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Synthesis and characterization of bis(*O,O'*-dipropylmonoselenophosphato) nickel (II) adducts

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ABSTRACT

Nitrogen containing Lewis base adducts of bis(O,O'-dialkylmonoselenophosphato)nickel(II) complexes of types, $Ni\{O(Se)P(OR)_2\}_2(L)_2$ *(where R = n-Pr, i-Pr; L =* C_5H_5N, NC_5H_4Me*-2,* NC_5H_4Me*-3) were synthesized by in situ reactions of* $NiCl_2.6H_2O$, $NaO(Se)P(OR)_2$ *and corresponding Lewis base. The spectroscopic studies (UV-Vis, IR,* $^1H/^{31}P$ *NMR), revealed that these adducts has distorted octahedral geometry and central nickel(II) atom has bidentate coordination with monoselenophosphate moieties and Lewis base. Elemental analyses and magnetic moment results also support octahedral coordination of these adducts.*

Keywords: Lewis base, monoselenophosphate, dialkylmonoselenophosphato nickel(II) complex, bidentate coordination.

INTRODUCTION

The thiophosphate ligands viz monothiophosphate, dithiophosphate and trithiophosphate are well studies and have attracted attention from last decade [1-3]. Fewer attentions have been made for coordination chemistry of monoselenophosphates complexes. In earlier days (1977), some metal complexes have been synthesized with di-isopropylphosphoroselenoate ligands [4]. The transition metal complexes of these ligands are highly unstable and showing decomposition by loss of selenium. Recently SC Bajia et al [5] have synthesized and well characterized adducts of bis(*O,O'*-dialkylmonoselenophosphato)cobalt(II) complexes.

Monoselenophosphate ligands are mixed chalchogeno ligands and monoselenophosphate moieties have stimulating structural potentials, such as monodentate (through oxygen/selenium) and bidentate [6].

The efforts made to synthesize nickel(II) complexes of dialkylmonoselenophosphate were unsuccessful. Several combinations of solvents and reaction conditions were espoused, but all unsuccessful. Finally adducts of heterocyclic nitrogen containing Lewis base of bis(*O,O'*-dialkylmonoselenophosphato)nickel(II) complexes (1-6) were synthesized by *insitu* reaction of $NiCl_2.6H_2O$, monoselenophosphate and Lewis bases.

MATERIALS AND METHODS

Solvents (benzene, carbon tetra chloride, diethyl ether hexane, 1-propanol, and 2-propanol) were dried using standard methods. All the reactions were carried out in anhydrous condition using pre dried and air tightening of the glasswares. The sodium salt of *O,O'*-dialkyl monothiophosphoric acid were prepared by using the reported method [9]. The carbon, hydrogen and nitrogen analysis is done on Vario EL elemental analyzer. UV-Visible spectra were recorded on a Perkin-Elmer UV-Vis-NIR spectrometer in pyridine, 2-picopine and 3-picoline solvent to avoid decomposition in solution and or dilution. Infrared spectra were recorded by Perkin-Elmer 983G spectrometer as Nujol mulls between CsI discs over the range 4000-180 cm^{-1}.

Preparations

$Ni\{O(Se)P(O^nPr)_2\}_2(C_5H_5N)_2$ (1): The $NiCl_2.6H_2O$ (1 mmol) and pyridine (2 mmol) was added in methanol (25 ml) and the reaction mixture was stirred for 30 minutes. The ethanol solution of $NaSe(O)P(O^nPr)_2$ (2 mmol) was added in the above reaction mixture. The resultant reaction mixture was refluxed for one hour. The brownish coloured solution was obtained and then solvent was pumped off. The metal complex was dried under vacuum. Brown; Yield: 88.4%; Anal. Calc. for $C_{22}H_{38}Se_2P_2O_6N_2Ni$: C, 37.47; H, 5.43; N, 3.97. Found: C, 37.40; H, 5.39; N, 3.93. UV-Vis spectral data [$\lambda_{max.}$, (nm); ε(Lmole^{-1}cm^{-1})] in 0.004 M pyridine solution 410 (140), 720 (280), 990(200); IR (cm^{-1}) 1598m, 1570m ν(C-N), 982s ν[(P)-O-C], 759s ν[P-O-(C)], 510s ν(P-Se), 416 ν(Ni-O), 350 ν(Ni-Se); ^{1}H NMR ($CDCl_3$, δ ppm,): 0.90-1.12 (t, 12H, CH_3), 1.34-1.37 (m, 8H, CH_2) 2.80-2.92 (t, 8H, CH_2), 21.6 (*o*-Py), 16.1 (*m*-Py), 9.3 (*p*-Py); ^{31}P NMR ($CDCl_3$, δ ppm): 47.5(s); μeff 3.0 B.M.

