

Preparation of Thiocarboxylate, Thiocarbamate and Xanthate Complexes of Pentacoordinate Nickel(II): Insertion of Heterocumulenes Into Nickel(II) Hydroxido Complexes

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The hydroxido complexes $[\text{Ni}(\text{N}_3\text{-mc})(\mu\text{-OH})_2][\text{PF}_6]_2$ [$\text{N}_3\text{-mc}$ = 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene ($\text{N}_3\text{-mc1}$) or 2,4,4,9-tetramethyl-1,5,9-triazacyclododec-1-ene ($\text{N}_3\text{-mc2}$)] react in the presence of alcohols with CS_2 or PhNCS to yield xanthate $[(\text{N}_3\text{-mc})\text{Ni}(\text{S}_2\text{C}(\text{OR}'))][\text{PF}_6]$ or *O*-alkyl *N*-phenylthiocarbamate $[(\text{N}_3\text{-mc})\text{Ni}(\text{PhNC}(\text{OR}')\text{S})][\text{PF}_6]$ complexes; these compounds represent the first examples of N,S-chelating thiocarbamates bound to nickel(II). The reactions of $[\text{Ni}(\text{N}_3\text{-mc})(\mu\text{-OH})_2][\text{PF}_6]_2$ with thiocarboxylic acids yield the

corresponding thiocarboxylate derivatives $[(\text{N}_3\text{-mc})\text{Ni}(\text{S-C}(\text{O})\text{R}')][\text{PF}_6]$. These paramagnetic nickel(II) complexes were characterized by both one- and two-dimensional (COSY) ^1H NMR spectroscopic techniques. The crystal structures of $[(\text{N}_3\text{-mc2})\text{Ni}(\text{S}_2\text{COCH}_3)][\text{PF}_6]$ (**2**), $[(\text{N}_3\text{-mc2})\text{Ni}(\text{PhNC}(\text{OCH}_2\text{-CH}_3)\text{S})][\text{PF}_6]$ (**8**), $[(\text{N}_3\text{-mc2})\text{Ni}(\text{SC}(\text{O})\text{CH}_3)][\text{PF}_6]$ (**10**) and $[(\text{N}_3\text{-mc1})\text{Ni}(\text{SC}(\text{O})\text{Ph})][\text{PF}_6]$ (**11**) were determined. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2007)

Introduction

Dimeric hydroxido complexes $[\text{Ni}(\text{N}_3\text{-mc})(\mu\text{-OH})_2][\text{PF}_6]_2$ [$\text{N}_3\text{-mc}$ = 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene ($\text{N}_3\text{-mc1}$) or 2,4,4,9-tetramethyl-1,5,9-triazacyclododec-1-ene ($\text{N}_3\text{-mc2}$)] have been shown to be good precursors in the synthesis of new coordination compounds. The acid–base reaction of these hydroxido complexes with protic acids leads to the formation of mono-^[1–3] or dinuclear^[4–6] complexes depending on the nature of the deprotonated ligand.

Dithioacid ligands have rich coordination and organo-metallic chemistry.^[7] These ligands and their metal complexes deserve continuous attention due to their interesting structural and chemical properties, as well as their wide range of applications, for example, industrially as pesticides, vulcanization accelerators, lubricants but also as potent biological pesticides.^[8] Those metal complexes were generally prepared by metathesis reactions of transition halides with the alkali metal salt of the corresponding thioacid.^[8]

In the past decade, growing interest has been directed towards nickel as a biological and spectroscopically relevant metal. The nickel-containing enzyme urease degrades urea to ammonia and carbamate (and finally CO_2). The widely

accepted mechanism for urease activity suggests that urea is activated by coordination to one nickel(II) ion in conjunction with extensive hydrogen bonding within the active-site pocket of the protein, and it is subsequently attacked by nucleophilic hydroxide ion bound to the opposite nickel(II) centre; the resulting carbamate species then decomposes further to yield carbonic acid and another molecule of ammonia.^[9] Bioinorganic synthetic complexes are particularly relevant to the study of the active site of metalloenzymes, because they provide spectroscopic information against which theoretical results can be compared, and they can also be used to carry out hydrolytic transformations at dinuclear nickel(II) cores that mimic the urease active site.^[10]

In previous studies we described the preparation of binuclear carbonate complexes $[\{\text{Ni}(\text{N}_3\text{-mc})\}_2(\mu\text{-CO}_3)][\text{PF}_6]_2$ when CO_2 was bubbled (or taken up directly from the atmosphere) through a solution of $[\text{Ni}(\text{N}_3\text{-mc})(\mu\text{-OH})_2][\text{PF}_6]_2$ in acetone [or if $(\text{NH}_4)\text{HCO}_3$ was added].^[11] Following our systematic study of the reactivity of hydroxido complexes of nickel, we next investigated the reactivity of nonorganometallic hydroxido nickel complexes such as $[\text{Ni}(\text{N}_3\text{-mc})(\mu\text{-OH})_2][\text{PF}_6]_2$ with related heterocumulenes; carbon disulfide, CS_2 , or phenylisothiocyanate, PhCNS , in the presence of alcohols $\text{R}'\text{OH}$, to form *O*-alkyl dithiocarbonate (xanthate) or *O*-alkyl *N*-phenylthiocarbamate pentacoordinate nickel(II) complexes, respectively. We report herein the first crystal structure of a N,S-chelating *N*-phenylthiocarbamate nickel complex (3D Search using the Cambridge Structural Database, CSD version 5.27, Aug. 2006 release). Thiocarboxylate complexes were also prepared by the acid–base re-

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X-ray diffraction studies were carried out on $[(N_3\text{-mc}2)\text{-Ni}(\text{S}_2\text{COCH}_3)]\text{PF}_6 \cdot 1/2 (\text{CH}_3)_2\text{CO}$ (**2**). A thermal ellipsoid drawing of the cation of **2** with a partial labelling scheme is shown in Figure 1. Selected geometric data are given in Table 1. The Ni^{II} ion in **2** adopts a distorted square-pyramidal geometry, and the parameter $\tau^{[24]}$ shows a value of 0.16. The three nitrogen atoms of the macrocyclic ligand constitute a trigonal face of the pyramid. The two sulfur atoms from the xanthate and the two nitrogen atoms of the macrocycle form the basal plane (rmsd 0.0591). The nickel ion lies above this plane and is displaced 0.3976 Å toward the N3 nitrogen, which constitutes the axial donor. The plane of the chelate moiety defined by S1, S2, C14 and O1 (rms 0.0015) is inclined by 17.19(6)° to the basal plane. The Ni–N distances lie within the range reported in complexes containing the $\{\text{Ni}(\text{N}_3\text{-mc})\}$ moiety.^[11] The Ni–S bond lengths are slightly different [2.3930(9) and 2.5119(9) Å]; thus the xanthate ligand is bonded in an asymmetric chelating mode. These bond lengths are longer than those reported for other crystallographically characterized nickel–xanthate complexes with iminophosphanes in a distorted square-planar geometry.^[25] Octahedral nickel–xanthate complexes containing phenanthroline^[26] or pyrazine,^[27] as well as penta-coordinate nickel–xanthate complexes containing triphosphanes,^[28] have shorter Ni–S bond lengths. The bite angle of the chelating xanthate anion shows values of 73.46(3)°. The distortion from square-pyramidal geometry is also reflected in the bond angles between the *trans* ligands. The N1–Ni–S2 and N2–Ni–S1 bond angles are 162.05(9) and 152.61(8)°, respectively. The deviation of these angles from the idealized square-pyramidal geometry is also due to the four-membered chelating ring of the xanthate ligand.

