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Spectroscopic and structural characterization of *O,O′*-(diphenylphosphineoxide)-amidate and acetylacetonate complexes of pentacoordinate nickel(II)

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ABSTRACT

Heteroleptic nickel pentacoordinate complexes with the macrocyclic ligands 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene (Me_3-mcN_3) or its 9-methyl derivative (Me_4-mcN_3), as ancillary ligands, and *O,O′*-(diphenylphosphineoxide)amidate ligands, [RC(O)NP(O)Ph_2] (R = C_6H_6 (**1**), C_5H_4N (**2**), C_4H_3S (**3**)), have been prepared as well as related acetylacetonate derivatives. The complexes have been studied by spectroscopic methods (IR, UV–Vis and ^{1}H NMR). In acetone solution, the complexes exhibit isotropically shifted ^{1}H NMR resonances. The full assignment of these resonances has been achieved using one- and two-dimensional ^{1}H NMR techniques. The single-crystal structures of {(Me_4-mcN_3)Ni[OP(Ph_2)NC(Tf)O]}[PF_6] (**9**) and {(Me_3-mcN_3)Ni(acac)}[PF_6] (**10**) have been established by X-ray diffraction.

1. Introduction

The chemistry of metal phosphonates, [RPO_3M], has been a well-investigated area since the 1970s because of application of these compounds in ion-exchange, catalysis, chemical-sensing, and electrooptic processes [1]. The structure and properties of these hybrid materials, which integrate organic and inorganic characteristics within a single extended framework, can often be modified by incorporation of additional functions such as hydroxyl, amino, carboxylate, and pyridyl in the R group [2]. Thus, the synthesis and characterization of phosphoramidate ligands has been recently developed due to their biological activity [3] and their coordination chemistry [4]. Some of them with RC(O)N(H)P(O)R'_2 formula were used as *O,O′*-donor ligands for metal ions [5]. Ligands with donor oxygen atoms in 1,3-positions are normally found to be good chelating groups for the trivalent lanthanide and actinide ions. Ligands with two P=O or P=O and C=O groups in 1,3-positions have been found to form many coordination complexes which display useful extraction applications [6,7]. In order to design improved extractants, it is helpful to understand the molecular structure-function characteristics of multifunctional ligands [8].

The incorporation of additional donor substitutes in the ligand frame allows generating a novel self-complementary system for the needs of supramolecular synthesis [9]. Although crystal structures of several phosphoramidate and their complexes are already known [4,10], there are little discussions about the substituents effects on the structural and NMR parameters and the nickel(II) complexes are scarce [9]. Herein, we present the synthesis of some phosphoramides with general formula RC(O)N(H)P(O)Ph_2, R = C_6H_6 (**1**), C_5H_4N (**2**), C_4H_3S (**3**), the preparation of the first heteroleptic nickel pentacoordinated complexes with *O,O′*-(diphenylphosphineoxide)amidate ligands, and the related acetylacetonate derivatives, together with the macrocyclic ligands 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene or its 9-methyl derivative, as ancillary ligands, in continuation of our work on reactivity studies of hydroxo nickel complexes [11]. Furthermore, we discussed on structural, NMR and other spectroscopic (IR, UV–Vis) parameters in these compounds. ^{1}H NMR spectroscopy has become an excellent technique to study structural and magnetic properties of paramagnetic metal ions in both coordination complexes and biological systems [12–14] and a wealth of structural and magnetic information can be obtained on the local environment of the paramagnetic metal center. However, a scarcely explored issue is the determination of the structural and magnetic properties of mononuclear and binuclear nickel(II) ions in both biological and model systems using ^{1}H NMR spectroscopy [15].

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2. Experimental

2.1. General methods

C, H, and N analyses were carried out with a microanalyzer Carlo Erba model EA 1108. Infrared spectra were recorded on a Perkin–Elmer 16F PC FT-IR spectrophotometer using Nujol mulls between polyethylene sheets. The ^{1}H and ^{31}P NMR spectra were recorded on a Bruker (AC 200E or AC 300E) spectrometer. Chemical shifts (in ppm) were reported with respect to the residual solvent signal or H_3PO_4 as standard. The ^{1}H COSY spectra were obtained at 20 °C for **5** and **6** with 512 data points in the F1 dimension and 1024 data points in the F2 dimension with a delay time of 150 and 50 ms for **5** and **6**, respectively. An unshifted sine-bell-squared weighting function was applied prior to Fourier transformation followed by baseline correction in both dimensions and symmetrization. Fast atom bombardment (FAB) mass spectra were run on a Fisons VG Autospec spectrometer operating in the FAB$^+$ mode. All chemicals were purchased from Aldrich and were used without further purification. Solvents were dried and distilled by general methods before use. The complexes $[Ni(mcN_3)(\mu\text{-}OH)]_2(PF_6)_2$ (mcN_3 = 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene (Me_3-mcN_3) and its 9-methyl derivative (Me_4-mcN_3)) were prepared by procedures previously described [16,17].

2.2. Ligands preparation (**1**–**3**)

The ligands *N-(diphenylphosphineoxide)amide* were synthesized by the following experimental procedure [18]: in separate experiments, chlorodiphenylphosphine (5 mL, 27.9 mmol) was added to a solution of the corresponding amide (26 mmol): benzamide ($PhC(O)NH_2$) (**1**), nicotinamide (3-$PyC(O)NH_2$) (**2**) or 2-thiophenecarboxamide (**3**), triethylamine (3.9 mL, 28 mmol) and DMAP (240 mg, 20 mmol) in THF (100 mL). A drop of aqueous H_2O_2 (30% w/w) was added and this solution was refluxed overnight. The reaction mixture was filtered to remove a white solid (Et_3NHCl) and washed with THF (50 mL). The solvent was removed in vacuo leaving a pale yellow solid. This solid was recrystallised by cooling a concentrated dichloromethane/ether solution overnight.

