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Dimeric *versus* monomeric nickel(II) complexes with tetraorganodichalcogenoimidodiphosphinato ligands: Crystal structures of $Ni_2[(OPPh_2)_2N]_4 \cdot CH_2Cl_2$, $Ni[(OPPh_2)_2N]_2(DMF)_2 \cdot 2H_2O$ and $[KNi[(SPPh_2){OP(OEt)_2}N]_3]_2$

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ABSTRACT

Nickel(II) complexes of the type Ni $[(XPR_2)(YPR'_2)N]_2$ [X = S (1) or O (2), Y = O, R = Ph, R' = OEt] and $Ni_2[(OPPh_2)_2N]_4$ (3) were prepared by reacting either anhydrous $NiCl_2$ or $NiCl_2 \cdot 6H_2O$ with the potassium salt of the appropriate tetraorganodichalcogenoimidodiphosphinic acid, in 1:2 molar ratio. Recrystallization of **3** from dimethylformamide resulted in Ni[(OPPh₂)₂N]₂(DMF) (**4**). Reaction between NiCl₂ and K[(SPPh₂){OP(OEt)₂}N] in an 1:3 molar ratio resulted in the ionic species KNi[(SPPh₂)-{OP(OEt)₂}N]₃ (5). Compounds 1–5 were characterized by IR, electronic spectroscopy and mass spectrometry. The molecular structures of $3 \cdot CH_2Cl_2$, $4 \cdot 2H_2O$ and 5 were determined by singlecrystal X-ray diffraction. A dimeric structure was found in case of complex 3 CH₂Cl₂, with both monometallic biconnective and homobimetallic triconnective $[(OPPh_2)_2N]^-$ units, while an octahedral environment around nickel was established in the monomeric complex 4 2H₂O by monometallic biconnective $[(OPPh_2)_2N]^-$ and DMF ligands, respectively. The crystal of the ionic species 5 contains discrete tetranuclear units in which the phosphorus ligands act heterobimetallic, either (0,0,S)triconnective or (S,O,O,O_{Et})-tetraconnective, and (N,O,O,S)-heterotrimetallic tetraconnective, resulting in an octahedral environment around nickel and a square-pyramidal one around potassium, respectively. Powder X-ray diffraction studies on 5 are in agreement with the single-crystal investigation.

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1. Introduction

Metal complexes of tetraorganodichalcogenoimidodiphosphinato ligands, $[(XPR_2)(YPR'_2)N]^-$, attracted an increased interest for many years, due to their properties and potential applications as catalysts in organic synthesis, components in optical or electronic devices and sensors, NMR shift reagents, as well as derivatives with biological activity. Inorganic and organometallic derivatives either of Main Group [1] or transition metal complexes [2] were previously described. Several nickel(II) complexes of type Ni[(XPR₂)(YPR'₂)N]₂ were reported so far. For compounds containing the same chalcogen atoms, *e.g.* Ni[(SPR₂)₂N]₂ (R = Me [3,4], Ph [5,6]) and Ni[(SePPh₂)₂N]₂ [7], monomeric structures with a tetrahedral NiE₄ core (E = S, Se) were found by single-crystal X-ray diffraction, while in the case of the derivative Ni $[(SPMe_2)(SPPh_2)N]_2$ [5] a square-planar NiS₄ core was observed. The monothio derivatives Ni[(OPPh_2)(SPR_2)N]_2 (R = Me, Ph) are also monomeric, with chelating monometallic biconnective ligands, resulting in tetrahedral NiO₂S₂ cores [8]. For the dioxo derivative Ni[(OPPh_2)₂N]₂, a dimeric structure was previously proposed in benzene solution according to the molecular mass measurements [9].

Here we report on the synthesis and spectroscopic characterization of the new derivatives Ni[(SPPh₂){OP(OEt)₂}N]₂ (1) and Ni[(OPPh₂){OP(OEt)₂}N]₂ (2), the ionic species KNi[(SPPh₂){OP(OEt)₂}N]₃ (5) as well as the adduct Ni[(OPPh₂)₂N]₂(DMF)₂ · 2H₂O ($\mathbf{4} \cdot 2H_2O$). The crystal and molecular structure of the dimeric Ni₂[(OPPh₂)₂N]₄ · CH₂Cl₂ ($\mathbf{3} \cdot CH_2Cl_2$), its adduct $\mathbf{4} \cdot 2H_2O$ and the ionic derivative 5 are also discussed.

2. Experimental

The organophosphorus ligands were prepared according to literature methods: $K[(SPPh_2){OP(OEt)_2}N]$, $K[(OPPh_2){OP(OEt)_2}N]$

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[10]. K[(OPPh₂)₂N] was obtained by stirring the free acid with KOBu^t in diethyl ether. NiCl₂ was dehydrated by keeping $NiCl_2 \cdot 6H_2O$ for two weeks in the oven at 120 °C and subsequently stored under argon. Solvents were dried (THF on potassium, EtOH and MeOH on magnesium and CH₂Cl₂ on CaCl₂) and distilled under argon prior to be used. IR spectra were recorded in the range 4000-400 cm⁻¹ in KBr pellets on a Jasco FT/IR-615 equipment, while the electronic spectra were recorded on a Jasco V-550 spectrometer. Mass spectra were recorded on a FINNIGAN MAT 8200 (CI), a FINNIGAN MAT 8222 (FAB) and a Bruker Esquire LC instrument (ESI), respectively. Magnetic moments were determined on a Sherwood MSB AUTO instrument and elemental analvsis were performed on a VarioEL analyzer. The experimental powder diffraction pattern was obtained with a Shimadzu XRD-6000 diffractometer using a Cu Ka X-ray radiation, while the simulated X-ray powder diffraction pattern was obtained with the MERCURY CSD 2.0 program [11].