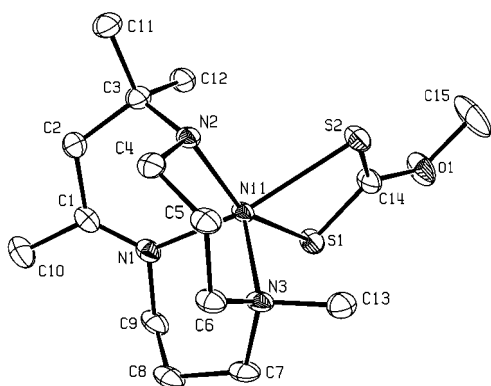


Figure 1. ORTEP drawing of the cation of complex **2** (ellipsoids at 50% probability level) with atom-labelling scheme. For clarity hydrogen atoms are omitted.

Structural studies were also carried out for the complex $[(N_3\text{-mc}2)\text{-Ni}\{\text{PhNC}(\text{OCH}_2\text{CH}_3)\text{S}\}]\text{PF}_6$ (**8**). As shown in Figure 2 (selected bond lengths and angles in Table 2) the Ni atom has a distorted square-pyramidal geometry with a value of 0.14 for τ . Distortions from the idealized square pyramidal geometry are almost localized in the equatorial plane where the bidentate ligand subtends an angle of 68.17(6)° to the metal. The Ni atom lies above of the basal

Table 1. Selected bond lengths and angles for complex **2**.^[a]

Bond lengths [Å]			
Ni1–N2	2.038(3)	Ni1–S1	2.3930(9)
Ni1–N1	2.039(3)	Ni1–S2	2.5119(9)
Ni1–N3	2.062(3)		
Bond angles [°]			
N2–Ni1–N1	90.46(11)	N3–Ni1–S1	102.64(8)
N2–Ni1–N3	102.71(11)	N2–Ni1–S2	90.26(8)
N1–Ni1–N3	92.87(11)	N1–Ni1–S2	162.05(9)
N2–Ni1–S1	152.61(8)	N3–Ni1–S2	104.45(8)
N1–Ni1–S1	98.48(8)	S1–Ni1–S2	73.46(3)

[a] Symmetry transformations used to generate equivalent atoms: #1: $-x + 1, y, -z + 5/2$.

plane (rmsd 0.0330) by 0.3642 Å. The plane of the chelate moiety defined by the S1, N4, C14 and O1 (rmsd 0.0066) atoms is inclined by 9.49(9)° to the basal plane, and the attached phenyl ring is somewhat rotated [65.33(7)°] about the N4–C17 axis. The C14–O1–C15 angle of 119.26(19)° suggests that the oxygen atom can be considered to be in the sp^2 -hybridized state, and the C–O bond lengths agree with the values expected for a $\text{C}(\text{sp}^2)\text{--O--C}(\text{sp}^3)$ system.^[29] The C14–S1 bond length of 1.722(2) Å is indicative of a $\text{C}(\text{sp}^2)\text{--S}$ single bond,^[30] whereas double bond character is well-defined in the N4–C14 bond of 1.301(3) Å. Thus, the negative charge within the bidentate ligand seems to be mainly localized on the sulfur atom.^[31]

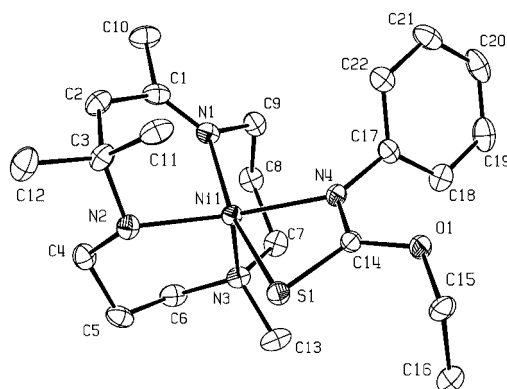


Figure 2. ORTEP drawing of the cation of complex **8** (ellipsoids at 50% probability level) with atom-labelling scheme. For clarity hydrogen atoms are omitted.

Table 2. Selected bond lengths and angles for complex **8**.

Bond lengths [Å]			
Ni1–N1	2.034(2)	Ni1–N3	2.089(2)
Ni1–N2	2.048(2)	Ni1–S1	2.4927(6)
Ni1–N4	2.067(2)		
Bond angles [°]			
N1–Ni1–N2	90.42(9)	N4–Ni1–N3	101.95(8)
N1–Ni1–N4	100.95(8)	N1–Ni1–S1	161.37(6)
N2–Ni1–N4	152.82(8)	N2–Ni1–S1	93.68(6)
N1–Ni1–N3	93.39(8)	N4–Ni1–S1	68.17(6)
N2–Ni1–N3	101.91(8)	N3–Ni1–S1	103.50(6)

