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Mendeleev Commun., 2007, **17**, 222–223
Mendeleev Communications

Unusual structure of an *N*-phosphoryl-*N'*-isopropylthiourea chelate with the nickel(II) cation

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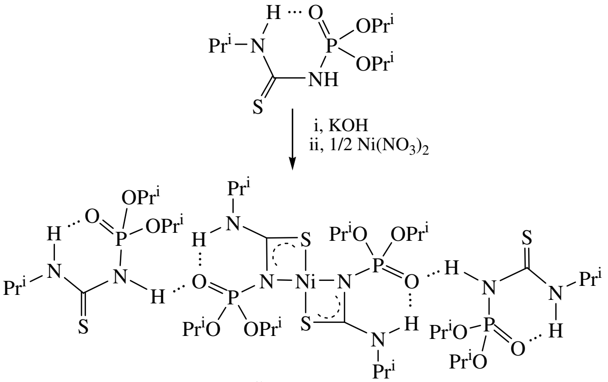
DOI: 10.1016/j.mencom.2007.06.013

The reaction of the potassium salt of N-phosphorylated thiourea $Pr^iN'HC(S)NHP(O)(OPr^i)_2$ (HL) with the Ni^{II} cation leads to the complex $[NiL_2(HL)_2]$; according to X-ray analysis, two neutral HL molecules are coordinated in the second sphere of the planar 1,3-N,S-chelate $[NiL_2]$ *via* (HL) PNH···O=P (NiL_2) hydrogen bonds.

The competitive coordination[1] of polyfunctional ligands with metal cations is of interest in modern coordination chemistry. Recently, we found that *N*-phosphorylthioureas $RNHC(S)NHP(O)(OPr^i)_2$ (R = Ph, cyclohexyl) can form 1,3-N,S-chelates with Ni^{II}, Pd^{II} and Cu^{II} cations.[2] The 1,5-O,S-coordination of such a type of ligands[3] is not favourable in these cases due to higher crystal field stabilization energies for the square-planar d^8 and d^9 complexes $[M\{RNHC(S)NP(O)(OPr^i)_2\text{-}N,S\}_2]$ caused by stronger ligand field of the amide N atom in comparison with the P=O oxygen atom. The second stabilising factor for 1,3-N,S-chelates is the formation of intramolecular NH···O=P hydrogen bonds.

The synthesis of a Ni^{II} complex with thiourea $Pr^iNHC(S)NHP(O)(OPr^i)_2$ (HL) has led to an interesting result: light violet crystals corresponding to the stoichiometry of $[NiL_2(HL)_2]$ **1** were isolated from the reaction mixture.† The crystals are readily soluble in benzene and chlorinated alkanes and insoluble in water and *n*-hexane. The stoichiometry of complex **1** is preserved after multiple crystallizations from benzene and dichloromethane.



Scheme 1

Spectral analyses‡ and X-ray data§ undoubtedly indicate the 1,3-N,S-type of coordination by two anionic ligand molecules in this case (Scheme 1). Only the examples of 1,5-O,S-coordination of the thiourea HL in $[ML_2]$ chelates with cobalt(II)[4] and zinc(II)[5] cations have been reported earlier.

One could presume that complex **1** should contain a six-coordinated Ni^{II} cation. Indeed, such a type of the square-bipyramidal complexes $[M(QH)_2Q_2]$ of thioamide $PhC(S)NHP(O)(OPr^i)_2$ (HQ) with Ni^{II} and Co^{II} cations was isolated and investigated by X-ray analysis.[6] The $[Q^-]$ ligands in these complexes exhibit a 1,5-O,S-coordination with the central ion in the equatorial positions of the bipyramide, while neutral ligands [HQ] are coordinated *via* oxygen atoms of the phosphoryl group in axial positions.

However, the unusual 1,3-N,S-coordination of the thiourea ligand $[L^-]$ leads to interesting changes in complex structure. X-ray analysis has clearly shown that neutral ligands in adduct **1** do not interact directly with the metal ion and being in the second sphere interact *via* hydrogen bonds between the P(O)NH protons of free ligands and the P=O oxygen atoms of coordinated ligand (Figure 1). The strong ligand field of 1,3-N,S-coordinated thiourea moieties, stabilising the square-planar low-spin complex species, does not allow the axial coordination of the HL molecules.

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† Thiourea HL was prepared according to the previously described method.[5] *Synthesis of $[NiL_2(HL)_2]$:* a suspension of HL (1.410 g, 5 mmol) in aqueous ethanol (20 ml) was mixed with an ethanol solution of potassium hydroxide (0.28 g, 5 mmol). An aqueous (20 ml) solution of $Ni(NO_3)_2\cdot 6H_2O$ (0.815 g, 2.8 mmol) was added dropwise with vigorous stirring to the resulting potassium salt. The mixture was stirred at room temperature for 5 h and left overnight. The resulting complex was extracted with CH_2Cl_2, washed with water and dried with anhydrous $MgSO_4$. The solvent was removed *in vacuo*. The precipitate was isolated from CH_2Cl_2 by *n*-hexane.