2.1. Preparation of bis[P,P-diethoxi-P',P'-diphenyl-P'thioimidodiphosphinato]nickel, Ni[(SPPh₂){OP(OEt)₂}N]₂ (1)

A mixture of K[(SPPh₂){OP(OEt)₂}N] (0.511 g, 1.25 mmol) and NiCl₂ (0.148 g, 0.62 mmol) was stirred for 8 h in a mixture of THF (40 ml) and ethanol (10 ml) at reflux. The solvent was removed in vacuum and the solid was treated with CH₂Cl₂. KCl was filtered off and the solution was concentrated in vacuum. A yellow-brown solid product was isolated. Yield: 0.39 g (78%), M.p. 99 °C. *Anal.* Calc. for $C_{32}H_{40}N_2O_6P_4S_2Ni$: C, 48.33; H, 5.03; N, 3.52. Found: C, 47.98; H, 5.16; N, 3.48%. IR (cm⁻¹): 1255vs [$\nu_{as}(P_2N)$], 1105s [ν (PO)], 1043vs, br [ν (POC)], 596s [ν (PS)]. λ_{max} (cm⁻¹), CH₂Cl₂ (blue): 14620, 16129, 17921, 21209; THF (yellow): 12048, 22026. CI_{neg} MS (m/z, %): 794 (85) [M⁻], 368 (100) [{(SPPh₂}{OP(OEt)₂}N⁻], 336 (38) [{(PPh₂}{OP(OEt)₂}N⁻]. μ = 1.88 BM.

2.2. Preparation of bis[P,P-diethoxi-P',P'-diphenyl-imidodiphosphinato]nickel, Ni[(OPPh₂){OP(OEt)₂}N]₂ (**2**)

A mixture of K[(OPPh₂){OP(OEt)₂}N] (0.720 g, 1.84 mmol) and NiCl₂ (0.119 g, 0.92 mmol) was stirred for 8 h in a mixture of THF (40 ml) and ethanol (10 ml) at reflux, under argon atmosphere. The solvent was removed in vacuum and the solid was treated with CH₂Cl₂. KCl was filtered off and the solution was concentrated in vacuum. A pale yellow solid product was isolated. Yield: 0.63 g (90%), M.p. 108–110 °C. *Anal.* Calc. for C₃₂H₄₀N₂O₈P₄Ni: C, 50.36; H, 5.25; N, 3.67. Found: C, 5.31; H, 5.17; N 3.52%. IR (cm⁻¹): 1261vs [$\nu_{as}(P_2N)$], 1103vs [ν (PO)], 1041vs, 1028vs [ν (POC)]. λ_{max} (cm⁻¹), CH₂Cl₂ (blue): 14652, 16181, 18099, 21276; THF (yellow): 12706, 22321. CI_{neg} MS (*m*/*z*, %): 762 (92) [M⁻], 352 (100) [{(OPPh₂}(OP(OEt)₂]N}⁻], 336 (23) [{(PPh₂}(OP(OEt)₂]N]⁻]. μ = 2.19 BM.

2.3. Preparation of tetrakis[tetraphenylimidodiphosphinato]dinickel, Ni₂[(OPPh₂)₂N]₄ (**3**) and bis(dimethylformamide)bis(tetraphenylimidodiphosphinato)nickel, Ni[(OPPh₂)₂N]₂(DMF)₂ (**4**)

A solution of NiCl₂ · 6H₂O (0.24 g, 1.0 mmol) in methanol (15 ml) was added to a solution of K[(OPPh₂)₂N] (0.88 g, 2.0 mmol) in methanol (15 ml). The reaction mixture was stirred at room temperature for 12 h. The solvent was removed in vacuum and the solid was extracted with benzene (20 ml). The benzene solution was concentrated in vacuum to ca. 10 ml and layered with hexane. Yellow crystals of **3** were isolated by filtration. Yield 0.80 g (86%), M.p. 290 °C. *Anal.* Calc. for C₄₈H₄₀N₂O₄P₄Ni: C, 64.66; H, 4.53; N, 3.14. Found: C, 64.58; H, 4.37; N, 3.16%. IR (cm⁻¹): 1232vs [ν_{as} (P₂N)], 1136vs [ν (PO)], 1097vs [ν (PO)]. λ_{max}

(cm⁻¹), CH₂Cl₂ (yellow): 11904, 18182, 22727; THF (yellow): 12670, 23614. Cl_{neg} MS (*m/z*, %): 890 (100) [Ni{(OPPh₂)₂N}₂⁻], 416 (7) [{(OPPh₂)₂N]⁻], 216 (5) [{(OPPh₂)N}⁻]. FAB + MS (*m/z*, %): 1783 (15) [{Ni₂[(OPPh₂)₂N]₄ + 2H}⁺], 1366 (38) [{Ni₂-[(OPPh₂)₂N]₃ + 2H}⁺], 891 (100) [{Ni[(OPPh₂)₂N]₂ + H}⁺]. μ = 3.26 BM.

Compound **3** was dissolved at room temperature in dimethylformamide. The yellow solution was concentrated in vacuum. Yellow-green crystals of **4** quantitatively formed at $-5 \,^{\circ}$ C. M.p. 115 $^{\circ}$ C (dec.). *Anal.* Calc. for C₅₄H₅₄N₄O₆P₄Ni: C, 62.52; H, 5.21; N, 5.40. Found: C, 62.83; H, 5.32; N, 5.28%. IR (cm⁻¹): 1643vs [ν (CO)], 1230vs, br [$\nu_{as}(P_2N)$], 1130vs [ν (PO)], 1105vs [ν (PO)]. λ_{max} (cm⁻¹), CH₂Cl₂ (yellow): 11904, 14706, 18248, 22727; THF (yellow): 12658, 23809. Cl_{neg} MS (m/z, %): 890 (100) [{Ni-[(OPPh₂)₂N]₂]-], 416 (7) [{(OPPh₂)₂N}-], 216 (5) [{(OPPh₂)N}-]. μ = 3.10 BM.

2.4. Preparation of potassium [tris{P,P-diethoxi-P',P'-diphenyl-P'-thioimidodiphosphinato}nickel], KNi[(SPPh₂){OP(OEt)₂}N]₃ (**5**)

(a) A mixture of K[(SPPh₂){OP(OEt)₂}N] (0.766 g, 1.86 mmol) and NiCl₂ (0.148 g, 0.62 mmol) was stirred for 16 h in methanol (40 ml) at room temperature. The solvent was removed in vacuum and the solid was treated with CH₂Cl₂. KCl was filtered off and the solvent was removed in vacuum, resulting in a yellow-brown solid product. Yield: 0.58 g (77%). M.p. 118–119 °C. *Anal.* Calc. for C₄₈H₆₀N₃O₉P₆ S₃KNi: C, 47.94; H, 4.99; N, 3.50. Found: C, 48.21; H, 4.82; N, 3.24%.