The ^1H NMR spectra of complexes **1–8** exhibit sharp isotropically shifted signals from 375 to -40 ppm, in acetone solution. The spectra show the resonance line pattern observed for the $\text{N}_3\text{-mc}$ ligands that was assigned on the basis of previous studies of nickel macrocyclic complexes.^[1–6] A representative ^1H NMR spectrum for complex **1** is shown in Figure 3. The eight resonance signals due to the $\alpha\text{-CH}$ protons were shifted downfield, whereas the six resonance signals for the $\beta\text{-CH}$ protons were shifted upfield relative to the diamagnetic position because of a dominant spin polarization mechanism.^[32] Moreover, the equatorial protons were expected to experience larger contact shifts than the axial protons because of the angular dependence of the hyperfine coupling constant,^[33] and therefore, the most downfield resonances are due to the $\alpha\text{-CH}_{\text{eq}}$ protons and the most upfield ones to the $\beta\text{-CH}_{\text{eq}}$ protons. The isotropically shifted ^1H NMR signals observed for the methyl groups [2-Me, 4-Me(a, b) and 9-Me-N] and the alkyl groups of the xanthates and thiocarbamates can be initially assigned by inspection of their peak areas. Therefore, on the basis of X-ray structures of **2** and **8**, the larger distortions in the square-pyramid for **8** as a result of the small bite of the N,S-chelating thiocarbamate moiety (68.17°) results in a larger magnetic anisotropy that in turn induces a larger dipolar shift^[34] for the *O*-alkyl substituents. The complete assignment of these isotropically shifted signals required the use of two-dimensional ^1H NMR spectroscopic techniques. A magnitude COSY spectrum of **6** (Figure 4), recorded at 25°C , clearly shows cross signals between the resonances at $\delta = 27.2$ and 17.8 ppm and also between resonances at 17.8 , -0.9 and -4.8 ppm. These signals can be assigned to the $\text{CH}_3\text{O-}$ and *N*-phenyl *m*-H (17.8), *o*-H (-0.9) and *p*-H (-4.8) protons, respectively, of the *O*-alkyl *N*-phenylthiocarbamate ligand. The shift direction alternation of the *N*-phenyl protons is characteristic if the π -contact shift is dominant. The net spin density in the d_π orbitals could be polarized by the unpaired electrons in the $d_{x^2-y^2}$ and d_{z^2} orbitals through spin-orbit coupling. A similar behaviour was observed elsewhere.^[35]

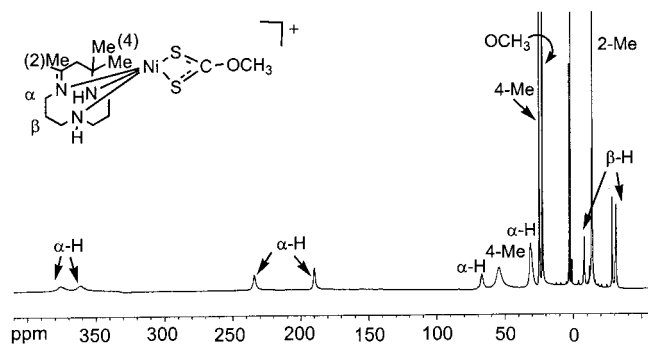


Figure 3. ^1H NMR spectra [in $(\text{CD}_3)_2\text{CO}$ solution at room temperature] of complex **1**.

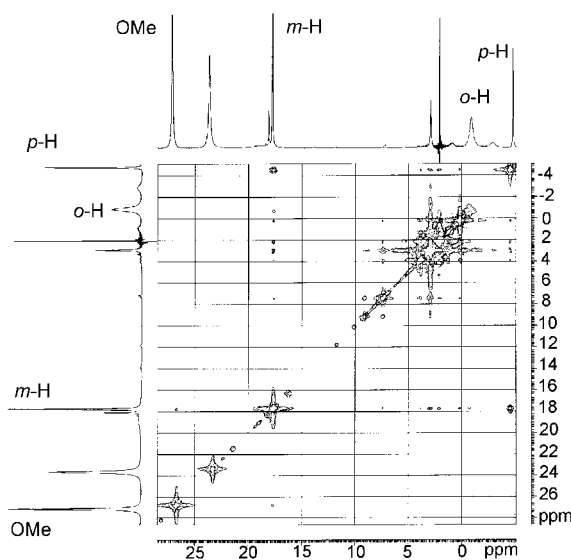


Figure 4. Portion of the ^1H COSY spectrum of complex **6** [in $(\text{CD}_3)_2\text{CO}$ solution at 25°C]. Only the relevant region to assign the *O*-alkyl *N*-phenylthiocarbamate resonances is shown in the top trace.

Thiocarboxylate Complexes

When $[\text{Ni}(\text{N}_3\text{-mc})(\mu\text{-OH})_2][\text{PF}_6]_2$ was treated with thioacids $\text{HSC}(\text{O})\text{CH}_3$ or $\text{HSC}(\text{O})\text{Ph}$ in acetone, complexes **9–12** were obtained in moderate-to-high yields (Scheme 1). The acid–base reaction occurred at room temperature in acetone with the concomitant liberation of water for complexes **9–12**. The thiocarboxylate anions, $\text{RC}(\text{O})\text{S}^-$, constitute an interesting class of ligand having a soft sulfur donor site and a hard oxygen donor site.^[36] Furthermore, the chemistry of these ligands was relatively unexplored relative to thiolate or thiocarbamate ligands.^[37,38] The IR spectra of complexes **9–12** show characteristic absorptions for the $\text{N}_3\text{-mc}$ ligands at $3294\text{--}3264\text{ cm}^{-1}$ $\nu(\text{N-H})$ and ca. 1660 cm^{-1} $\nu(\text{C=N})$, and two strong bands due to the presence of the PF_6^- ion at 840 and 560 cm^{-1} are also observed. The thiocarboxylate ligand in compounds **9–12** exhibits a κ^2 -coordination mode to the nickel atom, which is suggested by the IR spectra. The spectra show strong absorption bands at ca. 1500 and ca. 980 cm^{-1} , which can be assigned to $\nu(\text{CO})$ and $\nu(\text{CS})$, respectively, and they are consistent with a symmetrical bidentate coordination.^[39] This coordination mode was authenticated by X-ray crystal structure determination on **10** and **11** (vide infra). The crystal structures of cations $[(\text{N}_3\text{-mc}2)\text{Ni}\{\text{SC}(\text{O})\text{CH}_3\}][\text{PF}_6]$ (**10**) and $[(\text{N}_3\text{-mc}1)\text{Ni}\{\text{SC}(\text{O})\text{Ph}\}][\text{PF}_6]$ (**11**) are shown in Figures 5 and 6. Selected distances and angles for these complexes are given in Tables 3 and 4. In each crystallized cation, the nickel atom is five-coordinate, with a square-pyramid arrangement of the chelating atoms. The structure of complex **10** shows the presence of two independent molecules. In each one, the Ni atom shows τ values of 0.26 and 0.27 for **10** and 0.35 for **11**. The three nitrogen atoms of the N_3 -macrocyclic hold the apical position and two adjacent basal ones, whereas the other two basal positions correspond to the *S,O*-thiocarboxylate group. The basal plane is