$Ni\{O(Se)P(O^nPr)_2\}_2(NC_5H_4Me\text{-}2)_2$ (2): Prepared same as (1). Brown; Yield: (83%); Anal. Calc. for $C_{24}H_{42}Se_2P_2O_6N_2Ni$: C, 39.32; H, 5.77; N, 3.82. Found: C, 39.35; H, 5.72; N, 3.80 %. UV-Vis spectral data [$\lambda_{max.}$, (nm); ε(Lmole^{-1}cm^{-1})] in 0.005 M 2-picoline solution 425 (125), 740 (300), 1022 (178); IR (cm^{-1}) 1593m, 1577m ν(C-N), 982s ν[(P)-O-C], 772s ν[P-O-(C)], 470s ν(P-Se), 410 ν(Ni-O), 325 ν(Ni-Se); ^{31}P NMR ($CDCl_3$, δ ppm): 46.8 (s); μ_{eff} 3.2 B.M.

$Ni\{O(Se)P(O^nPr)_2\}_2(NC_5H_4Me\text{-}3)_2$ (3): Prepared same as (1). Brown; Yield: (86%); Anal. Calc. for $C_{24}H_{42}Se_2P_2O_6N_2Ni$: C, 39.32; H, 5.77; N, 3.82. Found: C, 39.30; H, 5.75; N, 3.85 %. UV-Vis spectral data [λ_{max}(nm); ε(Lmole^{-1}cm^{-1})] in 0.004 M 3-picoline solution 460 (98), 750 (198), 1040 (102); IR (cm^{-1}) 1598m, 1580m ν(C-N), 1015s ν[(P)-O-C], 760s ν[P-O-(C)], 482s ν(P-Se), 430 ν(Ni-O), 330 ν(Ni-Se); ^{31}P NMR ($CDCl_3$, δ ppm): 46.9 (s); μ_{eff} 3.2 B.M.

$Ni\{O(Se)P(O^iPr)_2\}_2(C_5H_5N)_2$ (4): Prepared same as (1). Brown; Yield: (89%); Anal. Calc. for $C_{22}H_{38}Se_2P_2O_6N_2Ni$: C, 37.47; H, 5.43; N, 3.97. Found: C, 37.43; H, 5.40; N, 3.95 %. UV-Vis spectral data [λ_{max} (nm); ε(Lmole^{-1}cm^{-1})] in 0.005 M pyridine solution 402 (106), 710 (189), 982 (155); IR (cm^{-1}) 1595m, 1575m ν(C-N), 1006s ν[(P)-O-C], 767s ν[P-O-(C)], 516s ν(P-Se), 420 ν(Ni-O), 335 ν(Ni-Se); ^{1}H NMR ($CDCl_3$, δ ppm,): 1.22 (d, 24H, CH_3), 3.01 (m, 4H, CH), 21.6 (*o*-Py), 16.4 (*m*-Py), 10.1 (*p*-Py); ^{31}P NMR ($CDCl_3$, δ ppm): 47.3 (s); μ_{eff} 3.1 B.M.

