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# Ligand Condensation of $P(CH_2OH)_3$: Synthesis and Structure of $[Ni_3S_2\{(CH_2OH)_2PCH_2OP(CH_2OH)_2\}_3][Mo_6Cl_{14}] \cdot 0.8H_2O$[1]

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**Abstract**—Reaction of $NiCl_2 \cdot 6H_2O$ and $P(CH_2OH)_3$ (THP) with $H_2S$ and $(H_7O_3)_2[Mo_6Cl_{14}] \cdot 3H_2O$ in ethanol produces new trinuclear nickel sulphide complex $[Ni_3(\mu_3\text{-}S)_2\{(HOCH_2)_2PCH_2OP(CH_2OH)_2\}_3][Mo_6Cl_{14}] \cdot 0.8H_2O$ (**I**) with new bidentate phosphine-phosphinite ligand resulted from THP condensation. It was characterized by X-ray structure analysis.

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## INTRODUCTION

Stable water soluble transition metal complexes for catalytic and biomedical purposes are one of the hot topics in modern coordination chemistry [1–5]. Phopshines functionalized with hydroxo or sulfonate groups are the ligands of choice [1, 6]. Phosphines with hydroxyalkyl groups such as tris(hydroxymethyl)phosphine ($P(CH_2OH)_3$ THP), form stable water-soluble complexes with Pd, Pt, Rh, Re, Ru, Ir [7–11]. Sulfide clusters of Mo with hydroxyalkyl-functionalized diphosphines have also been reported [12]. However, sulfide-bridged complexes and clusters of 3*d* metals with THP are unknown.

## EXPERIMENTAL

All manipulations with $P(CH_2OH)_3$ were carried out in argon atmosphere used Schlenk technique. Ethanol was purified according standard procedure prior to use. Silica gel L 100/160 (Chemapol), $P(CH_2OH)_3$ and $CoCl_2 \cdot 6H_2O$ (Sigma-Aldrich) were used as supplied. $\{^1H\}^{31}P$ (202 MHz) spectra of **I** in $EtOH–D_2O$ solution were recorded on a Bruker Avance 500 spectrometer at room temperature. $\{^1H\}^{31}P$ NMR shifts were referenced to external 85% $H_3PO_4$ in $D_2O$. IR spectra were recorded on a Scimitar FTS 2000 spectrometer in KBr pill at 4000–400 $cm^{-1}$. X-ray diffraction data were collected on a Bruker X8 Apex diffractometer.

Element analysis (C, H, S) was carried out in Analytic laboratory (Nikolaev Institute of Inorganic Chemistry) on Euro EA 3000 analyzer. Absorption spectra in solution were recorded on Helios γ spectrophotometer.

[1] The article was translated by the authors.

**Preparation of $[Ni_3(\mu_3\text{-}S)_2\{(HOCH_2)_2PCH_2OP(CH_2OH)_2\}_3][Mo_6Cl_{14}] \cdot 0.8H_2O$ (I).** $NiCl_2 \cdot 6H_2O$ (0.24 g, 0.10 mmol) and $P(CH_2OH)_3$ (0.25 g, 0.20 mmol) were dissolved in ethanol (10 $cm^3$) under argon and then hydrogen sulfide was bubbled through the solution for 4 h. The solution became dark-red and was stirred for another 12 h, filtered, and $(H_7O_3)_2[Mo_6Cl_{14}] \cdot 3H_2O$ was added to the filtrate. Slow evaporation of the solvent in air gave orange needle-shaped crystals of **I**; they were collected and dried in vacuo. Yield 0.12 g, 18%.

| For $C_{15}H_{43.6}O_{15.8}S_2P_6Cl_{14}Ni_3Mo_6$ | | | |
|---|---|---|---|
| anal. calcd., %: | C, 9.12; | H, 2.23; | S, 3.25. |
| Found, %: | C, 9.15; | H, 2.19; | S, 3.27. |

IR (ν, $cm^{-1}$): 445, 505, 560, 677, 750, 846, 873, 1030, 1179, 1283, 1374, 1408, 1619, 1729, 2051, 2897, 3355.

**X-ray crystallography.** The diffraction data were collected on a Bruker X8Apex CCD diffractometer with Mo$K_\alpha$ radiation (λ = 0.71073 Å) by doing φ- and ω scans of narrow (0.5°) frames at 296 K. Structure of **I** was solved by direct methods and refined by full-matrix least-squares treatment against $|F|^2$ with SHELXTL programs set [13]. Absorption corrections were applied empirically with SADABS program [14]. For structure determination APEX 2 (Bruker AXS, 2004), SAINT (Bruker-AXS, 2004), SHELXS-97 (Sheldrick, 1998), SHELXL-97 (Sheldrick, 1998), CIFTAB-97 (Sheldrick, 1998) programs were used. Coordinated {P,P-$PCH_2OP$} ligands were refined isotropically, because refinement of fully disordered model in anisotropical aproximation was unstable. The hydrogen atoms were refined in their geometri-