‡ The IR spectra (Nujol) were recorded with a Specord M-80 spectrometer in the range 400–3600 cm^{-1}. The NMR spectra were obtained on a Varian Unity-300 NMR spectrometer at 25 °C. The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded at 299.948 and 121.420 MHz, respectively. Chemical shifts are reported with reference to $SiMe_4$ (^1H) and H_3PO_4 ($^{31}P\{^1H\}$). The mass spectra were measured on a TRACE MS Finnigan MAT instrument. The electron ionisation energy was 70 eV. The substance was injected directly into the ion source at 150 °C. Heating was carried out in a programmed mode from 35–200 °C at a rate of 35 K min^{-1}. Elemental analyses were performed on a Perkin-Elmer 2400 CHN micro-analyser.

For $[NiL_2(HL)_2]$: yield 0.784 g (53%), mp 82 °C. ^1H NMR ($CDCl_3$) δ: 1.16 (d, 12H, Me [Pr^iN, L], $^3J_{HH}$ 6.5 Hz), 1.33–1.47 (m, 48H, Me [$Pr^iO + Pr^iN$]), 1.58 (d, 12H, Me [Pr^iO, L], $^3J_{HH}$ 6.2 Hz), 3.91 (d sept., 2H, [NCH, L], $^3J_{CHCH}$ 6.5 Hz, $^3J_{CHNH}$ 8.2 Hz), 4.53–4.72 (overlapped m, 10H, [NCH + OCH]), 6.86 (br. s, 2H, [NHP, HL]), 8.33 (d, 2H, [$NHPr^i$, L], $^3J_{CHNH}$ 8.2 Hz), 10.36 (br. s, [$NHPr^i$, HL]). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: –3.8 (HL), 2.9 (L). IR (ν/cm^{-1}): 1016 (POC), 1200 (P=O), 1560 (SCN), 3176, 3232 (NH). EI-MS, *m/z* (%): 621 (5) $[M - 2HL]^+$. Found (%): C, 40.59; H, 7.60; N, 9.42. Calc. for $C_{40}H_{90}N_8O_{12}P_4S_4Ni$ (1184.39) (%): C, 40.51; H, 7.65; N, 9.45.

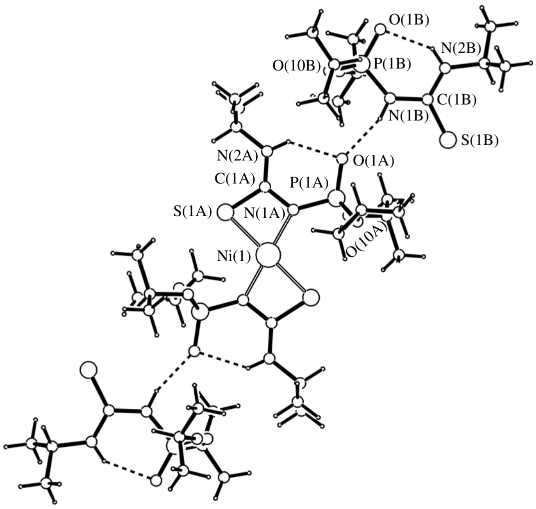

Figure 1 Molecular structure and hydrogen bonding of complex $[NiL_2(HL)_2]$ **1**. Selected bond lengths (Å) and angles (°): Ni(1)–S(1A) 2.221(2), Ni(1)–N(1A) 1.900(2), C(1A)–S(1A) 1.726(3), C(1A)–N(1A) 1.342(3), C(1A)–N(2A) 1.307(3), P(1A)–N(1A) 1.636(2), P(1A)–O(1A) 1.465(2), C(1B)–S(1B) 1.667(3), C(1B)–N(1B) 1.381(4), C(1B)–N(2B) 1.317(3), N(1B)–P(1B) 1.654(3), O(1B)–P(1B) 1.455(2); C(1A)–S(2A)–Ni(1) 77.46(11), N(1A)–C(1A)–S(1A) 108.7(2), S(1A)–Ni(1)–N(1A) 74.36(8).