formed by N1, N2, O1 and S1, with a rms deviation of fitted atoms of 0.1076, by N4, N5, O2 and S2, rmsd 0.1132, for **10** and by N1, N2, O1 and S1, rmsd 0.1448, for complex **11**. The Ni atoms are 0.3850(17) and 0.3888(18) Å above of the corresponding basal plane towards the apical N3 or N6 atom in complex **10** and 0.3346(8) Å in **11**. The Ni–O bond lengths in **10** are 2.119(3) and 2.121(3) Å; in complex **11** the Ni–O bond length is 2.1000(15) Å. These bond lengths are comparable to those reported for other crystallographically characterized homoleptic nickel–thiobenzoate complexes with distorted octahedral^[38] geometries. The bite angle of the carboxylate anion shows values of 68.73(10) and 68.42(10)° for complex **10** and 69.05(4)° for **11**. The plane of the chelate moiety defined by S1, O1, C14 and C15 (rmsd 0.0066) is inclined 13.93(15)° with respect to the basal plane N1, N2, O1 and S1; and the plane S2, O2, C29 and C30 (rmsd 0.0020) is inclined by 18.96(16)° to the basal N4, N5, O2 and S2 in complex **10**. In complex **11**, the plane of the chelate moiety defined by S1, O1, C13 and C14 (rmsd 0.0041) is inclined by 18.51(8)° to the basal plane N1, N2, O1 and S1, and the angle between the phenyl ring and the nickel-bounded thiocarboxylate group is 16.29(10)°.

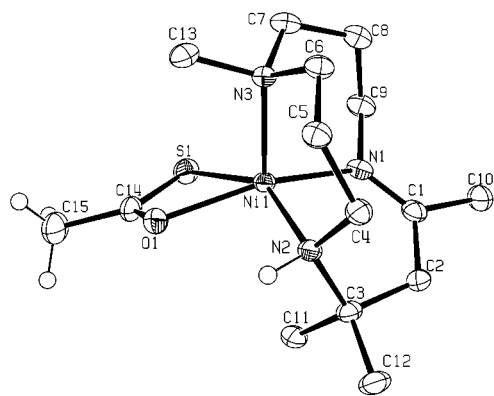


Figure 5. ORTEP drawing of the cation of complex **10** (ellipsoids at 50% probability level) with atom-labelling scheme. For clarity hydrogen atoms are omitted.

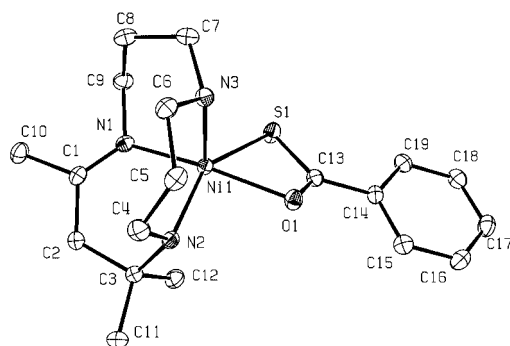


Figure 6. ORTEP drawing of the cation of complex **11** (ellipsoids at 50% probability level) with atom-labelling scheme. For clarity hydrogen atoms are omitted.

Complexes **9–12** exhibit relatively sharp hyperfine-shifted ¹H NMR signals in acetone solution spanning from 390 to –35 ppm. The spectra were assigned on the basis of our previous studies of paramagnetic nickel(II) macrocyclic

Table 3. Selected bond lengths and angles for complex **10**.

Bond lengths [Å]			
Ni1–N1	2.013(4)	Ni2–N4	2.014(4)
Ni1–N2	2.030(4)	Ni2–N5	2.017(4)
Ni1–N3	2.047(4)	Ni2–N6	2.054(4)
Ni1–O1	2.119(3)	Ni2–O2	2.121(3)
Ni1–S1	2.4045(13)	Ni2–S2	2.4047(13)
Bond angles [°]			
N1–Ni1–N2	92.25(15)	N4–Ni2–N5	91.93(16)
N1–Ni1–N3	94.47(15)	N4–Ni2–N6	94.45(16)
N2–Ni1–N3	102.78(15)	N5–Ni2–N6	102.31(15)
N1–Ni1–O1	163.40(14)	N4–Ni2–O2	163.65(14)
N2–Ni1–O1	89.70(14)	N5–Ni2–O2	89.50(14)
N3–Ni1–O1	101.17(14)	N6–Ni2–O2	101.16(15)
N1–Ni1–S1	102.17(11)	N4–Ni2–S2	102.87(12)
N2–Ni1–S1	148.10(11)	N5–Ni2–S2	147.34(11)
N3–Ni1–S1	104.24(11)	N6–Ni2–S2	105.31(11)
O1–Ni1–S1	68.73(10)	O2–Ni2–S2	68.42(10)

Table 4. Selected bond lengths and angles for complex **11**.

Bond lengths [Å]			
Ni1–N1	2.0016(18)	Ni1–O1	2.1000(15)
Ni1–N3	2.0202(18)	Ni1–S1	2.4028(6)
Ni1–N2	2.0274(17)		
Bond angles [°]			
N1–Ni1–N3	93.21(7)	N2–Ni1–O1	88.41(6)
N1–Ni1–N2	93.04(7)	N1–Ni1–S1	104.65(5)
N3–Ni1–N2	101.79(7)	N3–Ni1–S1	104.33(5)
N1–Ni1–O1	168.51(7)	N2–Ni1–S1	147.34(5)
N3–Ni1–O1	97.66(7)	O1–Ni1–S1	69.05(4)

complexes. The spectra show the expected resonance line pattern because of a dominant spin-polarization mechanism.^[32] The spectra of thiocarboxylate derivatives **9–12** are similar to those of corresponding complexes **1–8** in signals and magnitudes of contact shifts. The mean difference is the large isotropic shift for the –CH₃ and –Ph protons, which are consistent with the close proximity of these groups to the paramagnetic nickel(II) centre. The spectrum of complex **12** is shown in Figure 7, and from its inspection it can be seen that all the resonances of the phenyl rings

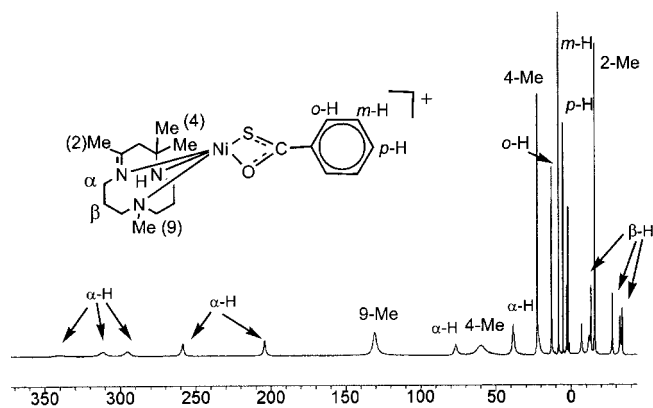


Figure 7. ¹H NMR spectra [in (CD₃)₂CO solution at room temperature] of complex **12**.

are shifted downfield relative to TMS in accordance with a dominant σ -delocalization pattern of spin density that is consistent with the ground state of nickel(II) although the unpaired electrons could polarize the net spin density in the d_{π} orbitals.^[6]

Conclusions

Because many questions still remain about the mechanism of action of the urease metalloenzyme, such as the nature of the hydrolytic attack^[40] and the feasibility of carbamate as the first intermediate formed in the reaction,^[41] this study investigated the possibility of attack on cumulated double bond systems. In these reactions the proposed first step is the addition of OH across one double bond followed by esterification; however, the external attack by $R'O^-$ of the coordinated heterocumulene cannot be ruled out. Moreover, the proton resonances of the synthetic mononuclear pentacoordinate nickel(II) complexes of relevance to urease were completely assigned by using 1D and 2D 1H NMR spectroscopic methods.