(b) Alternatively, **5** was obtained by stirring a 1:1 mixture of **1** (0.794 g, 1 mmol) and K[(SPPh₂){OP(OEt)₂}N] (0.407 g, 1 mmol) in methanol (50 ml) at room temperature, for 24 h. The solvent was removed in vacuum from the blue-green solution, resulting quantitatively in a yellow-brown solid. M.p. 118–119 °C. *Anal.* Calc. for C₄₈H₆₀N₃O₉S₃P₆KNi: C, 47.94; H, 4.99; N, 3.50. Found: C, 47.82; H, 4.92; N, 3.53%. IR (cm⁻¹): 1261vs [$\nu_{as}(P_2N)$], 1103s [$\nu(PO)$], 1033vs, br [$\nu(POC)$], 590s [$\nu(PS)$]. λ_{max} (cm⁻¹), CH₂Cl₂ (blue): 14652, 16168, 17746, 21459; THF (yellow): 12053, 22321. Cl_{neg} MS (m/z, %): 794 (78) [M-K[(SPPh₂){OP(OEt)₂}N]⁻], 407 (5) [K[(SPPh₂){OP(OEt)₂}N]⁻] 368 (100) [{(SPPh₂){OP(OEt)₂}N]⁻], 36 (38) [{(PPh₂){OP(OEt)₂}N]⁻], 833 (82) [K₂Ni[(SPPh₂){OP(OEt)₂}-N]₂⁻], 407 (35) [K[(SPPh₂){OP(OEt)₂}N]⁻]. μ = 3.36 BM.

2.5. Crystal structure determinations

Block crystals of Ni₂[(OPPh₂)₂N]₄ · CH₂Cl₂ (**3** · CH₂Cl₂) (yellow), Ni[(OPPh₂)₂N]₂(DMF)₂ · 2H₂O (**4** · 2H₂O) (yellow-green) and KNi[(SPPh₂){OP(OEt)₂}N]₃ (**5**) (yellow-brown) were attached with epoxy glue on cryoloops. The data were collected at room temperature on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo K α radiation (λ = 0.71073 Å). The details of the crystal structure determination and refinement are given in Table 1.

The structures were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter. For structure solving and refinement the software package SHELX-97 was used [12]. The drawings were created with the DIAMOND program [13].

3. Results and discussion

The title nickel(II) complexes were obtained by salt metathesis reactions between anhydrous $NiCl_2$ or $NiCl_2 \cdot 6H_2O$ and the potassium salt of the corresponding tetraorganodichal-cogenoimidodiphosphinic acid, according to the following equations:



The reactions between $K[(XPR_2)(YPR'_2)N]_2$ and nickel dichloride were performed using either dehydrated NiCl₂ or NiCl₂ · 6H₂O in a tetrahydrofurane/ethanol mixture (**1** and **2**), or methanol as solvent (**3** and **5**), respectively. The use of anhydrous NiCl₂ and argon atmosphere resulted in a considerable increase in the yields of compounds **1** and **2**. The formation of the ionic species **5** through both methods of preparation was confirmed by powder X-ray diffraction studies. The experimental spectrum is in a good agreement with the simulated one based on the single-crystal X-ray diffraction data (Fig. 1). All isolated compounds are stable as solids in open atmosphere for weeks. They are paramagnetic in solid state. Attempts to characterize these compounds as CDCl₃ solutions by NMR spectroscopy failed suggesting their paramagnetic nature in solution too.

The CI_{neg} mass spectra of compounds **1** and **2** show the molecular ion with high intensity (85% for **1** and 92% for **2**, respectively). In case of compounds **3** and **4** the $[Ni\{(Ph_2PO)_2N\}_2]^-$ ion appeared with 100% intensity in CI_{neg} mass spectra. The dimeric species **3** was confirmed by FAB mass spectroscopy, while the formation of **5** was revealed by ESI mass spectra.

Table 1

 $Crystal \ data \ and \ structure \ refinement \ for \ Ni_2[(OPPh_2)_2N]_4 \\ \cdot CH_2Cl_2 \ (\textbf{3} \cdot CH_2Cl_2), \ Ni[(OPPh_2)_2N]_2(DMF)_2 \\ \cdot 2H_2O \ (\textbf{4} \cdot 2H_2O) \ and \ KNi[(SPPh_2)\{OP(OEt)_2\}N]_3 \ (\textbf{5}) \\ \cdot CH_2Cl_2 \ (\textbf{3} \cdot CH_2Cl_2), \ Ni[(OPPh_2)_2N]_2(DMF)_2 \\ \cdot 2H_2O \ (\textbf{4} \cdot 2H_2O) \ and \ KNi[(SPPh_2)_2N]_3 \ (\textbf{5}) \\ \cdot CH_2Cl_2 \ (\textbf{3} \cdot CH_2Cl_2), \ Ni[(OPPh_2)_2N]_2(DMF)_2 \\ \cdot CH_2Cl_2 \ (\textbf{3} \cdot CH_2Cl_2), \ Ni[(OPPh_2)_2N]_2(DMF)_2 \ (\textbf{3} \cdot CH_2Cl_2), \ Ni[(OPPh_2)_2N]_2(DMF)_2 \ (\textbf{3} \cdot CH_2Cl_2) \ (\textbf{3} \cdot CH_2Cl_2), \ Ni[(OPPh_2)_2N]_2(DMF)_2 \ (\textbf{3} \cdot CH_2CL_2), \ Ni[(OPPh_2)_$