The IR spectrum of **1** contains two absorption bands assigned to NH at 3176 and 3232 cm^{-1}, which are characteristic of the NH-stretching vibrations of Pr^iNH and NHP(S) groups, respectively. At the same time, the P=O absorption band practically does not change the position when compared to the free ligand. The lack of the shift of a P=O band in the IR spectrum is characteristic of the 1,3-N,S-chelate formation.[2]

There are two singlet ^{31}P signals of identical intensities at δ –3.9 and 2.8 ppm observed for **1**. The signal at δ –3.9 ppm is in the region characteristic of neutral N-phosphorylated thioamides and thioureas, whereas the other signal corresponds to the amidophosphate environment in complexes of *N*-acylamidophosphate anions. The ^1H NMR spectrum also contains the double set of signals for metal-coordinated and unbound ligand molecules. The assignment of ^1H NMR signals was proved by ^1H COSY spectra. The slow (in an NMR scale) exchange between neutral and anionic forms of the ligand in $CDCl_3$ has been found by ^1H NOESY experiment.

According to X-ray analysis data, a molecule of **1** is centrosymmetric in a crystal. The Ni^{II} atom and all 24 atoms of the N–C(S)–N–P=O backbones of $[L^-]$ and [HL] belong to the same plane. The structure of the chelate core $[NiL_2]$ is similar to those of the other 1,3-N,S-chelates of Ni^{II} and Pd^{II}.[2(*a*)] The central ion has got *trans*-square-planar environment NiN_2S_2. Valent angles at Ni(1) and S(1A) atoms in four-membered M–S–C–N metallocycles are sufficiently sharper in comparison with six-membered chelate rings.[3]

As expected, a comparison of interatomic distances for $[L^-]$ and [HL] moieties has shown a lengthening of CS and a shortening of CN bonds upon complexation, while minor changes have been observed for the P–N and P=O bond values.

The P=O oxygen atoms of $[L^-]$ moieties form intramolecular hydrogen bonds with the Pr^iNH protons and an intermolecular hydrogen bond with HNP(O) of neutral [HL] ligand. The [HL] moieties are in a typical of *N*-phosphorylthioureas flatten *syn*,*syn*-conformation of the N–C–N–P–O backbone, stabilised by the intramolecular hydrogen bond $Pr^iNH\cdots O{=}P$. The parameters of hydrogen bonds are the following: N(1B)–H(1B)···O(1A) [*d*(D–H) 0.86 Å, *d*(H···O) 2.05 Å, *d*(N···O) 2.834(4) Å, ∠NHO 150°], N(2A)–H(2A)···O(1A) [*d*(D–H) 0.86 Å, *d*(H···O) 2.07 Å, *d*(N···O) 2.773(4) Å, ∠NHO 138°], N(1B)–H(1B)···O(1B) [*d*(D–H) 0.86 Å, *d*(H···O) 2.05 Å, *d*(N···O) 2.771(4) Å, ∠NHO 141°].

According to the CCDC database (CSD version 5.27), these interactions of the *N*-phosphorylthiourea chelates with the neutral ligand have not been described. The above H-bonding pattern is possible only for 1,3-N,S-chelates of *N*-phosphorylthioureas; thus, it could be used for the design of thiourea-based receptor molecules capable of selectively binding 1,3-N,S-complexes from a mixture with 1,5-O,S-analogues.

This work was supported by the Russian Foundation for Basic Research (grant nos. 03-03-32372-a and 03-03-96225-r2003tatarstan_a) and the joint programme of CRDF and the Russian Ministry of Education (BHRE 2004 Y2-C-07-02, grant no. REC-007).

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Received: 20th February 2007; Com. 07/2879

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§ Crystals of $C_{20}H_{44}N_4NiO_6P_2S_2$ [or $2(C_{10}H_{23}N_2O_3PS)$] are monoclinic, space group *C*2/*c* (no. 15); *M* = 1186.05; *a* = 19.451(18), *b* = 9.557(9) and *c* = 34.85(2) Å, β = 99.17(7)°, *V* = 6396(9) $Å^3$, *Z* = 4, d_{calc} = 1.232 g cm^{-3}, *F*(000)= 2536, μ = 0.588 mm^{-1}. Reflections collected/unique (R_{int}): 6224/6224 [0.0623]; R_1 = 0.04317, wR_2 = 0.112 [$I > 2\sigma(I)$].

The X-ray diffraction data for the complex $[NiL_2(HL)_2]$ were collected on an Enraf-Nonius CAD4 automatic diffractometer using graphite monochromated MoKα (0.71073 Å) radiation. The stability of crystals and experimental conditions was checked every 2 h using three control reflections, while the orientation was monitored every 200 reflections by centering two standards. No significant decay was observed. The structure was solved by a direct method using the SIR[7] program and refined by the full-matrix least-squares using the SHELXL97 program. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were calculated and refined as riding atoms. All calculations were performed using the WinGX[8] program. Cell parameters, data collection and data reduction were performed on an Alpha Station 200 computer using the MoLEN[9] program. All figures were made using the PLATON[10] program.

CCDC 625741 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2007.