Experimental Section

Materials: Chemicals were purchased from Aldrich and were used without further purification. Solvents were dried and distilled by general methods before use. The complexes $[Ni(N_3\text{-mc})(\mu\text{-OH})_2][PF_6]_2$ [$N_3\text{-mc}$ = 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene ($N_3\text{-mc1}$) or 2,4,4,9-tetramethyl-1,5,9-triazacyclododec-1-ene ($N_3\text{-mc2}$)] were prepared by previously described procedures.^[42,43]

Physical Measurements: C, H, N and S analyses were carried out with a microanalyzer Carlo Erba model EA 1108. Fast atom bombardment (FAB) mass spectra were obtained with a Fisons VG Autospec spectrometer operating in the positive mode. Infrared spectra were recorded with a Perkin–Elmer 16F PC FTIR spectrophotometer by using Nujol mulls between polyethylene sheets. UV/Vis spectra (in acetone) were recorded with a UNICAM 520 spectrophotometer equipped with matched quartz cells in the 300–800 nm range. 1H NMR spectra were recorded with a Bruker model AV 200E or AV 300 spectrometer. Chemical shifts (in ppm) are reported with respect to the residual solvent signal. The 1H COSY spectrum was obtained at 25 °C for **6** with 512 data points in the F^1 dimension and 4096 data points in the F^2 dimension with a delay time of 150 ms. An unshifted sine-bell-squared weighting function was applied prior to Fourier transformation followed by baseline correction in both dimensions and symmetrization. Molar conductivities were measured in acetone solutions (ca. 10^{-3} mol L $^{-1}$) with a Crison 525 conductimeter.

$[N_3\text{-mc})Ni(S_2COCH_3)] [PF_6]$ (1**):** To a suspension of $[Ni(N_3\text{-mc})(\mu\text{-OH})_2][PF_6]_2$ (0.15 mmol) in methanol (60 mL) was added CS_2 (0.30 mmol). The mixture was stirred at room temperature for 24 h, and the solvent was partially evaporated under reduced pressure to ca. 15 mL. The mixture was filtered and the addition of diethyl ether caused the precipitation of a green solid, which was collected by filtration, washed with diethyl ether and air-dried.

$[N_3\text{-mc1})Ni(S_2COCH_3)] [PF_6]$ (1**):** Yield: 46 mg (36%). $M_M = 142$ Ω^{-1} cm 2 mol $^{-1}$. 1H NMR [300 MHz, $(CD_3)_2CO$, TMS]: δ = 375.8 (α -H), 361.7 (α -H), 234.1 (α -H), 189.9 (α -H), 67.0 (α -H), 54.5 (4-Me, 3 H), 31.3 (2 α -H), 24.8 (4-Me, 3 H), 24.0 (α -H), 22.5 (CH_3O -, 3 H), -7.9 (β -H), -13.3 (2 β -H), -13.9 (2-Me, 3 H), -28.5 (β -H), -31.0 (β -H), -31.4 (β -H) ppm. IR (nujol): $\tilde{\nu}$ = 3271, 3237 (N–H), 1658 (C=N), 1238 (COC), 1178 (CO), 1046 (CS) cm $^{-1}$. UV/Vis (acetone): λ (ϵ , M $^{-1}$ cm $^{-1}$) = 611 (100), 384 (446) nm. MS (FAB+): m/z (%) = 376 (100) $[M]^+$. $C_{14}H_{28}F_6N_3NiOPS_2$ (522.18): calcd. C 32.20, H 5.40, N 8.05, S 12.28; found C 32.33, H 5.26, N 7.97, S 11.84.

$[N_3\text{-mc2})Ni(S_2COCH_3)] [PF_6]$ (2**):** Yield: 62 mg (51%). $M_M = 139$ Ω^{-1} cm 2 mol $^{-1}$. 1H NMR [300 MHz, $(CD_3)_2CO$, TMS]: δ = 286.2 (α -H), 243.3 (α -H), 173.3 (α -H), 113.8 (9-Me, 3 H), 59.2 (α -H), 49.4 (4-Me, 3 H), 34.1 (α -H), 30.6 (α -H), 24.3 (4-Me, 3 H), 22.6 (α -H), 20.7 (CH_3O -, 3 H), 18.9 (α -H), -6.4 (β -H), -11.2 (β -H), -14.4 (2-Me, 3 H), -17.6 (β -H), -26.9 (β -H), -29.4 (β -H), -33.3 (β -H) ppm. IR (nujol): $\tilde{\nu}$ = 3271 (N–H), 1651 (C=N), 1228 (COC), 1170 (CO), 1044 (CS) cm $^{-1}$. UV/Vis (acetone): λ (ϵ , M $^{-1}$ cm $^{-1}$) = 639 (100), 392 (395) nm. MS (FAB+): m/z (%) = 390 (100) $[M]^+$. Green crystals suitable for X-ray diffraction studies were obtained by diffusion of diethyl ether into an acetone solution of the compound. $C_{15}H_{30}F_6N_3NiOPS_2$ (536.21): calcd. C 33.60, H 5.64, N 7.84, S 11.96; found C 33.15, H 5.57, N 8.00, S 11.53.

$[N_3\text{-mc})Ni(S_2COCH_2CH_3)] [PF_6]$ (3**):** To a suspension of $[Ni(N_3\text{-mc})(\mu\text{-OH})_2][PF_6]_2$ (0.15 mmol) in ethanol (50 mL) CS_2 (0.30 mmol) was added and the resulting mixture was refluxed for 3 h. The solvent was partially evaporated under reduced pressure until ca. 10 mL and then the suspension was filtered. On addition of Et_2O the blue-green complexes precipitated. The solids were filtered off and air-dried.