	$3 \cdot CH_2Cl_2$	4 · 2H ₂ O	5
Molecular formula	C97H82Cl2N4Ni2O8P8	C ₅₄ H ₅₈ N ₄ NiO ₈ P ₄	C ₉₆ H ₁₁₆ K ₂ N ₆ Ni ₂ O ₁₈ P ₁₂ S ₆
Μ	1867.75	1073.61	2401.60
Temperature (K)	293(2)	297(2)	297(2)
Crystal size (mm)	$0.30 \times 0.28 \times 0.21$	$0.60 \times 0.55 \times 0.44$	$0.35 \times 0.29 \times 0.23$
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	P2(1)/n	P2(1)/n	Pbca
Radiation	Mo Kα, 0.71073 Å	Mo Kα, 0.71073 Å	Mo Kα, 0.71073 Å
Unit cell dimension			
a (Å)	16.433(3)	9.4672(15)	24.9858(10)
b (Å)	21.222(3)	20.951(3)	17.6058(7)
<i>c</i> (Å)	26.375(4)	13.363(2)	25.8683(10)
α (°)	90	90	90
β (°)	104.266(3)	94.442(3)	90
γ (°)	90	90	90
$V(Å^3)$	8915(2)	2642.6(7)	11379.3(8)
Ζ	4	2	4
$D_{\text{calc}} (\text{g cm}^{-3})$	1.392	1.349	1.402
F000	3864	1124	4992
μ (Mo K α) (mm ⁻¹)	0.686	0.545	0.746
θ Range for data collections (°)	1.25-26.37	1.81-26.37	1.62-25.00
Reflections collected	71288	20850	79397
Independent reflections [R _{int}]	18241 [0.0465]	5387 [0.0362]	10020 [0.1005]
Maximum and minimum transmissions	0.87 and 0.803	0.7954 and 0.7356	0.8471 and 0.7802
Refinement method		Full-matrix least-squares on F^2	
Data/restraints/parameters	18241/0/1095	5387/0/332	10020/0/646
Goodness-of-fit on F ²	1.210	1.220	1.243
	$R_1 = 0.0709$	$R_1 = 0.0503$	$R_1 = 0.1129$
	$wR_2 = 0.1472$	$wR_2 = 0.1088$	$wR_2 = 0.2344$
R indicies (all data)	$R_1 = 0.0832$	$R_1 = 0.0530$	$R_1 = 0.1317$
	$wR_2 = 0.1528$	$wR_2 = 0.1101$	$wR_2 = 0.2444$
Largest difference peak and hole (e $Å^{-3}$)	0.629 and -0.761	0.449 and -0.440	0.798 and -1.458



Fig. 1. (a) Experimental powder diffraction pattern and (b) the simulated X-ray powder diffraction spectrum obtained from the single-crytal cif file of **5**.

Strong infrared absorptions were observed for all complexes in the region 1260–1230, 1140–1100, 1050–1030 and about 600 cm⁻¹ and they were assigned to $v_{as}(P_2N)$, v(PO), v(POC) and v(PS)stretching vibrations, respectively, by comparison with the IR spectra of the free acids and their alkali metal salts [1,10,14], thus suggesting the coordination of the ligand units through both chalcogen atoms. For the adduct **4** the coordination of the DMF molecules to the metal atom is reflected in a shift of the C=O vibration from 1675 cm⁻¹ in the free DMF to 1643 cm⁻¹ in the adduct spectrum.

All derivatives are well soluble in CH_2Cl_2 , resulting in bluegreen (1, 2 and 5) or yellow (3 and 4) solutions, respectively. The solutions of all compounds in coordinating solvents, *i.e.* tetrahydrofurane or methanol, are yellow. The electronic spectra of compounds 1, 2 and 5 exhibit four absorption maxima in CH_2Cl_2 solutions, around 21000, 18000, 16000 and 14600 cm⁻¹, assignable to tetracoordinate species [5,8]. According to the magnetic moments (about 2.0 BM) found for compounds **1** and **2** in solid state, the formation of a mixture of tetrahedral and square-planar species might be suggested [15]. It can be mentioned here that the crystal of the related copper(II) complex, Cu[(OPPh₂)(SPPh₂)N]₂, was reported to contain both tetrahedral and square-planar isomers [16].

For the derivative **3** in CH_2Cl_2 solution the observed absorptions (22727, 18182 and 11904 cm⁻¹) are similar to those reported previously for the dimeric Ni₂[(OPPh₂)₂N]₄ species in benzene solution [9], while in case of its adduct with dimethylformamide (**4**) a fourth absorption appeared around 14700 cm⁻¹. This behavior might be consistent with a mixture of octahedral and pentacoordinate species in solution. The magnetic moments recorded in solid state for compounds **3–5** (3.26, 3.10 and 3.36 BM, respectively) are consistent with paramagnetic species with two unpaired electrons. In THF all compounds gave strong absorptions in the region 22000-24000 cm⁻¹.

3.1. Crystal and molecular structure of $Ni_2[(OPPh_2)_2N]_4 \cdot CH_2Cl_2 \cdot (\mathbf{3} \cdot CH_2 \ Cl_2)$ and $Ni[(OPPh_2)_2N]_2(DMF)_2 \cdot 2H_2O \ (\mathbf{4} \cdot 2H_2O)$

Single crystals of $Ni_2[(OPPh_2)_2N]_4 \cdot CH_2Cl_2$ (**3** $\cdot CH_2Cl_2$), suitable for X-ray diffraction studies, were obtained from CH_2Cl_2/n -hexane (1:4, v:v).

The crystal of **3** consists of distinct dinuclear units separated by normal van der Waals distances between heavy atoms. An ORTEP-like view with the atoms numbering scheme is given in Fig. 2. Selected bond lengths and angles are listed in Table 2.

Three of the phosphorus ligands act as homobimetallic triconnective units, bridging the two metal centers, while the fourth one acts monometallic biconnective. The result is a fused polycyclic system formed by three six-membered NiO_2P_2N rings and three non-planar four-membered Ni_2O_2 rings [dihedral angles:



Fig. 2. ORTEP plot of the dinuclear unit in the crystal of 3 · CH₂Cl₂. The atoms are drawn with 40% probability ellipsoids. Hydrogen atoms and CH₂Cl₂ are omitted.