N-(diphenylphosphineoxide)phenylamide (**1**): Yield: 53%. M.p. = 157 °C. Anal. Calc. for $C_{19}H_{16}NO_2P$: C, 71.0; H, 5.0; N, 4.4. Found: C, 71.2; H, 5.1; N, 4.4%. FAB: *m/z* 322.2 $[M]^+$, 219.1 $[P(OH)Ph_2NH_2]^+$. IR $\nu_{max}(cm^{-1})$: 3309, 1666, 1590, 1499, 1198, 1128,1108, 1072, 876, 524. ^{1}H NMR ($CDCl_3$, ppm): δ 9.12 (d,1H, NH, $^2J_{PNH}$ = 4.83 Hz), 8.02 (d, 2H, Ph), 7.94–7.87 (m, 3H, Ph), 7.58–7.38 (m, 10H, PPh_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ 28.5 (s).

N-(diphenylphosphineoxide)nicotinamide (**2**): Yield: 59%. M.p. = 188 °C. Anal. Calc. for $C_{18}H_{15}N_2O_2P$: C, 67.1; H, 4.7; N, 8.7. Found: C, 67.0; H, 4.6; N, 8.6%. FAB: *m/z* 323.2 $[M]^+$, 219.1 $[P(OH)Ph_2NH_2]^+$. IR $\nu_{max}(cm^{-1})$: 3372, 1654, 1588, 1410, 1270, 1186, 1125, 1097, 1023, 530. ^{1}H NMR ($CDCl_3$, ppm): δ 9.31 (d, 1H, NH, $^2J_{PNH}$ = 4.68 Hz), 8.71 (d, 1H, PyC[6]H), 8.44 (d, 1H, PyC[2]H), 7.89 (m, 4H, $OPPh_2$), 7.59–7.54 (m, 1H, PyC[5]H), 7.54–7.42 (m, 6H, $OPPh_2$), 7.30 (m, 1H, PyC[4]H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ 29.8 (s).

N-(diphenylphosphineoxide)-2-thiophenecarboxamide (**3**): Yield: 64%. M.p. = 219 °C. Anal. Calc. for $C_{17}H_{14}NO_2SP$: C, 62.4; H, 4.3; N, 4.3; S, 9.8. Found: C, 62.1; H, 4.2; N, 4.2; S, 9.6%. FAB: *m/z* 328.1 $[M]^+$, 219.1 $[P(OH)Ph_2NH_2]^+$. IR $\nu_{max}(cm^{-1})$: 3295, 1657, 1589, 1524, 1202, 1090, 1036, 528–519. ^{1}H NMR ($CDCl_3$, ppm): δ 9.83 (1H, NH), 8.10 (d, 1H, TfC[3]H), 7.88 (m, 4H, PPh_2), 7.54–7.44 (m, 6H+1H, PPh_2, TfC[5]H), 7.00 (m, 1H, TfC[4]H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): δ 29.5 (s).

2.3. Synthesis of the O,O′-(diphenylphosphineoxide)amidate complexes (**4**–**6**)

In separate experiments, the corresponding *N*-(diphenylphosphineoxide)amide (0.232 mmol) was added to a solution of $[Ni(Me_3\text{-}mcN_3)(\mu\text{-}OH)]_2(PF_6)_2$ (100 mg, 0.116 mmol) in acetone (40 mL) and the mixture was stirred at room temperature for 4 h. The solvent was removed under reduced pressure to approximately 10 mL. Addition of diethyl ether (20 mL) resulted in the precipitation of the expected solid which was filtered off, washed with diethyl ether and air-dried.

{(Me_3-mcN_3)Ni[$OP(Ph_2)NC(Ph)O$]}[PF_6] (**4**): Yield: 70.8 mg, 73%. Anal. Calc. for $C_{31}H_{40}N_4O_2NiP_2F_6$: C, 50.6; H, 5.4; N, 7.6. Found: C, 50.3; H, 5.3; N, 7.9%. Λ_M: 153.7 S cm^2 mol^{-1}. FAB: *m/z* 486.4 $[M]^+$. UV–Vis in acetone: λ (nm), (ε, M^{-1} cm^{-1}): 633 (40.4), 386 (117.8). IR $\nu_{max}(cm^{-1})$: 3268, 1657, 1590, 1190, 1130, 1044. ^{1}H NMR ($(CD_3)_2CO$, ppm): δ 362.0 (H_α), 335.1 ($2H_\alpha$), 235.6 (H_α), 199.6 (H_α), 87.1 (H_α), 42.3 (4-Me, 3H), 37.0 (H_α), 28.7 (H_α), 21.7 (4-Me, 3H), 11.4 (O-C-Ph, 2H), 9.9 (O-C-Ph + O-P-Ph_2, 9H), 7.6 (O-P-Ph_2, 4H), −10.0 (H_β), −13.4 ($2H_\beta$), −17.4 (2-Me, 3H), −28.0 (H_β), −34.0 (H_β),−35.6 (H_β).

{(Me_3-mcN_3)Ni[$OP(Ph_2)NC(3\text{-}py)O$]}[PF_6] (**5**): Yield: 74.8 mg, 82%. Anal. Calc. for $C_{30}H_{39}N_5O_2NiP_2F_6$: C, 48.9; H, 5.3; N, 9.5. Found: C, 48.6; H, 5.4; N, 9.3%. Λ_M: 120.6 S cm^2 mol^{-1}. FAB: *m/z* 590.0 $[M]^+$. UV–Vis in acetone: λ (nm), (ε, M^{-1} cm^{-1}): 610 (43.7), 379 (120.4). IR $\nu_{max}(cm^{-1})$: 3274, 1660, 1607, 1587, 1536, 1133, 1089, 1052. ^{1}H NMR ($(CD_3)_2CO$, ppm): δ 366.4 (H_α), 344.3 ($2H_\alpha$), 239.0 (H_α), 205.7 (H_α), 93.2 (H_α), 52.4 (4-Me, 3H), 35.0 (H_α), 30.8 (H_α), 21.4 (4-Me, 3H), 13.7 (PyC[6]H), 12.9 (PyC[5]H), 11.7 (PyC[4]H), 10.7 (PyC[2]H), 9.0 (O-P-Ph_2, 2H), 8.5 (O-P-Ph_2, 2H), 7.7 (O-P-Ph_2, 2H), 7.4 (O-P-Ph_2, 2H), 6.4 (O-P-Ph_2, 2H), −9.5 (H_β), −13.1 ($2H_\beta$), −16.0 (2-Me, 3H), −28.2 (H_β), −32.5 (H_β), −33.9 (H_β).