**Table 1.** Crystallographic data and refinement details for **I**

| Parameter | Value |
|---|---|
| $M$ | 1974.91 |
| Crystal system | Triclinic |
| Space group, $Z$ | $P\bar{1}$, 2 |
| Temperature, K | 296 |
| $a$, Å | 11.0506 (3) |
| $b$, Å | 12.3111 (3) |
| $c$, Å | 21.9626 (7) |
| α, deg | 96.896 (1) |
| β, deg | 94.778 (1) |
| γ, deg | 112.356 (1) |
| $V$, Å | 2716.14 (13) |
| $F$(000) | 1912 |
| μ, $mm^{-1}$ | 3.35 |
| Crystal size, mm | 0.15 × 0.05 × 0.05 |
| $T_{min}$, $T_{max}$ | 0.634, 0.851 |
| Range of $h$, $k$, $l$ | $-12 \le h \le 12$, $-13 \le k \le 14$, $-24 \le l \le 24$ |
| Number of measured reflections | 38145 |
| Number of independent reflections ($R_{int}$) | 8301 (0.042) |
| Number of reflections with ($I > 2\sigma(I)$) | 6858 |
| GOOF | 1.054 |
| Number of parameters refined | 2 |
| $R$ ($F^2 > 2\sigma(F^2)$), $wR$ ($F^2$); $S$ | 0.040, 0.115; 1.05 |
| Weighting scheme | $w = 1/[\sigma^2(F_o^2) + (0.0509P)^2 + 15.2203P]$, where $P = (F_o^2 + 2F_c^2)/3$ |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$, $e$ Å$^{-3}$ | 1.23, −0.91 |

cally calculated positions; a riding model was used for this purpose. Crystallographic data and refinement details are given in Table 1, geometrical parameters of **I** are given in Table 2. Further details may be obtained from the Cambridge Crystallographic Data Centre [15] on quoting depository number CCDC 857936. Copies of this information may be obtained free of charge from http://www.ccdc.cam.ac.uk.

## RESULTS AND DISCUSSIONS

Reaction of $NiCl_2 \cdot 6H_2O$ and $P(CH_2OH)_3$ in ethanol with hydrogen sulfide, similar to the preparation of $[Ni_3S_2(PEt_3)_6]^{2+}$ from $Ni(BF_4)_2 \cdot 6H_2O$ and $H_2S$ [16] produced red-brown solution. Addition of $(H_7O_3)_2[Mo_6Cl_{14}] \cdot 3H_2O$ [17] followed by slow crystallization yielded orange crystals suitable for X-ray structure determination. Crystal structure of **I** contains trinuclear cations $[Ni_3(\mu_3\text{-}S)_2(\{P,P\text{-}PCH_2OP\})_3]^{2+}$ (Fig. 1), $PCH_2OP$ = $(HOCH_2)_2PCH_2OP(CH_2OH)_2$, cluster anions $[Mo_6Cl_{14}]^{2-}$ and solvent water molecules which form hydrogen bonds with OH groups of the {*P*,*P*-$PCH_2OP$} ligands—{$PCH_2OH$}···$H_2O$ (O···O 2.522(1)–2.660(1) Å). In crystal packing of **I** layers of cluster cations alternate with layers of cluster anions (Fig. 2).

Cationic cluster $[Ni_3(\mu_3\text{-}S)_2(\{P,P\text{-}PCH_2OP\})_3]^{2+}$ has triangular $\{Ni_3S_2\}^{2+}$ core with average Ni···Ni distance of 2.78 Å, which are appreciably shorter than the Ni–Ni distance found in $[Ni_3S_2(PEt_3)_6](BPh_4)_2$ (**II**) (2.91(2) Å) [16]. However, this value is much shorter than the Ni–Ni bond length calculated from the covalent radius of Ni (2.48 Å) [18, 19]. Other distances (Ni–S(av.) 2.204(2) Å, Ni–P(av.) 2.151(6) Å) also differ from those reported for the $PEt_3$ complex (2.15(2) and 2.27(4) Å, respectively), indicating considerable non-rigidity of the $\{Ni_3(\mu_3\text{-}S)_2\}^{2+}$ core. Each Ni atom has square planar environment and is coordinated with two sulfur atoms and two phosphorus atoms of the bidentate phosphine-phosphite $(HOCH_2)_2PCH_2OP(CH_2OH)_2$ ligand. All valence angles P–Ni–P are close to 85°, thus being much smaller than 98° observed in $[Pt_3S_2(P(CH_2OH)_3)_6]Cl_2$ [16] and 97° in $[Pt_3S_2(THP)_6]Cl_2$ [18], most probably do to constraints required by formation of five-membered ring in **I**. Curiously, the Ni–S–Ni angles are smaller (78°) and S–Ni–S angles are larger (85°) than those observed in $[Ni_3S_2(PEt_3)_6](BPh_4)_2$ (85° and 77°, respectively).