Table 2								
Selected	interatomic	distances	(Å)	and	angles	(°)	in	$Ni_2[(OPPh_2)_2N]_4 \cdot CH_2Cl_2$
$(3, \mathbf{CH}_{2}\mathbf{C})$	2)							

(2 2 2)			
Ni(1)-O(1)	1.982(3)	Ni(2)-O(3)	1.997(2)
Ni(1)-O(2)	1.970(3)	Ni(2)-O(4)	2.208(2)
Ni(1) - O(4)	2.031(2)	Ni(2) - O(5)	2.011(2)
Ni(1)-O(6)	2.052(2)	Ni(2) - O(6)	2.086(2)
Ni(1)-O(8)	2.062(2)	Ni(2)-O(7)	2.020(2)
		Ni(2)-O(8)	2.131(2)
P(1)-O(1)	1.513(3)	P(5)-O(5)	1.499(2)
P(1) - N(1)	1.589(3)	P(5)-N(3)	1.592(3)
P(2) - N(1)	1.583(4)	P(6)-N(3)	1.578(3)
P(2)-O(2)	1.512(3)	P(6)-O(6)	1.520(2)
P(3)-O(3)	1.505(2)	P(7)-O(7)	1.506(3)
P(3) - N(2)	1.589(3)	P(7)-N(4)	1.589(3)
P(4) - N(2)	1.579(3)	P(8)-N(4)	1.570(3)
P(4)-O(4)	1.524(2)	P(8)-O(8)	1.517(2)
O(1)-Ni(1)-O(6)	174.99(11)	O(3)-Ni(2)-O(8)	165.77(10)
O(2)-Ni(1)-O(8)	149.00(11)	O(4) - Ni(2) - O(5)	165.54(10)
		O(6)-Ni(2)-O(7)	169.25(10)
O(4) - Ni(1) - O(1)	102.09(11)	O(3)-Ni(2)-O(4)	90.97(9)
O(4) - Ni(1) - O(2)	125.46(11)	O(3) - Ni(2) - O(5)	95.50(10)
O(4) - Ni(1) - O(6)	80.30(10)	O(3) - Ni(2) - O(6)	93.23(10)
O(4) - Ni(1) - O(8)	81.52(10)	O(3)-Ni(2)-O(7)	96.41(10)
O(1) - Ni(1) - O(2)	93.23(11)	O(8) - Ni(2) - O(4)	76.02(9)
O(2) - Ni(1) - O(6)	88.86(10)	O(8) - Ni(2) - O(5)	95.95(10)
O(6) - Ni(1) - O(8)	80.49(9)	O(8) - Ni(2) - O(6)	78.14(9)
O(8)-Ni(1)-O(1)	95.45(10)	O(8)-Ni(2)-O(7)	91.46(10)
		O(4) - Ni(2) - O(6)	75 57(9)
		O(6) - Ni(2) - O(5)	91 13(10)
		O(5) - Ni(2) - O(7)	92 67(10)
		O(7)-Ni(2)-O(4)	99.45(10)
$N_{i}(1) = O(1) = P(1)$	131 79(17)	Ni(2) = O(5) = P(5)	122 77(14)
O(1) - P(1) - N(1)	116 97(17)	O(5) - P(5) - N(3)	118 92(15)
P(1) - N(1) - P(2)	124 2(2)	P(5) - N(3) - P(6)	126 88(19)
O(2) - P(2) - N(1)	11640(17)	O(6) - P(6) - N(3)	116.00(15)
$N_{i}(1) = O(2) = P(2)$	132 17(16)	Ni(2) = O(6) = P(6)	124 13(14)
10(1) 0(2) 1(2)	152.17(10)	Ni(1) - O(6) - P(6)	148.47(15)
$N_{i}(2) = O(3) = P(3)$	121 25(14)	$N_{i}(2) = O(7) = P(7)$	120 27(14)
O(3) = P(3) = N(2)	121.23(14) 11834(15)	O(7) - P(7) - N(4)	117 67(15)
P(3) = N(2) = P(4)	128 3(2)	P(8) = N(4) = P(7)	126 5(2)
O(4) - P(4) - N(2)	115 59(15)	O(8) - P(8) - N(4)	1157(15)
$N_{i}(2) = O(A) = P(A)$	121 08(13)	$N_{i}(2) = O(8) = D(8)$	122.06(12)
$N_{1}(2) = O(4) = F(4)$ $N_{1}(1) = O(4) = P(4)$	153.97(16)	Ni(2) = O(0) = F(0) Ni(1) = O(8) = P(8)	152 09(15)
	155.57(10)	11(1) = 0(0) = 1(0)	152.03(13)
Ni(1) - O(4) - Ni(2)	84.57(9)	Ni(1)-O(8)-Ni(2)	85.83(9)
NI(1) = O(6) = NI(2)	87.24(9)		

O(4)Ni(1)O(6)/O(4)Ni(2)O(6) 54.6°; O(4)Ni(1)O(8)/O(4)Ni(2)O(8) 57.8°; O(4)Ni(1)O(8)/O(4)Ni(2)O(8) 54.2°]. The two nickel atoms are in different environments: Ni(1) has a distorted square-pyramidal coordination geometry, with O(4) atom in apical position and the nickel atom out of the best O(1)O(2)O(6)O(8) plane (0.29 Å), while Ni(2) has a distorted octahedral geometry being surrounded by six oxygen atoms. The Ni₂O₈ core may be considered as resulted from a Ni(1)O₅ square pyramid and a Ni(2)O₆ octahedron, with a common trigonal face described by the O(4), O(6)and O(8) atoms (Fig. 3). The two nickel atoms are brought very close each other, at a distance less than the sum of their van der Waals radii [Ni(1)···Ni(2) 2.8552(8) Å versus \sum_{vdW} (Ni,Ni) 3.20 Å [17]. This compound displays a different structure compared with the related dimeric manganese(II) derivative, $[Mn{(OPPh_2)_2N}_2]_2$, where both metal centers have the same coordination geometry. i.e. trigonal bipyramidal, with two of the imidodiphosphinato ligands acting as monometallic biconnective units, with a cis orientation with respect to the four-membered Mn₂O₂ ring; the other two phosphorus ligands are homobimetallic triconnective, the result being a fused tricyclic Mn₂O₄P₄N₂ system [18].

The nickel-oxygen distances are different. The shorter bonds $[Ni(1)-O(1) \ 1.982(3), Ni(1)-O(2) \ 1.970(3) \text{ Å}]$ are established by



Fig. 3. View of the $Ni_2O_8P_8N_4$ core in the crystal of $3 \cdot CH_2Cl_2$.

the isobidentate, monometallic biconnective ligand which coordinate the Ni(1) atom. They are considerably shorter than the corresponding metal-oxygen bonds in the adduct $4 \cdot 2H_2O$ in which the phosphorus ligands exhibit an anisobidentate, monometallic biconnective pattern [Ni(1)–O(1) 2.1133(17), Ni(1)–O(2) 2.0542(17) Å]. The bridging Ni–O–Ni systems are not symmetric (Table 2), with Ni(1)–O distances shorter than Ni(2)–O distances. The remaining, terminal, Ni(2)–oxygen bond distances are of intermediate magnitude between the bridging metal–oxygen and Ni(1)–O bonds established by the monometallic biconnective ligand, respectively.