{(Me_3-mcN_3)Ni[$OP(Ph_2)NC(Tf)O$]}[PF_6] (**6**): Yield: 72.2 mg, 79%. Anal. Calc. for $C_{29}H_{38}N_4O_2SNiP_2F_6$: C, 47.0; H, 5.1; N, 7.6; S, 4.3. Found: C, 46.9; H, 5.9; N, 7.5; S, 4.2%. Λ_M: 158.1 S cm^2 mol^{-1}. FAB: *m/z* 595.6 $[M]^+$. UV–Vis in acetone: λ (nm), (ε, M^{-1} cm^{-1}): 612 (51.8), 378 (135.6). IR $\nu_{max}(cm^{-1})$: 3271, 1658, 1529, 1513, 1130, 1089, 1034. ^{1}H NMR ($(CD_3)_2CO$, ppm): δ 359.1 (H_α), 340.4 ($2H_\alpha$), 237.3 (H_α), 202.0 (H_α), 92.6 (H_α), 50.5 (4-Me, 3H), 35.2 (H_α), 31.5 (H_α), 21.5 (4-Me, 3H), 13.8 (TfC[3]H), 11.0 (TfC[4]H), 10.2 (TfC[5]H), 8.7 (O-P-Ph_2, 2H), 8.4 (O-P-Ph_2, 2H), 7.9 (O-P-Ph_2, 2H), 7.2 (O-P-Ph_2, 2H), 6.6 (O-P-Ph_2, 2H), −9.7 (H_β), −13.0 ($2H_\beta$), −15.8 (2-Me, 3H), −27.8 (H_β), −31.8 (H_β), −33.1 (H_β).

2.4. Synthesis of the O,O′-(diphenylphosphineoxide)amidate complexes (**7**–**9**)

The experimental procedure was similar to that described above using $[Ni(Me_4\text{-}mcN_3)(\mu\text{-}OH)]_2(PF_6)_2$ (100 mg, 0.112 mmol) and the corresponding *N*-(diphenylphosphino)amide oxide (0.224 mmol) in acetone (40 mL).

{(Me_4-mcN_3)Ni[$OP(Ph_2)NC(Ph)O$]}[PF_6] (**7**): Yield: 68.5 mg, 74%. Anal. Calc. for $C_{32}H_{42}N_4O_2NiPF_6$: C, 51.3; H, 5.6; N, 7.5. Found: C, 50.9; H, 5.6; N, 7.6%. Λ_M: 150.7 S cm^2 mol^{-1}. FAB: *m/z* 500.7 $[M]^+$. UV–Vis in acetone: λ (nm), (ε, M^{-1} cm^{-1}): 648 (44.4), 392 (118.4). IR $\nu_{max}(cm^{-1})$: 3265, 1656, 1592, 1578, 1193, 1129, 1096, 1040. ^{1}H NMR ($(CD_3)_2CO$, ppm): δ 294.3 (H_α), 272.1 (H_α), 256.3 (H_α), 195.0 (H_α), 183.3 (H_α), 118.6 (9-Me, 3H), 85.0 (H_α), 48.3 (4-Me, 3H), 36.6 (H_α), 34.5 (H_α), 22.7 (4-Me, 3H), 12.7 (O-C-Ph, 2H), 10.5 (O-C-Ph, 2H), 10.1 (O-C-Ph), 9.1 (O-P-Ph_2, 4H), 8.6 (O-P-Ph_2, 4H), 7.2 (O-P-Ph_2,2H), −9.8 (H_β), −11.8 (H_β), −12.9 (H_β), −17.6 (2-Me, 3H), −27.6 (H_β), −33.8 (H_β), −34.9 (H_β).

{(Me_4-mcN_3)Ni[$OP(Ph_2)NC(3\text{-}py)O$]}[PF_6] (**8**): Yield: 72.2 mg, 83%. Anal. Calc. for $C_{31}H_{41}N_5O_2NiP_2F_6$: C, 49.6; H, 5.5; N, 9.3. Found: C,

49.5; H, 5.6; N, 9.0%. Λ_M: 162.8 S cm^2 mol^{-1}. FAB: *m/z* 604.7 [M]$^+$. UV–Vis in acetone: λ (nm), (ε, M^{-1} cm^{-1}): 622 (50.8), 381 (139.4). IR ν_{max}(cm^{-1}): 3266, 1656, 1585, 1523, 1133, 1084, 1067. ^{1}H NMR ((CD$_3$)$_2$CO, ppm): δ 294.3 (H$_\alpha$), 276.4 (H$_\alpha$), 262.8 (H$_\alpha$), 193.1 (2H$_\alpha$), 116.6 (9-Me, 3H), 84.8 (H$_\alpha$), 55.5 (4-Me, 3H), 36.0 (2H$_\alpha$), 22.1 (4-Me, 3H), 12.9 (PyC[6]H + PyC[5]H), 11.2 (PyC[4]H), 9.7 (PyC[2]H), 9.6 (O-P-Ph$_2$, 2H), 9.0 (O-P-Ph$_2$, 2H), 7.7 (O-P-Ph$_2$, 2H), 7.5 (O-P-Ph$_2$, 2H), 6.4 (O-P-Ph$_2$, 2H), −9.0 (H$_\beta$), −9.9 (H$_\beta$), −12.9 (H$_\beta$), −16.8 (2-Me, 3H), −27.4 (H$_\beta$), −33.2 (H$_\beta$), −34.5 (H$_\beta$).

