}P NMR resonance (ca. 1600 Hz at the base) obscures the ^{77}Se satellites [typical ^1J(P−Se) values are in the range 500–600 Hz].[37] Meanwhile, the ^{31}P NMR spectrum of crystals of **3** reveals two peaks at 32.1 and −873.2 ppm in an integrated ratio of ca. 42:1. The predominance of the resonance at 32.1 ppm shows that this complex retains the SP $Ni^{II}Te_4$ core in solution. While it is possible to obtain a ^{125}Te NMR spectrum from diamagnetic **3**, the paramagnetism of **2** in solution precludes the observation of a ^{77}Se NMR resonance.

In summary, a comparison of the structures of $Ni[(EP^iPr_2)_2N]_2$ complexes (E = S, Se, Te) reveals a chalcogen-dependent trend from a $\mathrm{T_d}$ (**1**, E = S) to SP (**3**, E = Te) $Ni^{II}E_4$ core.[38] We note that complexes **1**−**3** are not isomorphous (Table S1 in the Supporting Information). The isolation of both $\mathrm{T_d}$ and SP stereoisomers for **2** (E = Se) from the same reaction is a novel feature of Ni^{II} coordination chemistry; the mononuclear planar $Ni^{II}Te_4$ site in complex **3** is also unprecedented. In solution, the $\mathrm{T_d}$ and SP geometries are preserved for **1** and **3**, respectively, but $\mathbf{2_{SP}}$ isomerizes to $\mathbf{2_{Td}}$. Relevant magnetic measurements, UV–vis spectra, and theoretical calculations will be combined in a full paper.

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Supporting Information Available: Table of crystallographic data for $\mathbf{2_{Td}}$, $\mathbf{2_{SP}}$, and **3** and details for an alternative synthesis of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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