$Ni\{O(Se)P(O^iPr)_2\}_2(NC_5H_4Me\text{-}2)_2$ (5): Prepared same as (1). Brown; Yield: (82%); Anal. Calc. for $C_{24}H_{42}Se_2P_2O_6N_2Ni$: C, 39.32; H, 5.77; N, 3.82. Found: C, 39.29; H, 5.80; N, 3.80%. UV-Vis spectral data [λ_{max} (nm); ε(Lmole^{-1}cm^{-1})] in 0.006 M 2-picoline 462 (96), 736 (198), 1038 (147); IR (cm^{-1}) 1595m, 1579m ν(C-N), 995s ν[(P)-O-C], 772s ν[P-O-(C)], 472s ν(P-Se), 422 ν(Ni-O), 336 ν(Ni-Se); ^{31}P NMR ($CDCl_3$, δ ppm): 47.4 (s); μ_{eff} 3.0 B.M.

$Ni\{O(Se)P(O^iPr)_2\}_2(NC_5H_4Me\text{-}3)_2$ (6): Prepared same as (1). Brown; Yield: (85%); Anal. Calc. for $C_{24}H_{42}Se_2P_2O_6N_2Ni$: C, 39.32; H, 5.77; N, 3.82. Found: C, 39.34; H, 5.74; N, 3.81%. UV-Vis spectral data [λ_{max} (nm); ε(Lmole^{-1}cm^{-1})] in 0.005 M 3-picoline solution 465 (140), 755 (188), 1058 (98); IR (cm-1) 1595m, 1579m ν(C-N), 995s ν[(P)-O-C], 772s ν[P-O-(C)], 472s ν(P-Se), 422 ν(Ni-O), 336 ν(Ni-Se); ^{31}P NMR ($CDCl_3$, δ ppm): 47.1 (s); μ_{eff} 3.2 B.M.

We have successfully synthesized and characterized bis(*O,O*'-dialkylmonoselenophosphato)nickel(II) adducts (1-6). The spectroscopic studies (IR, UV-Visible, and ^{1}H/^{31}P NMR) of adducts (1-6) are consistent with proposed octahedral geometry. The octahedral coordination is further confirmed from elemental analyses magnetic susceptibility measurement.

RESULTS AND DISCUSSION

Attempts to synthesize bis(*O,O'*-dialkylmonoselenophosphato)nickel(II) complexes by reactions of $NiCl_2.6H_2O$ and sodium salt of *O,O'*-dialkyl monoselenophosphates were unproductive. Lewis base adducts (1-6) of bis(*O,O'*-dialkylmonoselenophosphato)nickel(II) complexes were synthesized using indirect and alternative method by *insitu* reaction of $NiCl_2.6H_2O$, Lewis base and sodium salt of *O,O'*-dipropyl/diisopropyl monoselenophosphate. The reactions are quite fast and completion of reaction was ensured by one hour reflux of reaction mixture.

$$NiCl_2.6H_2O + 2L \longrightarrow Ni(L)_2Cl_2$$

$$Ni(L)_2Cl_2 + 2NaO(Se)P(OR)_2 \longrightarrow Ni\{O(Se)P(OR)\}_2(L)_2 + 2NaCl$$

(where R = n-Pr, i-Pr; L = pyridine, 2-picoline, 3-picoline)

After completion of reaction, solvent was pump off and dried under vacuum yielded brown coloured compounds. Attempts are made for recrystallization of these adducts by using different solvents and mixtures of solvents, but good quality of crystals were not obtained which are required for single crystal X-ray diffraction study.

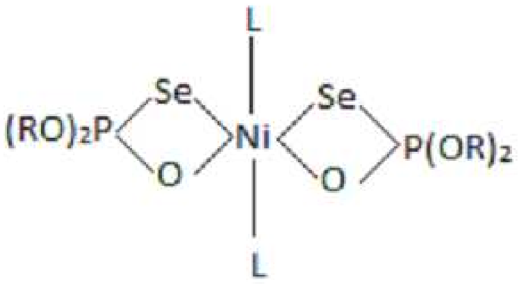

Figure-1 Octahedral structure of adducts Ni{O(Se)P(OR)$_2$}$_2$(L)$_2$ (1-6)
(where R = n-Pr, i-Pr; L = C_5H_5N, NC_5H_4Me-2, NC_5H_4Me-3)

These nickel(II) adducts (1-6) are stable in inert atmosphere, but showing decomposition in open environmental condition and or during recrystallization. In some cases adducts were decomposed in solid state over a period of time. These nickel(II) adducts (1-6) were characterized by elemental analysis, spectroscopy techniques (IR, UV-Visible and ^{1}H/^{31}P NMR) and magnetic susceptibility measurement.