{(Me$_4$-mcN$_3$)Ni[OP(Ph$_2$)NC(Tf)O]}[PF$_6$] (**9**): Yield: 69.7 mg, 70%. Anal. Calc. for $C_{30}H_{40}N_4O_2SNiP_2F_6$: C, 47.7; H, 5.3; N, 7.4; S, 4.2. Found: C, 47.9; H, 5.4; N, 7.5; S, 4.0%. Λ_M: 155.6 S cm^2 mol^{-1}. FAB: *m/z* 609.6 [M]$^+$. UV–Vis in acetone: λ (nm), (ε, M^{-1} cm^{-1}): 623 (62.1), 379 (166). IR ν_{max}(cm^{-1}): 3260, 1657, 1533, 1508, 1131, 1091, 1066. ^{1}H NMR ((CD$_3$)$_2$CO, ppm): δ 293.4 (H$_\alpha$), 276.6 (H$_\alpha$), 263.9 (H$_\alpha$), 191.8 (2H$_\alpha$), 116.5 (9-Me, 3H), 85.2 (H$_\alpha$), 53.1 (4-Me, 3H), 36.0 (2H$_\alpha$), 22.2 (4-Me, 3H), 13.7 (TfC[3]H), 10.8 (TfC[4]H), 9.1 (TfC[5]H), 8.8 (O-P-Ph$_2$, 4H), 7.9 (O-P-Ph$_2$, 4H), 7.2 (O-P-Ph$_2$), 6.6 (O-P-Ph$_2$), −9.5 (2H$_\beta$), −13.1 (H$_\beta$), −16.8 (2-Me, 3H), −27.2 (H$_\beta$), −33.0 (H$_\beta$), −34.3 (H$_\beta$).

2.5. Synthesis of the acetylacetonate complexes (**10, 11**)

2,4-Pentanodione (0.232 mmol) was added to a solution of [Ni(mcN$_3$)(μ-OH)]$_2$(PF$_6$)$_2$ (0.116 mmol) in acetone (40 mL) and the mixture was stirred at room temperature for 4 h. The solvent was removed under reduced pressure to approximately 10 mL. Addition of diethyl ether (20 mL) resulted in the precipitation of blue solids which were filtered off, washed with diethyl ether and air-dried.

{(Me$_3$-mcN$_3$)Ni(acac)}[PF$_6$] (**10**): Yield: 76%. Anal. Calc. for $C_{17}H_{32}N_3O_2NiPF_6$: C, 39.5; H, 6.8; N, 8.1. Found: C, 39.8; H, 6.6; N, 8.2%. Λ_M: 159.1 S cm^2 mol^{-1}. FAB: *m/z* 368.0 [M]$^+$. UV–Vis in acetone: λ (nm), (ε, M^{-1} cm^{-1}): 579 (90.4). IR ν_{max}(cm^{-1}): 3272, 1660, 1594, 1530. ^{1}H NMR ((CD$_3$)$_2$CO, ppm): δ 353.9 (H$_\alpha$), 347.3 (H$_\alpha$), 225.6 (H$_\alpha$), 191.5 (H$_\alpha$), 93.4 (H$_\alpha$), 49.0 (4-Me, 3H), 34.9 (H$_\alpha$), 31.3 (H$_\alpha$), 27.5 (H$_\alpha$), 21.4 (4-Me, 3H), 2.8 (OC-Me, 6H), −10.4 (2H$_\beta$), −13.2 (H$_\beta$), −16.8 (2-Me, 3H), −27.0 (–CH–), −27.5 (H$_\beta$), −32.1 (H$_\beta$), −33.2 (H$_\beta$).

{(Me$_4$-mcN$_3$)Ni(acac)}[PF$_6$] (**11**): Yield: 70%. Anal. Calc. for $C_{18}H_{34}N_3O_2NiPF_6$: C, 40.9; H, 6.5; N, 7.9. Found: C, 40.8; H, 6.6; N, 8.0%. Λ_M: 156.3 S cm^2 mol^{-1}. FAB: *m/z* 382.0 [M]$^+$. UV–Vis in acetone: λ (nm), (ε, M^{-1} cm^{-1}): 589 (93.2), 357 (470.6). IR ν_{max}(cm^{-1}): 3262, 1660, 1590, 1520. ^{1}H NMR ((CD$_3$)$_2$CO, ppm): δ 341.0 (H$_\alpha$), 284.2 (H$_\alpha$), 249.3 (H$_\alpha$), 181.6 (H$_\alpha$), 108.1 (9-Me, 3H), 86.7 (H$_\alpha$), 49.7 (4-Me, 3H), 37.2 (H$_\alpha$), 32.4 (H$_\alpha$), 21.6 (4-Me, 3H), 10.8 (H$_\alpha$), 1.3 (OC-Me, 6H), −7.3 (2H$_\beta$), −9.9 (H$_\beta$), −13.1 (H$_\beta$), −17.1 (2-Me, 3H), −26.5 (–CH–), −27.9 (H$_\beta$), −33.7 (H$_\beta$), −34.3 (H$_\beta$).