$[N_3\text{-mc1})Ni(S_2COCH_2CH_3)] [PF_6]$ (3**):** Yield: 50 mg (40%). $M_M = 133$ Ω^{-1} cm 2 mol $^{-1}$. 1H NMR [300 MHz, $(CD_3)_2CO$, TMS]: δ = 371.0 (α -H), 357.1 (α -H), 231.4 (α -H), 186.2 (α -H), 66.5 (α -H), 53.3 (4-Me, 3 H), 31.4 (2 α -H), 24.5 (4-Me, 3 H), 21.7 (α -H), 9.4 ($-CH_2O$ -, 2 H), 8.8 (CH_3 -, 3 H), -7.8 (β -H), -13.2 (2 β -H), -13.6 (2-Me, 3 H), -28.1 (β -H), -30.4 (β -H), -30.9 (β -H) ppm. IR (nujol): $\tilde{\nu}$ = 3274, 3247 (N–H), 1652 (C=N), 1237 (COC), 1159 (CO), 1031 (CS) cm $^{-1}$. UV/Vis (acetone): λ (ϵ , M $^{-1}$ cm $^{-1}$) = 616 (96), 385 (418) nm. MS (FAB+): m/z (%) = 390 (100) $[M]^+$. $C_{15}H_{30}F_6N_3NiOPS_2$ (536.21): calcd. C 33.60, H 5.64, N 7.84, S 11.96; found C 33.56, H 5.46, N 7.55, S 11.56.

$[N_3\text{-mc2})Ni(S_2COCH_2CH_3)] [PF_6]$ (4**):** Yield: 46 mg (37%). $M_M = 154$ Ω^{-1} cm 2 mol $^{-1}$. 1H NMR [300 MHz, $(CD_3)_2CO$, TMS]: δ = 289.2 (α -H), 246.5 (α -H), 173.8 (α -H), 113.9 (9-Me, 3 H), 59.7 (α -H), 49.8 (4-Me, 3 H), 34.2 (α -H), 30.7 (α -H), 24.6 (4-Me, 3 H), 22.3 (α -H), 18.8 (α -H), 8.3 ($-CH_2O$ -, 2 H), 7.4 (CH_3 -, 3 H), -6.5 (β -H), -11.4 (β -H), -14.5 (2-Me, 3 H), -17.0 (β -H), -27.3 (β -H), -29.7 (β -H), -33.6 (β -H) ppm. IR (nujol): $\tilde{\nu}$ = 3271 (N–H), 1651 (C=N), 1217 (COC), 1158 (CO), 1046 (CS) cm $^{-1}$. UV/Vis (acetone): λ (ϵ , M $^{-1}$ cm $^{-1}$) = 633 (115), 391 (454) nm. MS (FAB+): m/z (%) = 404 (100) $[M]^+$. $C_{16}H_{32}F_6N_3NiOPS_2$ (550.23): calcd. C 34.93, H 5.86, N 7.64, S 11.66; found C 35.03, H 5.76, N 7.38, S 11.39.

$[N_3\text{-mc})Ni(PhNC(OCH_3)S)] [PF_6]$ (5**):** To a suspension of $[Ni(N_3\text{-mc})(\mu\text{-OH})_2][PF_6]_2$ (0.15 mmol) in methanol (60 mL) was added PhNCS (0.30 mmol). The mixture was stirred at room temperature for 24 h. The solvent was removed under reduced pressure until a blue solid began to precipitate, and then diethyl ether was added to complete precipitation. The solid was filtered off, washed with diethyl ether and air-dried.

$[N_3\text{-mc1})Ni(PhNC(OCH_3)S)] [PF_6]$ (5**):** Yield: 94 mg (70%). $M_M = 133$ Ω^{-1} cm 2 mol $^{-1}$. 1H NMR [300 MHz, $(CD_3)_2CO$, TMS]: δ =

367.2 (α -H), 347.8 (α -H), 230.4 (2 α -H), 182.9 (α -H), 75.7 (α -H), 51.0 (4-Me, 3 H), 33.7 (α -H), 30.3 (α -H), 27.9 (CH₃O-, 3 H), 23.1 (4-Me, 3 H), 17.5 (2 m -H), -2.5 (2 o -H), -6.1 (p -H), -8.8 (2 β -H), -9.6 (β -H), -13.2 (2-Me, 3 H), -28.6 (β -H), -29.4 (2 β -H) ppm. IR (nujol): $\tilde{\nu}$ = 3290, 3253 (N-H), 1657 (C=N), 1537 (CN) cm⁻¹. UV/Vis (acetone): λ (ϵ , M⁻¹cm⁻¹) = 602 (70), 366 (272) nm. MS (FAB+): m/z (%) = 435 (100) [M]⁺. C₂₀H₃₃F₆N₄NiOPS (581.23): calcd. C 41.33, H 5.72, N 9.64, S 5.52; found C 40.71, H 5.52, N 9.73, S 5.41.

[(N₃-mc2)Ni{PhNC(OCH₃)S}][PF₆] (6): Yield: 105 mg (79%). A_M = 136 Ω^{-1} cm²mol⁻¹. ¹H NMR [300 MHz, (CD₃)₂CO, TMS]: δ = 290.4 (α -H), 281.7 (α -H), 251.7 (α -H), 163.5 (α -H), 151.0 (α -H), 112.4 (9-Me, 3 H), 66.2 (α -H), 47.3 (4-Me, 3 H), 38.7 (α -H), 34.1 (α -H), 27.2 (CH₃O-, 3 H), 23.7 (4-Me, 3 H), 17.8 (2 m -H), -0.9 (2 o -H), -4.8 (p -H), -7.5 (β -H), -10.6 (β -H), -11.8 (β -H), -13.9 (2-Me, 3 H), -25.8 (β -H), -27.5 (β -H), -31.7 (β -H) ppm. IR (nujol): $\tilde{\nu}$ = 3270 (N-H), 1659 (C=N), 1524 (CN) cm⁻¹. UV/Vis (acetone): λ (ϵ , M⁻¹cm⁻¹) = 629 (79) 384 (285) nm. MS (FAB+): m/z (%) = 449 (100) [M]⁺. C₂₁H₃₅F₆N₄NiOPS (595.25): calcd. C 42.37, H 5.93, N 9.41, S 5.39; found C 42.62, H 5.73, N 9.27, S 5.17.

[(N₃-mc)Ni{PhNC(OCH₂CH₃)S}][PF₆]: To a suspension of [Ni(N₃-mc)(μ -OH)]₂[PF₆]₂ (0.15 mmol) in ethanol (40 mL) was added PhNCS (0.30 mmol), and the resulting mixture was heated at reflux for 1 h. The solvent was partially evaporated under reduced pressure until a solid began to precipitate. Upon the addition of diethyl ether, the blue-green complexes precipitated completely. The solid was filtered off and air-dried.