IR spectra

The IR bands of these adducts (1-6) are compared free ligand NaO(Se)P(OR)$_2$ and adducts of bis(*O,O'*-dialkylmonoselenosphato)cobalt(II) complexes [5]. The shifting in peaks attributed to ν(P-O) and ν(P-Se) is the evidence of the coordination, which lies in range of 1042-1068 and 470-520 cm^{-1}, respectively. The ν[(P)-O-C] and ν[P-O-(C)] stretching vibrations are observed in region 1020-982 and 772-759 cm^{-1}, respectively. The bands in region 410-430 and 325-350 cm^{-1} is assigned for ν(Ni-O) and ν(Ni-Se) stretching vibration, respectively. The bands in range of 1598-1570 cm^{-1} is assigned for ν(C-N) stretching vibrations of Lewis base.

Electronic absorption spectra

In electronic absorption spectra adducts (1-6), are showing three absorption bands in region 1050-982, 755-710 and 465-410 nm that assigned for $^3A_{2g}\rightarrow{}^3T_{2g}$, $^3A_2g\rightarrow{}^3T_1g$ and $^3A_2g\rightarrow{}^3T_1g(P)$ transition, respectively are consistent with octahedral coordination. All most identical electronic absorption was observed for octahedral adducts of bis(*O,O*-dialkylmonothiophosphato)nickel(II) complexes [3].

NMR

Some representative complexes (1 and 4) have been characterized by ^{1}H NMR spectroscopy. Adducts (1 and 4) are para-magnetic and hence pyridine ring protons are showing downfield shifting [6, 7]. This downfield shifting may due to delocalization of unpaired electrons from metal ion to σ-orbital of pyridine ring. The alkyl protons are also showing slight downfield shifting in these complexes.

The coordination of nickel(II) metal with monoselenophosphato ligands is confirmed by ^{31}P NMR spectroscopy. For adducts (1-6) ^{1}J(PSe) is in range of 850-550 Hz, suggested bidentate coordination of monoselenophosphate ligands. A single peak in ^{31}P NMR spectra (46.8-47.5 ppm), suggested bidentate coordination.

Magnetic measurements

The magnetic moments values of adducts (1-6), are found in region of 3.0-3.2 BM. These magnetic moments values are resembles with two unpaired electrons and anticipated for octahedral geometry.

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REFERENCES

[1] S.C. Bajia, J.E. Drake, M.E. Light, M. Nirwan, S.K. Pandey, R. Ratnani, *Polyhedron*, **2009**, 28, 85.
[2] S. Bajia, R.J. Butcher, J.E. Drake, R. Ratnani, *Polyhedron*, **2009**, 28, 1556.

[3] A.L. Bingham, J.E. Drake, M.B. Hursthouse, M.E. Light, M. Nirwan, R. Ratnani, *Polyhedron*, **2008**, 27, 1673.
[4] C. Glidwell, *Inorg. Chim. Acta*, **1977**, 24, 255.
[5] S.C. Bajia, *J. Coord. Chem*., 2011, 64, 2631.
[6] C. Glidewell, E.J. Leslie, *J. C. S. Dalton*, **1977**, 527.
[7] R.H. Holm, G.W. Everett, W.D. Horrocks, *J. Am. Chem. Soc.*, **1966**, 88, 1071.
[8] M.M. Dhingra, G. Govil, C.R. Kanekar, *Chem. Phys. Lett.*, **1971**, 10, 86.
[9] T.S. Lobana, J.C. Wang, C.W. Liu, *Coord. Chem. Rev.*, **2005**, 251: 91.