2.6. Crystal structure determination of *{(Me$_4$-mcN$_3$)Ni[OP(Ph$_2$)-NC(Tf)O]}[PF$_6$]* (**9**) and *{(Me$_3$-mcN$_3$)Ni(acac)}[PF$_6$]* (**10**)

Crystals suitable for a diffraction study were prepared by a slow diffusion of diethyl ether into their acetone solutions. Crystallographic data are summarized in Table 1. Data collection for **10** was performed on a Siemens P4 diffractometer at −100 °C. Data collection for **9** was performed at −173 °C on a Bruker Smart CCD diffractometer, the diffraction frames were integrated using the SAINT package [19] and corrected for absorption with SADABS [20]. The structures were solved by direct methods [21] and refined by full-matrix least-squares techniques using anisotropic thermal parameters for non-H atoms. Hydrogen atoms were introduced in calculated positions and refined during the last stages of the refinement.

Table 1
Crystal data and structure refinement for **9** and **10**.

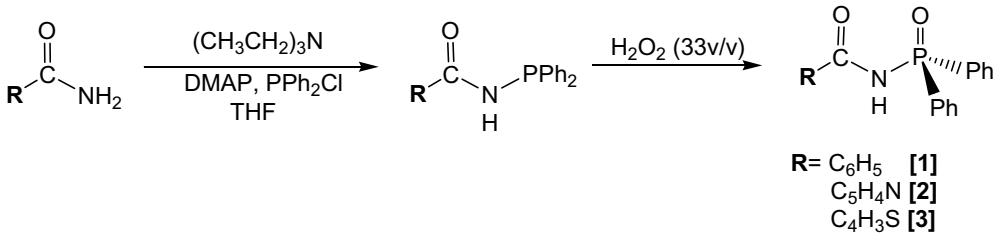
Complex	**9**	**10**
Empirical formula	$C_34H_5oF_6N_4Ni0_3P_2S$	$C_{17}H_{35}F_6N_3NiO_2P$
Formula weight	829.49	517.16
Temperature (K)	100(2)	173(2)
λ	0.71073 A	0.71073 A
Crystal system	Monoclinic	Monoclinic
Space group	*P*21/*n*	*P*21/*c*
Unit cell dimensions		
a (Å)	8.6550(3)	10.3168(6)
b (Å)	23.2308(9)	13.1119(8)
c (Å)	18.8819(7)	16.4372(10)
α (°)	90	90
β (°)	91.6350(10)	95.62
γ (°)	90	90
V (Å^3)	3794.9(2)	2212.8(2)
Z	4	4
$D_{calcd.}$ (mg m^{-3})	1.452	1.552
Absorption coefficient (mm^{-1})	0.720	1.018
F(000)	1736	1084
Crystal size (mm^3)	0.29 × 0.11 × 0.06	0.28 × 0.24 × 0.18
θ range for data collection (°)	1.39–28.26	3.03–25.00
Index ranges	$-11 \leqslant h \leqslant 10$, $-29 \leqslant k \leqslant 29$, $-24 \leqslant 1 \leqslant 25$	$-12 \leqslant h \leqslant 3{,}0 \leqslant k \leqslant 15$, $-19 \leqslant l \leqslant 19$
Reflections collected	43 633	5059
Independent reflections [$R_{(int)}$]	8822 (0.0601)	3885 (0.0302)
Absorption correction	None	0.8380 and 0.7637
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	8822/1/462	3885/0/271
Goodness-of-fit (GOF) on F^2	1.021	0.973
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0672, wR_2 = 0.1492	R_1 = 0.0517, wR_2 = 0.1363
R indices (all data)	R_1 = 0.0918, wR_2 = 0.1661	R_1 = 0.0758, wR_2 = 0.1461
Largest difference peak and hole (e Å^{-3})	0.957 and −0.707	0.665 and −0.810

3. Results and discussions

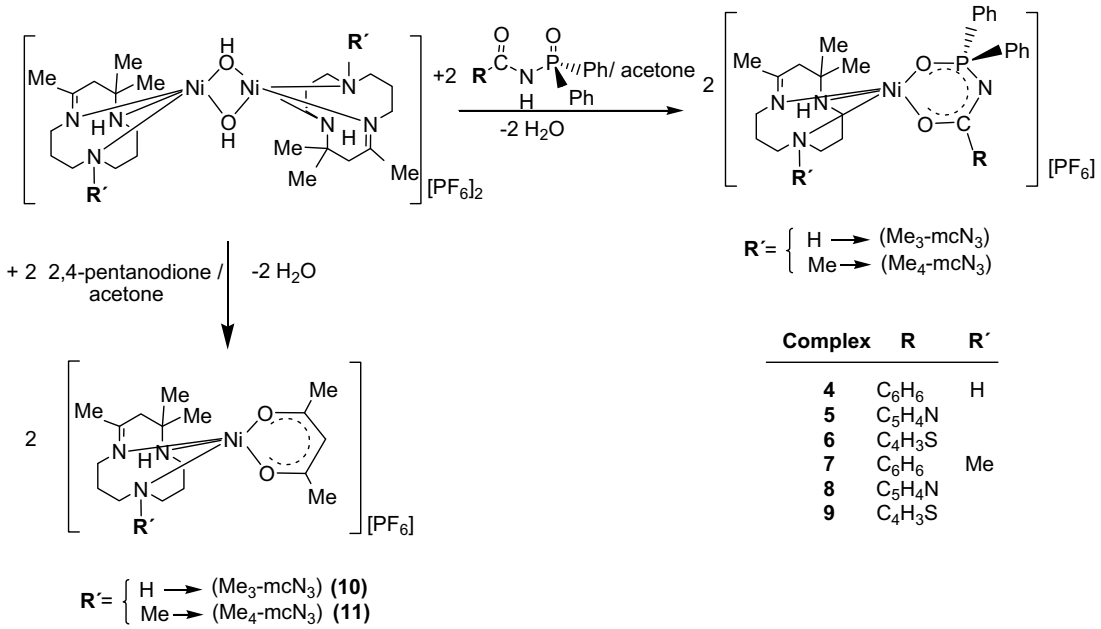
3.1. Syntheses and spectroscopic characterization