[(N₃-mc1)Ni{PhNC(OCH₂CH₃)S}][PF₆] (7): Yield: 54 mg (40%). A_M = 137 Ω^{-1} cm²mol⁻¹. ¹H NMR [300 MHz, (CD₃)₂CO, TMS]: δ = 363.9 (α -H), 344.5 (α -H), 228.7 (2 α -H), 180.3 (α -H), 74.9 (α -H), 49.9 (4-Me, 3 H), 33.4 (α -H), 30.0 (α -H), 22.9 (4-Me, 3 H), 17.5 (2 m -H), 13.7 (-CH₂O-, 2 H), 13.0 (CH₃-, 3 H), -2.3 (2 o -H), -6.0 (p -H), -8.7 (2 β -H), -9.5 (β -H), -13.0 (2-Me, 3 H), -28.3 (β -H), -29.1 (2 β -H) ppm. IR (nujol): $\tilde{\nu}$ = 3292, 3252 (N-H), 1659 (C=N), 1537 (CN) cm⁻¹. UV/Vis (acetone): λ (ϵ , M⁻¹cm⁻¹) = 607 (75), 364 (293) nm. MS (FAB+): m/z (%) = 449 (100) [M]⁺. C₂₁H₃₅F₆N₄NiOPS (595.25): calcd. C 42.37, H 5.93, N 9.41, S 5.39; found C 42.49, H 5.84, N 9.30, S 5.47.

[(N₃-mc2)Ni{PhNC(OCH₂CH₃)S}][PF₆] (8): Yield: 58 mg (42%). A_M = 134 Ω^{-1} cm²mol⁻¹. ¹H NMR [300 MHz, (CD₃)₂CO, TMS]: δ = 288.2 (α -H), 280.1 (α -H), 251.1 (α -H), 160.6 (α -H), 149.5 (α -H), 117.1 (9-Me, 3 H), 65.1 (α -H), 46.5 (4-Me, 3 H), 38.3 (α -H), 34.0 (α -H), 23.6 (4-Me, 3 H), 17.8 (2 m -H), 14.0 (-CH₂O-, 2 H), 12.2 (CH₃-, 3 H), -0.6 (2 o -H), -4.6 (p -H), -7.5 (β -H), -10.4 (β -H), -11.8 (β -H), -13.8 (2-Me, 3 H), -27.3 (β -H), -28.3 (β -H), -31.6 (β -H) ppm. IR (nujol): $\tilde{\nu}$ = 3279 (N-H), 1659 (C=N), 1537 (CN) cm⁻¹. UV/Vis (acetone): λ (ϵ , M⁻¹cm⁻¹) = 623 (78), 384 (281) nm. MS (FAB+): m/z (%) = 463 (100) [M]⁺. Green crystals suitable for X-ray diffraction studies were obtained by slow evaporation of the reaction mixture. C₂₂H₃₇F₆N₄NiOPS (609.28): calcd. C 43.37, H 6.12, N 9.20, S 5.26; found C 43.29, H 5.96, N 9.02, S 5.47.

[(N₃-mc)Ni(A)][PF₆] [N₃-mc = N₃-mc1, A = SC(O)CH₃ (9), SC(O)-Ph (11); N₃-mc = N₃-mc2, A = SC(O)CH₃ (10), SC(O)Ph (12)]: These complexes were prepared by reaction of [Ni(N₃-mc)(μ -OH)]₂[PF₆]₂ (0.12 mmol) with the corresponding thiocarboxylic acid [HSC(O)CH₃ or HSC(O)Ph, 0.24 mmol] in acetone (25 mL). After stirring for 1 h, the solution was filtered and concentrated under reduced pressure to ca. 8 mL. The addition of diethyl ether caused the precipitation of green solids, which were collected by filtration, washed with diethyl ether and air-dried.

[(N₃-mc1)Ni{SC(O)CH₃}[PF₆] (9): Yield: 90 mg (79%). A_M = 140 Ω^{-1} cm²mol⁻¹. ¹H NMR [300 MHz, (CD₃)₂CO, TMS]: δ =

370.1 (α -H), 357.9 (α -H), 235.5 (α -H), 213.6 (α -H), 87.0 (α -H), 81.9 (CH₃-, 3 H), 72.7 (α -H), 54.9 (4-Me, 3 H), 36.7 (α -H), 31.2 (α -H), 21.8 (4-Me, 3 H), -8.5 (2 β -H), -12.9 (β -H), -13.7 (2-Me, 3 H), -27.2 (β -H), -29.0 (β -H), -30.5 (β -H) ppm. IR (nujol): $\tilde{\nu}$ = 3294, 3269 (N-H), 1659 (C=N), 1503 (C=O), 978 (CS) cm⁻¹. UV/Vis (acetone): λ (ϵ , M⁻¹cm⁻¹) = 627 (84), 385 (181) nm. MS (FAB+): m/z (%) = 344 (100) [M]⁺. C₁₄H₂₈F₆N₃NiOPS (490.11): calcd. C 34.31, H 5.76, N 8.57, S 6.54; found C 34.55, H 5.80, N 8.63, S 6.44.

[(N₃-mc1)Ni{SC(O)Ph}[PF₆] (11): Yield: 120 mg (94%). A_M = 144 Ω^{-1} cm²mol⁻¹. ¹H NMR [200 MHz, (CD₃)₂CO, TMS]: δ = 384.7 (α -H), 364.5 (α -H), 239.6 (α -H), 240.7 (α -H), 220.3 (α -H), 89.8 (α -H), 56.7 (4-Me, 3 H), 37.5 (α -H), 32.2 (α -H), 22.2 (4-Me, 3 H), 12.2 (2 o -H), 8.6 (2 m -H), 5.0 (p -H), -8.7 (2 β -H), -13.1 (β -H), -13.8 (2-Me, 3 H), -27.6 (β -H), -29.3 (β -H), -30.8 (β -H) ppm. IR (nujol): $\tilde{\nu}$ = 3285, 3268 (N-H), 1656 (C=N), 1594 (C=C), 966 (CS) cm⁻¹. UV/Vis (acetone): λ (ϵ , M⁻¹cm⁻¹) = 631 (86), 387 (183) nm. MS (FAB+): m/z (%) = 406 (100) [M]⁺. C₁₉H₃₀F₆N₃NiOPS (552.18): calcd. C 41.33, H 5.48, N 7.61, S 5.81; found C 41.45, H 5.39, N 7.53, S 5.70.