The phosphorus–nitrogen [1.570(3)–1.592(3) Å] and phosphorus–oxygen [1.499(2)–1.524(2) Å] distances are intermediate between single and double bonds [cf. Ph₂P(=S)–N=P(–SMe)Ph₂ [19]: P=N 1.562(2) Å, P–N 1.610(2) Å, Ph₂P(O)OH [20]: P=O 1.486(6) Å, P–O 1.526(6) Å], thus suggesting some delocalization of the π electrons. However the resulting NiO₂P₂N rings are not planar. All ligands acting as homobimetallic triconnective units establish six-membered NiO₂P₂N rings which exhibit distorted boat conformation, with Ni(2) and nitrogen atoms in apices. The fourth six-membered NiO₂P₂N ring, established by the monometallic biconnective ligand, has an envelope conformation, folded on the imaginary P(1)···P(2) axis, with the nitrogen atom –0.31 Å out of the almost planar NiO₂P₂ skeleton.

Recrystallization of **3** from dimethylformamide led to isolation of the adduct Ni[(OPPh₂)₂N]₂(DMF)₂ \cdot 2H₂O (**4** \cdot 2H₂O). Its crystal consists of discrete molecules with Ni atom as inversion center, separated by normal van der Waals distances. An ORTEP-like view with the atoms numbering scheme is given in Fig. 4 and selected bond lengths and angles are listed in Table 3.

The two imidodiphosphinato ligands act as monometallic biconnective units, chelating the metal center through both oxygen atoms. This results in a spiro-bicyclic system with Ni as spiro atom, occupying an inversion center. The NiO₄ system is planar, with different Ni–O distances [Ni–O(1) 2.1134(16) Å, Ni–O(2) 2.0541(16) Å]. The six-membered NiO₂P₂N rings are of boat conformations [with Ni(1) and nitrogen atoms in apices] and folded along the imaginary $O(1) \cdots O(2a)$ and $O(1a) \cdots O(2)$ axis [dihedral angle of 16.4° between the best P₂O₂ and NiO₄ planes] on opposite sides of the planar NiO₄ core [deviations from NiO₄ plane: P(1) = -0.462, P(2a) = -0.385, N(1a) = -0.703 Å, and P(1a) 0.462, P(2) 0.385, N(1) 0.703 Å, respectively]. The phosphorus-oxygen [P(1)-O(1)]1.5106(18), P(2)–O(2) 1.5088(17) Å] and phosphorus–nitrogen [P(1)–N(1a) 1.593(2), P(2)–N(1) 1.582(2) Å] distances, respectively, are equivalent and intermediate between single P-E and double P=E (E = O, N) bonds. The two dimethylformamide groups complete the axial position of the octahedral environment around the metal center and the Ni-O_{DMF} bond lengths are intermediate between the short and the long metal-oxygen bonds established by

. . . .



Fig. 4. ORTEP plot at 30% probability and the atom numbering scheme for $4 \cdot 2H_2O$. The hydrogen atoms are omitted.

Table 3							
Selected interatomic	distances	(Å) a	nd	angles	(°)	in	$Ni[(OPPh_2)_2N]_2(DMF)_2\cdot 2H_2O$
$(4 \cdot 2H_2O)$							

Ni(1)–O(1) Ni(1)–O(3)	2.1133(17) 2.0921(19)	Ni(1)-O(2)	2.0542(17)
P(1)-O(1) P(1)-N(1a)	1.5106(18) 1.593(2)	P(2)-O(2) P(2)-N(1)	1.5088(17) 1.582(2)
O(1)-Ni(1)-O(1a) O(3)-Ni(1)-O(3a)	180.00 180.00	O(2)-Ni(1)-O(2a)	180.00
O(3)-Ni(1)-O(1) O(3)-Ni(1)-O(1a) O(1)-Ni(1)-O(2)	87.25(7) 92.75(7) 87.57(7)	O(3)-Ni(1)-O(2) O(3)-Ni(1)-O(2a) O(1)-Ni(1)-O(2a)	90.36(7) 89.64(7) 92.43(7)
Ni(1)-O(1)-P(1) O(1)-P(1)-N(1a) P(1)-N(1a)-P(2a)	127.49(10) 118.84(10) 127.92(13)	Ni(1)-O(2)-P(2) O(2)-P(2)-N(1)	129.92(10) 118.66(10)

Symmetry equivalent positions (2 - x, -y, -z) are given by "a".

a phosphorus ligand unit. The distortion of the octahedral NiO_6 core is reflected in the difference between the *endo* and *exo* cyclic O-Ni-O bond angles in the equatorial plane [O(1)-Ni(1)-O(2a) (*endo*) 92.43(7)°, O(1)-Ni(1)-O(2) (*exo*) 87.57(7)°].

3.2. Crystal and molecular structure of [KNi[(SPPh₂){OP(OEt)₂}N]₃]₂ (5)

Yellow-brown crystals of (5) were grown from a CH_2Cl_2/n -hexane (1:4, v:v) mixture.

Compound **5** displays a tetranuclear structure and its ORTEPlike diagram with the atom numbering scheme is depicted in Fig. 5. Selected bond distances and angles are given in Table 4.

The phosphorus ligands exhibit different bridging patterns. They are coordinated to the nickel center through the sulfur atoms



Fig. 5. ORTEP plot of the dimer unit in the crystal of 5. The atoms are drawn with 30% probability ellipsoids. For clarity, only *ipso* carbons of the phenyl groups are shown and the hydrogen atoms are omitted.