The *N*-(diphenylphosphineoxide)amides were synthesized by treating chlorodiphenylphosphine with the corresponding amide (R-C(O)NH$_2$) in THF with Et$_3$N and DMAP, a drop of H$_2$O$_2$ was also added (Scheme 1). These phosphoramides behave as weak acids towards dinuclear hydroxo-complexes. Thus the acid-basic reaction between [Ni(mcN$_3$)(μ-OH)]$_2^{2+}$ and the corresponding *N*-(diphenylphosphineoxide)amide or 2,4-pentanodione leads to the formation of the new *O,O′*-(diphenylphosphineoxide)amidate complexes (**4–9**) or acetylacetonate complexes (**10–11**). In these Ni(II) complexes the organic ligands are coordinated bidentately *via* oxygen atoms of phosphoryl and carbonyl groups forming six-membered chelates. The isolated nickel(II) compounds (**4–11**) are presented in Scheme 2. All of them are air-stable solids and their acetone solutions exhibit conductance values corresponding to 1:1 electrolytes [22], which are in good agreement with the proposed formulae. They have been characterized by partial elemental analyses, FAB$^+$ mass spectrometry and spectroscopic (IR, UV–Vis and ^{1}H NMR) methods.

The IR spectra of derivatives **4–11** show bands in the range 3275–3260 cm^{-1} assigned to ν(NH) and a sharp band at 1660–1655 cm^{-1} assigned to ν(C=N). Both of them are bands of the coordinated macrocycle Me$_3$-mcN$_3$ or Me$_4$-mcN$_3$ [23]. The IR spectra of the Ni(II) derivatives **4–9** show bands attributed to the *O,O′*-(diphenylphosphineoxide)amidate ligands: ν(C–O) 1595–1510 cm^{-1}, ν(P–O) 1195–1125 cm^{-1} and ν(N–P) 1090–1030 cm^{-1} [18]. This



Scheme 1. Ligands preparation.



Scheme 2. Synthesis of the *N*-(diphenylphosphineoxide)amidate and acetylacetonate complexes of nickel(II).

general pattern of the infrared spectra supports coordination *via* oxygen atoms of phosphoryl and carbonyl groups of the deprotonated $OCNPO^-$ group. Because of the electronic delocalization in the OCNPO fragments is expected to notice ν(N–P) band at frequencies higher than 995 cm^{-1} [18b]. The Ni(II) derivatives **10–11** show in their IR spectra the absorption attributed to the acetylacetonate ligand ν(C=O) at ~1590 cm^{-1}. The electronic spectra of **4–11** are quite similar and show two d–d transitions in acetone solution with λ_{max} around 630 nm (~50 $M^{-1}\,cm^{-1}$) and 380 nm (~120 $M^{-1}\,cm^{-1}$) which could be assigned to

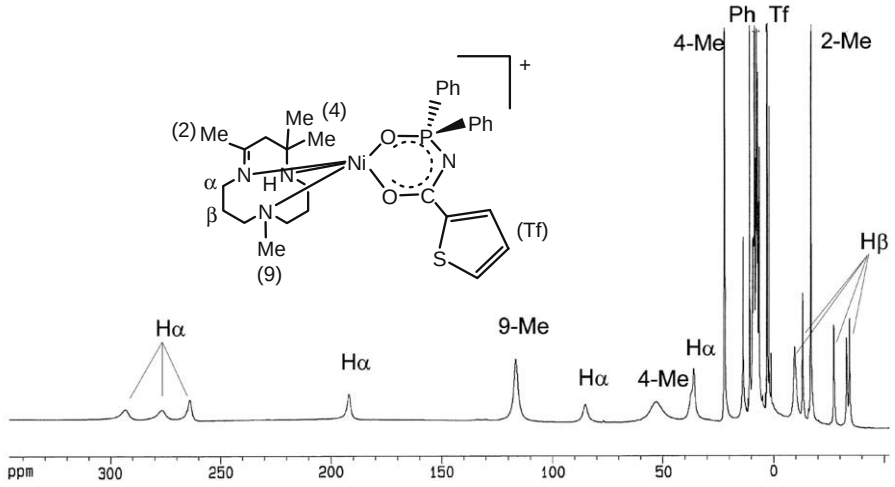


Fig. 1. ^{1}H NMR spectra (in d_6-acetone solution at r.t.) of **9**.

$^3B_1(F) \rightarrow {}^3E(F)$ and $^3B_1(F) \rightarrow {}^3A_2$, $^3E(P)$ transitions, respectively. Both λ_{max} values and molar absorptivities are consistent with a pentacoordinate environment around nickel(II) [24].

All of the complexes exhibit sharp hyperfine-shifted ^{1}H NMR signals in acetone solution in the 360 to −36 ppm chemical shift range. The ^{1}H NMR data for complexes **4–11** (see Section 2) are in good agreement with previous results for similar pentacoordinate nickel(II) complexes [25]. A representative proton NMR spectrum for complex **9** is shown in Fig. 1. The resonance line pattern observed for the macrocyclic ligands can be reasonably assigned based on the considerations used in previous studies of nickel(II) macrocyclic complexes [11b]. The α-methylenic protons shift downfield whereas the β-methylenic protons shift upfield with regard to the diamagnetic position, probably because of spin polarization mechanisms [26]. Equatorial protons are expected to experience larger contact shifts than axial protons and therefore the most downfield resonances are due to α-CH_{eq} and the most upfield ones to β-CH_{eq} [27]. All the resonances of the phenyl protons to the *N*-(diphenylphosphineoxide)amidate ligands are downfield to TMS in accordance with a dominant σ-delocalization pattern of spin density consistent with the nickel(II) ground state [28]. The definitive assignment of these isotropically shifted signals comes from two-dimensional ^{1}H NMR techniques. The magnitude COSY spectra of **5** (Fig. 2), recorded at 20 °C, clearly shows cross signals between resonances at 13.7, 12.9 and 11.7 ppm and also between resonances at 12.9, 11.7 and 10.7 ppm. These signals can be assigned to the pyridyl 6-H (13.7), 5-H (12.9), 4-H (11.7) and 2-H (10.7) protons, respectively, of the *O,O′*-(diphenylphosphineoxide)nicotinamide ligand. The magnitude COSY spectra of **6** (Fig. 3), recorded at 20 °C, shows cross signals between resonances at 13.8 and 11.0 and also between resonances at 13.8, 11.0 and 10.2 ppm. These signals can be assigned to the thiophenyl 3-H (13.8), 4-H (11.0) and 5-H (10.2) protons, respectively, of the *O,O′*-(diphenylphosphineoxide)-2-thiophenecarboxamide ligand.