[(N₃-mc2)Ni{SC(O)CH₃}[PF₆] (10): Yield: 87 mg (77%). A_M = 136 Ω^{-1} cm²mol⁻¹. ¹H NMR [300 MHz, (CD₃)₂CO, TMS]: δ = 340.0 (α -H), 304.0 (α -H), 290.5 (α -H), 252.6 (α -H), 198.6 (α -H), 128.6 (9-Me, 3 H), 79.6 (CH₃-, 3 H), 74.7 (α -H), 58.3 (4-Me, 3 H), 37.6 (2 α -H), 22.1 (4-Me, 3 H), -6.8 (β -H), -11.9 (β -H), -12.9 (β -H), -15.6 (2-Me, 3 H), -26.8 (β -H), -32.1 (β -H), -33.4 (β -H) ppm. IR (nujol): $\tilde{\nu}$ = 3264 (N-H), 1656 (C=N), 1519 (C=O), 980 (CS) cm⁻¹. UV/Vis (acetone): λ (ϵ , M⁻¹cm⁻¹) = 628 (88), 384 (164). MS (FAB+): m/z (%) = 358 (100) [M]⁺. C₁₅H₃₀F₆N₃NiOPS (504.14): calcd. C 35.74, H 6.00, N 8.33, S 6.36; found C 35.70, H 6.00, N 8.29, S 6.32.

[(N₃-mc2)Ni{SC(O)Ph}[PF₆] (12): Yield: 112 mg (88%). A_M = 138 Ω^{-1} cm²mol⁻¹. ¹H NMR [200 MHz, (CD₃)₂CO, TMS]: δ = 340.4 (α -H), 311.6 (α -H), 295.6 (α -H), 258.8 (α -H), 204.4 (α -H), 130.8 (9-Me, 3 H), 76.2 (α -H), 60.2 (4-Me, 3 H), 38.6 (2 α -H), 22.6 (4-Me, 3 H), 13.1 (2 o -H), 8.5 (2 m -H), 5.5 (p -H), -6.8 (β -H), -11.8 (β -H), -12.9 (β -H), -15.5 (2-Me, 3 H), -27.1 (β -H), -32.4 (β -H), -33.7 (β -H) ppm. IR (nujol): $\tilde{\nu}$ = 3267 (N-H), 1658 (C=N), 1495 (C=O), 967 (CS) cm⁻¹. UV/Vis (acetone): λ (ϵ , M⁻¹cm⁻¹) = 630 (87), 394 (186). MS (FAB+): m/z (%) = 420 (100) [M]⁺. C₂₀H₃₂F₆N₃NiOPS (566.21): calcd. C 42.42, H 5.70, N 7.42, S 5.66; found C 42.49, H 5.65, N 7.39, S 5.56.

Structure Determination and Refinement: Single crystals of complexes **2** (blue block), **8** (blue block), **10** (green block) and **11** (blue block) suitable for X-ray diffraction studies were obtained by slow diffusion of diethyl ether onto an acetone solution (**10**, **11** and **2**) or by slowly evaporation of the reaction solution (**8**) of the complex. Crystals were selected and mounted on a glass fibre for data collection. Diffraction data were measured with a Bruker SMART APEX by using Mo-K α radiation (λ = 0.71073 Å). Crystallographic data are summarized in Table 5. The diffraction frames were integrated by using the SAINT package^[44] and corrected for absorption with SADABS.^[45] The raw intensity data were converted (including corrections for Lorentz and polarization effects) to structure amplitudes and their esd by using the SAINT program. The structures were solved by direct methods^[46] and refined^[46] by full-matrix least-squares techniques by using anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were set at calculated positions. CCDC-645172 (for **2**), -645173 (for **8**), -645174 (for **10**) and -645175 (for **11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of

Table 5. Crystallographic data for complexes **2**, **8**, **10** and **11**.

Complex	2	8	10	11
Formula	C ₁₅ H ₃₀ F ₆ N ₃ NiOPS ₂ ·1/2Me ₂ CO	C ₂₂ H ₃₇ F ₆ N ₄ NiOPS	C ₁₅ H ₃₀ F ₆ N ₃ NiO ₁ PS·1/2Me ₂ CO	C ₁₉ H ₃₀ F ₆ N ₃ NiOPS
<i>M</i>	565.26	609.30	533.20	552.20
<i>T</i> [K]	100(2)	100(2)	100(2)	293(2) K
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	triclinic	monoclinic
Space group	<i>C</i> 2/ <i>c</i>	<i>P</i> 1	<i>P</i> 1̄	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> [Å]	22.773(2)	8.1229(4)	13.5659(11)	8.2180(4)
<i>b</i> [Å]	15.2834(15)	9.0655(5)	13.8759(11)	14.3034(6)
<i>c</i> [Å]	14.2077(14)	10.5412(6)	14.1725(11)	19.6944(9)
α [°]	90	74.3280(10)	77.0060(10)	90
β [°]	105.6810(10)	74.4370(10)	77.2380(10)	98.4990(10)
γ [°]	90	67.7310(10)	62.8690(10)	90
<i>V</i> [Å ³]	4760.9(8)	679.54(6)	2291.8(3)	2289.56(18)
<i>Z</i>	8	1	4	4
<i>D</i> _{calcd.} [Mg m ^{−3}]	1.577	1.489	1.545	1.602
μ [mm ^{−1}]	1.121	0.914	1.071	1.074
<i>F</i> (000)	2352	318	1112	1144
Reflections collected	26434	7946	26502	26189
Independent reflections	5487 (<i>R</i> _{int} = 0.0374)	5786 (<i>R</i> _{int} = 0.0159)	10217 (<i>R</i> _{int} = 0.0284)	5329 (<i>R</i> _{int} = 0.0222)
Goodness-of-fit on <i>F</i> ²	1.260	0.807	1.203	1.090
Final <i>R</i> indices	<i>R</i> ₁ = 0.0563	<i>R</i> ₁ = 0.0304	<i>R</i> ₁ = 0.0716	<i>R</i> ₁ = 0.0388
[<i>I</i> > 2σ(<i>I</i>)] ^[a,b]	<i>wR</i> ₂ = 0.1424	<i>wR</i> ₂ = 0.0730	<i>wR</i> ₂ = 0.1709	<i>wR</i> ₂ = 0.0938
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0572	<i>R</i> ₁ = 0.0319	<i>R</i> ₁ = 0.0765	<i>R</i> ₁ = 0.0395
	<i>wR</i> ₂ = 0.1430	<i>wR</i> ₂ = 0.0739	<i>wR</i> ₂ = 0.1737	<i>wR</i> ₂ = 0.0943
Max/min Δρ [e Å ^{−3}]	1.021/−0.572	0.515/−0.258	1.340/−0.654	0.767/−0.666

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ for reflections with $I > 2\sigma(I)$. [b] $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, in which $P = (2F_c^2 + F_o^2)/3$ and *a* and *b* are constants set by the program.

charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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