Table 4 Selected interatomic distances (Å) and angles (°) in KNi[(SPPh₂){OP(OEt)₂}N]₃ (5)

Ni(1)-O(4)	2.094(5)	K(1)-O(1)	2.362(6)
Ni(1)-O(7)	2.086(5)	K(1)–O(1a)	2.346(6)
Ni(1) - S(1)	2.464(2)	K(1)–O(4)	2.387(6)
Ni(1) - S(2)	2.477(2)	K(1)–O(7)	2.419(6)
Ni(1)-S(3)	2.422(2)	K(1)–O(8)	2.540(6)
Ni(1)–N(1)	2.238(6)		
P(1) - O(1)	1.480(6)	P(2)-S(1)	1.984(3)
P(1) - N(1)	1.610(7)	P(2) - N(1)	1.611(6)
P(1) - O(2)	1.583(6)		
P(1)–O(3)	1.568(6)		
P(3)-O(4)	1.489(6)	P(4)-S(2)	1.999(3)
P(3)–N(2)	1.551(8)	P(4) - N(2)	1.587(8)
P(3)-O(5)	1.577(7)		
P(3)–O(6)	1.565(7)		
P(5)-O(7)	1.485(5)	P(6)-S(3)	1.984(3)
P(5)–N(3)	1.565(6)	P(6)-N(3)	1.601(6)
P(5) - O(8)	1.591(6)		
P(5)–O(9)	1.574(6)		
O(4) - Ni(1) - S(1)	168.64(16)	O(7) - Ni(1) - S(2)	175.70(15)
N(1)-Ni(1)-S(3)	167.52(17)		
O(4)-Ni(1)-O(7)	84.2(2)	S(1)-Ni(1)-O(7)	92.89(15)
O(4) - Ni(1) - N(1)	93.5(2)	S(1)-Ni(1)-N(1)	75.30(17)
O(4) - Ni(1) - S(2)	91.86(16)	S(1)-Ni(1)-S(2)	90.67(8)
O(4)-Ni(1)-S(3)	98.94(16)	S(1)-Ni(1)-S(3)	92.25(8)
O(7) - Ni(1) - N(1)	86.4(2)	S(2)-Ni(1)-S(3)	87.03(7)
N(1) - Ni(1) - S(2)	92.18(18)	O(7)-Ni(1)-S(3)	95.24(15)
K(1) - O(1) - P(1)	123.7(3)	K(1a) - O(1) - P(1)	141.4(3)
O(1) - P(1) - N(1)	117.6(3)	K(1) - O(1) - K(1a)	87.9(2)
P(1)-N(1)-P(2)	133.0(4)		
S(1)-P(2)-N(1)	105.9(2)	Ni(1)-N(1)-P(1)	128.3(3)
Ni(1)-S(1)-P(2)	81.27(9)	Ni(1)-N(1)-P(2)	97.4(3)
Ni(1)-O(4)-P(3)	132.2(3)	Ni(1)-O(7)-P(5)	138.2(3)
O(4) - P(3) - N(2)	119.9(4)	O(7) - P(5) - N(3)	120.3(3)
P(3)-N(2)-P(4)	132.9(5)	P(5)-N(3)-P(6)	130.2(4)
S(2) - P(4) - N(2)	118.6(3)	S(3)-P(6)-N(3)	120.0(2)
Ni(1)-S(2)-P(4)	105.68(10)	Ni(1)-S(3)-P(6)	110.61(10)
K(1) - O(4) - P(3)	124.1(3)	K(1)-O(7)-P(5)	103.1(3)
K(1) - O(8) - P(5)	95.0(3)		
Ni(1) - O(4) - K(1)	100.1(2)	Ni(1)-O(7)-K(1)	99.3(2)
O(1)-K(1)-O(4)	90.2(2)	O(4)-K(1)-O(7)	71.32(19)
O(1)-K(1)-O(7)	92.3(2)	O(4) - K(1) - O(8)	110.8(2)
O(1)-K(1)-O(8)	132.2(3)	O(4)-K(1)-O(1a)	130.0(2)
O(1)-K(1)-O(1a)	92.1(2)		
O(7)-K(1)-O(8)	58.24(18)	O(8)-K(1)-O(81a)	104.0(2)
O(7)-K(1)-O(1a)	158.2(2)		

Symmetry equivalent positions (-x, -y, 1 - z) are given by "a".

which describe a triangular face of the distorted octahedral environment. The oxygen atoms of the SPNPO skeletons are involved in bridges between metal centers, *i.e.* O(4) and O(7) atoms bridge the metal atoms of a KNi[(SPPh₂){OP(OEt)₂}N]₃ unit, while O(1) atom is involved in a bridge between the two potassium atoms of the [KNi[(SPPh₂){OP(OEt)₂}N]₃]₂ dimer. The N(1) atom completes the octahedral coordination of the nickel atom (NiNO₂S₃ core), while the coordination sphere around the potassium atom is completed by an oxygen atom from an ethoxy group belonging to the KNi[(SPPh₂){OP(OEt)₂}N]₃ unit [K(1)–O(8) 2.540(6) Å]. Thus phosphorus ligands can be described as (0,0,5)-heterobimetallic triconnective, (S,O,O,O_{Ft})-heterobimetallic tetraconnective and (N,O,O,S)-heterotrimetallic tetraconnective, respectively. As far very few examples of complexes are known in which the nitrogen atom of the imidodiphosphinato ligand is involved in interaction with the metal center, i.e. S,N-monometallic biconnective in $Pd[(SPR_2){OP(OPh)_2}N]_2$ (R = Ph, Pr^i) [21], O,N-monometallic biconnective in the dimeric [PhHg{OP(OPh)₂}₂N]₂ [22] and X,X,Nmonometallic triconnective coordination in $[2-(Me_2NCH_2)C_6H_4]$

 $BiCl[(XPPh_2)_2N]$ (X = S, Se) [23]. As result of the coordination patterns of the phosphorus ligands different metalocycles are formed. The six-membered Ni(1)S(2)P(4)N(2)P(3)O(4) and Ni(1)S(3)-P(6)N(3)P(5)O(7) chelate rings have twisted boat or chair confor-

mations, with Ni(1)/N(2) and Ni(1)/N(3) atoms, respectively, in apices. The K₂O₂ ring is planar, while the NiKO₂ ring is folded [dihedral angle O(4)Ni(1)O(7)/O(4)K(1)O(7) 22.1°]. The dihedral angle between the K_2O_2 ring and the KO_2 fragment of the NiKO₂ is 88.6°.