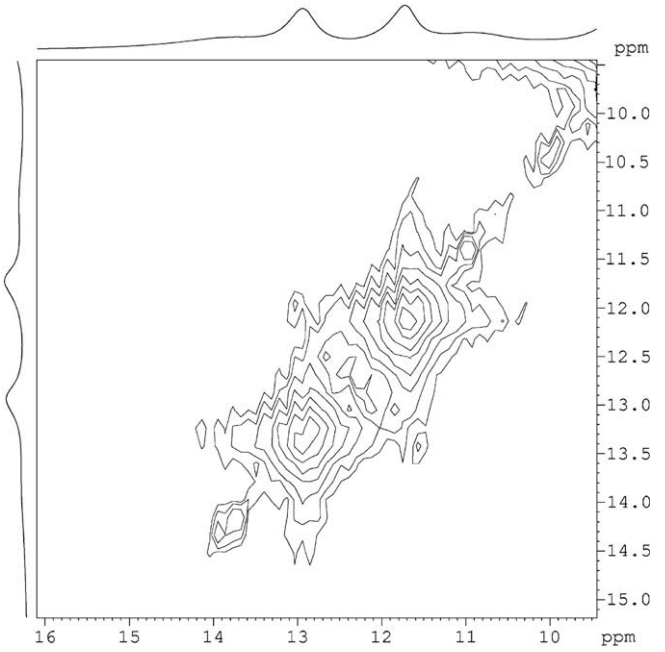


Fig. 2. Magnitude ^{1}H COSY spectrum of complex **5** at 200 MHz at 20 °C in d_6-acetone solution recorded with a delay time of 150 ms. Only the region relevant to the assignment of pyridyl resonances is shown in the top trace.

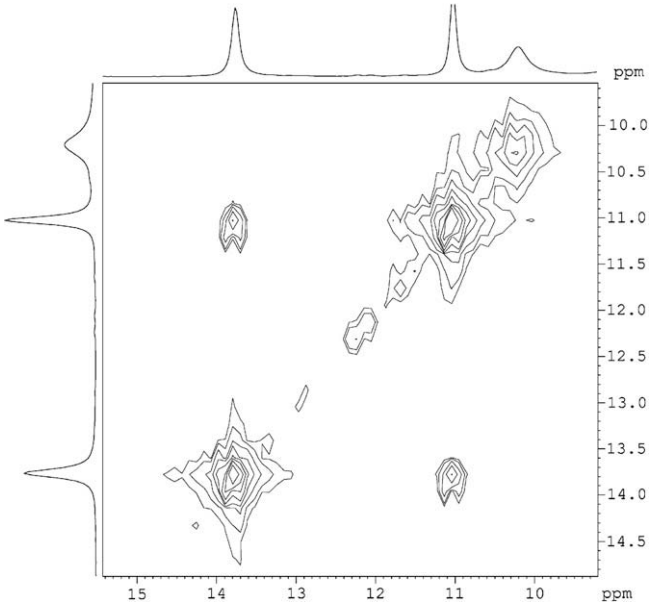


Fig. 3. Magnitude ^{1}H COSY spectrum of complex **6** at 200 MHz at 20 °C in d_6-acetone solution recorded with a delay time of 50 ms. Only the region relevant to the assignment of thiophenyl resonances is shown in the top trace.

3.2. X-ray diffraction study

The crystal structures of the cation of complexes **9** and **10** are shown in Figs. 4 and 5. In each crystallized cation, the nickel atom is five-coordinated, with a square pyramid arrangement of the chelating atoms. The structural index parameter τ for pentacoordinate complexes [29] ($\tau = 0$ and 1 for square pyramidal and trigonal bipyramidal structures, respectively) shows values of 0.142 and 0.182 for complexes **9** and **10**, respectively (see Table 2).

The three nitrogen atoms of the N_3-macrocycle hold the apical position and two adjacent basal ones, whereas the other two basal positions correspond to the *O,O′*-(diphenylphosphineoxide)amidate group in **9** and to the acetylacetonate ligand in **10**. The basal plane is formed by N(1), N(2), O(1) and O(2), with a rms deviation of fitted atoms of 0.0756 and 0.0970 Å, for complexes **9** and **10**, respectively. The Ni atom is 0.3168(15) and 0.2714(14) Å above of the corresponding basal plane towards the apical N(3) atom

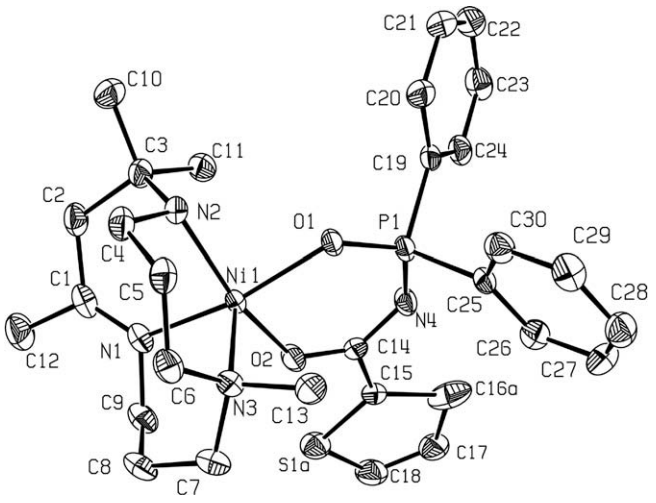


Fig. 4. ORTEP drawing of complex **9** showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The thien-2-yl fragment is disordered over two positions with occupation factors of 0.67 and 0.33. For clarity hydrogen atoms are omitted.

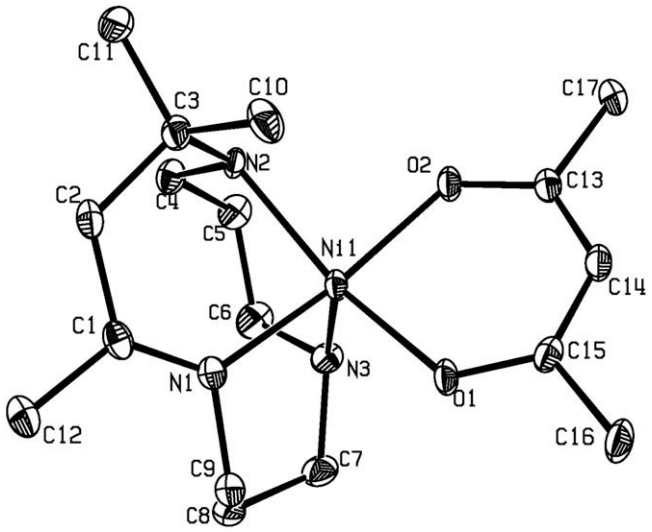


Fig. 5. ORTEP drawing of complex 10 showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. For clarity hydrogen atoms are omitted.

Table 2
Selected bond lengths (A) and angles (°) for **9** and **10**.

	9	**10**
Ni(1)–O(1)	2.042(2)	2.019(3)
Ni(1)–O(2)	2.032(3)	1.984(3)
Ni(1)–N(1)	2.047(3)	2.044(4)
Ni(1)–N(2)	2.038(3)	2.040(3)
Ni(1)–N(3)	2.067(3)	2.046(4)
O(2)–Ni(1)–N(2)	157.73(12)	158.79(13)
N(2)–Ni(1)–O(1)	85.47(11)	85.56(13)
N(2)–Ni(1)–N(1)	89.95(13)	89.68(14)
O(2)–Ni(1)–N(3)	100.63(12)	100.37(13)
O(1)–Ni(1)–N(3)	99.83(11)	96.68(14)
O(2)–Ni(1)–O(1)	90.85(10)	90.29(12)
O(2)–Ni(1)–N(1)	88.51(12)	90.88(13)
O(1)–Ni(1)–N(1)	166.30(12)	169.72(13)
N(2)–Ni(1)–N(3)	101.63(12)	100.77(14)
N(1)–Ni(1)–N(3)	93.74(12)	93.15(15)

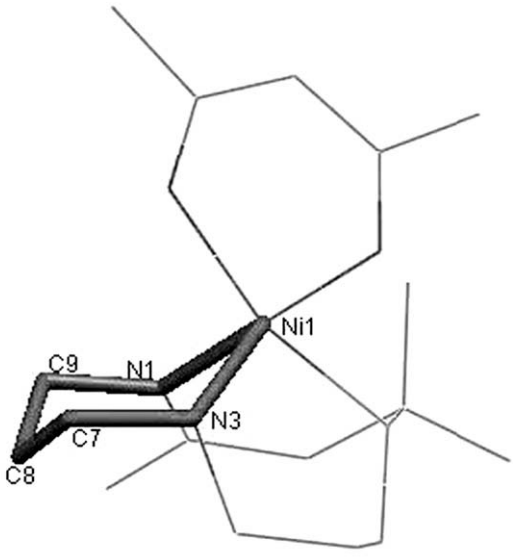


Fig. 6. Six-membered rings in complex **10**.

Table 3
Torsion angles of six-membered rings.

	9		**10**	
Six-membered rings	Conformation	Deformation	Conformation	Deformation
NiINI C1 C2 C3 N2	0.8136 HC	8°	0.8014 HC	7°
	0.1853 E		0.1893 E	
	0.0011 SB		0.0093 SB	
NiINI C9 C8 C7 N3	1.0000 C	8°	1.0000 C	9°
	0.9517 E	10°	0.7479 E	14°
NiIN2 C4 C5 C6 N3	0.0483 HC		0.2521 HC	
Ni1 O1 P1N4C14O2	0.9998 SB		–	
	0.0002 HC		0.9890 SB	–
Ni1 O1 C13C14C15O2			0.0103 HC	
			0.0007 E	

for complexes **9** and **10**, respectively. The plane of the chelate moiety defined by O1, P1, N4, C14 and O2 (rms 0.035) is inclined by 21.93(15)° to the basal plane in complex **9.** This complex is the first pentacoordinate *O,O′*-(diphenylphosphineoxide)amidate-nickel(II) derivative showing chelating fashion. In complex **10**, the plane of the chelate moiety defined by O1, C13, C14, C15 and O2 (rmsd 0.0056) is inclined by 17.58(18)° to the basal plane N1, N2, O1 and O2. The macrocycle shows the same configuration in both complexes. The six-membered rings involving N1 and N3 shows a *chair* conformation (C) when is evaluated by the classification method for $\sigma = 10$ [30] (Fig. 6). In both complexes the ring involving N2 and N3 shows a distorted conformation, the closest ideal conformation is the *envelope* (E) with a mean deviation from the ideal torsion angles in the *envelope* conformation of 10° and 14° for **9** and **10**, respectively (Table 3).

Acknowledgements

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Appendix A. Supplementary material

CCDC 693531 and 693532 contain the supplementary crystallographic data for **9** and **10**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.09.075.

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