The Ni-chalcogen distances are similar for the three ligand units. The Ni-S bond lengths [Ni(1)-S(1) 2.464(2), Ni(1)-S(2) 2.477(2), Ni(1)-S(3) 2.422(2) Å] are longer than in other Ni(II) thioato derivatives, i.e. the tetrahedral Ni[(OPPh₂)(SPR₂)N]₂ [2.306(4)/ 2.305(4) Å, R = Me; 2.306(4)/2.286(4) Å, R = Ph] [8] or Ni- $[(SPPh_2)_2N]_2$ [2.281(2)–2.316(2)Å] [5] and the square-planar $Ni[(SPMe_2)(SPPh_2)N]_2$ [2.231(1)/2.247(1)Å] [5], $Ni_3S_2(S_2COR)_2$ -(dppe) [2.170(1)-2.235(1) Å, R = Me; 2.151(4)-2.247(6) Å, R = Et]or Ni(S₂CO)(dppe) [2.1853(8)–2.1970(8)Å] [24] complexes. The Ni-O distances [Ni(1)-O(4) 2.094(5), Ni(1)-O(7) 2.086(5) Å] are similar to those found in compounds $3 \cdot CH_2Cl_2$ and $4 \cdot 2H_2O_1$, but slightly longer in comparison with the values found in $Ni[(OPPh_2)(SPR_2)N]_2$ [1.950(7)/1.959(7)Å, R = Me; 1.950(8)/ 1.956(7) Å, R = Ph] [8]. Significant differences were observed in case of the K–O distances [range 2.346(6)–2.540(6) Å]. The shortest bonds correspond to the K–O–K bridge [K(1)–O(1) 2.362(6), K(1)– O(1a) 2.346(6) Å], while the longest one corresponds to the K– O_{Et} interaction [K(1)–O(8) 2.540(6) Å]. It can be mentioned that only one OEt group is involved in interaction to each potassium center.

The phosphorus-nitrogen and phosphorus-chalcogen distances suggest that the monothioimidodiphosphinato ligands are primarily coordinated to nickel through sulfur. The phosphorus-sulfur [P(2)–S(1) 1.984(3), P(4)–S(2) 1.999(3) and P(6)–S(3) 1.984(3) Å] and terminal phosphorus-oxygen [P(1)-O(1) 1.480(6), P(3)-O(4) 1.489(6) and P(5)-O(7) 1.485(5) Å] bond lengths are equivalent in all three ligand units. Their magnitude is intermediate between single P–S and the double P=S bonds [cf. $Ph_2P(=S)-N=P(-SMe)Ph_2$ [19]: P-S 2.071(1) and P=S 1.954(1) Ål and consistent with double P=O bonds, respectively [cf. Ph₂P(O)OH [20]: P=O 1.486(6) Å. P-O 1.526(6)Å].

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Appendix A. Supplementary data

CCDC 612983, 612984 and 626929 contain the supplementary crystallographic data for $\mathbf{3} \cdot CH_2Cl_2$, $\mathbf{4} \cdot 2H_2O$ and $\mathbf{5}$. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033, or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2008.04.006.

References

- [1] C. Silvestru, J.E. Drake, Coord. Chem. Rev. 223 (2001) 117.
- J.D. Woollins, J. Chem. Soc., Dalton. Trans. (1996) 2893.
 M.R. Churchill, J. Cooke, J.P. Fennessey, J. Wormald, Inorg. Chem. 10 (1971) 1031.

- [4] M.R. Churchill, J. Cooke, J. Wormald, A. Davison, E.S. Switkes, J. Am. Chem. Soc. 91 (1969) 6518.
- [5] R. Roesler, C. Silvestru, G. Espinoza-Perez, I. Haiduc, R. Cea-Olivares, Inorg. Chim. Acta 241 (1996) 47.
- [6] P. Bhattacharyya, J. Novosad, J. Phillips, A.M.Z. Slawin, D.J. Williams, J.D. Woollins, J. Chem. Soc., Dalton Trans. (1995) 1607.
- [7] C. Papadimitriou, P. Veltsistas, J. Novosad, R. Cea-Olivares, A. Toscano, P. Garcia y Garcia, M. Lopez-Cardosa, A.M.Z. Slawin, J.D. Woollins, Polyhedron 16 (1997) 2727
- [8] A. Silvestru, D. Balc, R. Roesler, J.E. Drake, I. Haiduc, Inorg. Chim. Acta 305 (2000) 106.
- [9] A. Davison, E.S. Switkes, Inorg. Chem. 10 (1971) 837.
- [10] G. Balazs, J.E. Drake, C. Silvestru, I. Haiduc, Inorg. Chim. Acta 287 (1999) 61.
- [11] Mecury: visualization and analysis of crystal structures C.F. Macrae et al., J. Appl. Crystallogr. 39 (3) (2006) 453.
- [12] G.M. Sheldrik, SHELX-97, Universität Göttingen, Germany, 1997.
- [13] DIAMOND-Visual Crystal Structure Information System, Crystal Impact, Bonn, Germany, 2001.

- [14] I. Ghesner, C. Palotas, A. Silvestru, C. Silvestru, J.E. Drake, Polyhedron 20 (2001) 1101.
- [15] A. Deeg, W. Kuchen, D. Langsch, D. Mootz, W. Peters, H. Wunderlich, Z. Anorg, Allg. Chem. 606 (1991) 119.
- [16] A. Silvestru, A. Rotar, J.E. Drake, M.B. Hursthouse, M.E. Light, S.I. Farcas, R. Rösler, C. Silvestru, Can. J. Chem. 79 (2001) 983.
- [17] J. Huheey, E. Keiter, R. Keiter, Anorganische Chemie. Prinzipien von Struktur und Reaktivitaet, 2. Auflage, Walter de Gruyter, Berlin, 1995, p. 335.
- [18] I. Szekely, C. Silvestru, J.E. Drake, G. Balazs, S.I. Farcas, I. Haiduc, Inorg. Chim. Acta 299 (2000) 247.
- [19] I. Ghesner, A. Soran, C. Silvestru, J.E. Drake, Polyhedron 22 (2003) 3395.
- [20] D. Fenske, R. Mattes, J. Loens, K.-F. Tebbe, Chem. Ber. 106 (1973) 1139.
- [21] M. Necas, M.R. St J. Foreman, J. Marek, J.D. Woollins, J. Novosad, New J. Chem. 25 (2001) 1256.
- [22] H. Richter, E. Fluck, H. Riffel, H. Hess, Z. Anorg. Allg. Chem. 491 (1982) 266.
- [23] L. Balazs, O. Stanga, H.J. Breunig, C. Silvestru, Dalton Trans. (2003) 2237.
 [24] I. Haiduc, R.F. Semeniuc, M. Campian, V.Ch. Kravtsov, Y.A. Simonov, J. Lipkowski, Polyhedron 22 (2003) 2895.