The bidentate phosphine-phosphite ligand $(HOCH_2)_2PCH_2OP(CH_2OH)_2$ can be regarded as condensation product of two $P(CH_2OH)_3$ molecules. All these ligands are disordered over two positions with relative occupancy ratio 0.5/0.5. This disorder is due to flexibility of the –P–O–C–P– bridge and can indicate presence of two chiral isomers with $D_3$ point group symmetry in the same structure. This disorder makes impossible to split bridging atoms into individual C and O positions in the {*P*,*P*-$PCH_2OP$} ligand.

Reaction of $NiCl_2$ with two equivalents of THP in ethanol smoothly gives dark-orange solution of $[Ni(THP)_2Cl_2]$ as the only product, as evidenced by reaction monitoring with $\{^1H\}^{31}P$ NMR (sole peak at −6.2 ppm). Bubbling $H_2S$ through this solution gives dark-red solution ($\lambda_{max}$ 347 nm; reported [16] for $[Ni_3S_2(PEt_3)_6]^{2+}$ 360 nm) with only one $\{^1H\}^{31}P$ NMR signal at +14.0 ppm, in good agreement with $[Ni_3S_2(P(CH_2OH)_3)_6]^{2+}$ formulation. After 3 days signal of $[P(CH_2OH)_4]^+$ at +24.0 ppm appears, together with two other signals of equal intensity at +14.5 and at +42.3 ppm, attributable to ({*P*,*P*-$\underline{P}CH_2OP$}) and to

**Table 2.** Selected bond lengths and valence angles for complex **1***

| Bond | *d*, Å | Bond | *d*, Å |
|---|---|---|---|
| Ni(2)–Ni(1) | 2.7832 (12) | Mo(4)–Mo(6) | 2.6062 (8) |
| Ni(3)–Ni(1) | 2.7786 (12) | Mo(4)–Mo(6)$^{ii}$ | 2.6100 (9) |
| Ni(3)–Ni(2) | 2.7872 (12) | Mo(5)–Mo(4) | 2.6090 (9) |
| Ni(1)–S(11) | 2.1968 (19) | Mo(5)–Mo(4)$^{ii}$ | 2.6119 (8) |
| Ni(1)–S(12) | 2.2071 (19) | Mo(5)–Mo(6) | 2.6052 (9) |
| Ni(2)–S(11) | 2.2056 (19) | Mo(5)–Mo(6)$^{ii}$ | 2.6056 (8) |
| Ni(2)–S(12) | 2.2110 (19) | Mo(6)–Mo(4)$^{ii}$ | 2.6100 (9) |
| Ni(3)–S(11) | 2.2045 (19) | Mo(6)–Mo(5)$^{ii}$ | 2.6056 (8) |
| Ni(3)–S(12) | 2.1996 (19) | Ni(1)–P(11*A*) | 2.132 (2) |
| Mo(1)–Mo(2) | 2.6052 (9) | Ni(1)–P(12*B*) | 2.122 (6) |
| Mo(1)–Mo(2)$^{i}$ | 2.6094 (9) | Ni(1)–P(12*A*) | 2.155 (7) |
| Mo(1)–Mo(3) | 2.6039 (9) | Ni(2)–P(21*B*) | 2.077 (6) |
| Mo(1)–Mo(3)$^{i}$ | 2.6055 (9) | Ni(2)–P(21*A*) | 2.197 (5) |
| Mo(2)–Mo(1)$^{i}$ | 2.6094 (9) | Ni(2)–P(22*B*) | 2.177 (6) |
| Mo(2)–Mo(3) | 2.6075 (9) | Ni(2)–P(22*A*) | 2.107 (5) |
| Mo(2)–Mo(3)$^{i}$ | 2.6143 (9) | Ni(3)–P(31*B*) | 2.116 (7) |
| Mo(3)–Mo(1)$^{i}$ | 2.6055 (9) | Ni(3)–P(31*A*) | 2.150 (7) |
| Mo(3)–Mo(2)$^{i}$ | 2.6143 (9) | Ni(3)–P(32*B*) | 2.118 (6) |
| Mo(4)–Mo(5)$^{ii}$ | 2.6119 (8) | Ni(3)–P(32*A*) | 2.155 (6) |
| Angle | ω, deg | Angle | ω, deg |
| Ni(1)S(11)Ni(2) | 78.42 (6) | P(21*A*)Ni(2)S(11) | 89.86 (16) |
| Ni(1)S(11)Ni(3) | 78.29 (6) | P(21*A*)Ni(2)S(12) | 176.03 (16) |
| Ni(3)S(11)Ni(2) | 78.40 (6) | P(22*B*)Ni(2)S(11) | 176.62 (17) |
| Ni(1)S(12)Ni(2) | 78.09 (6) | P(22*B*)Ni(2)S(12) | 90.56 (17) |
| Ni(3)S(12)Ni(1) | 78.18 (6) | P(22*A*)Ni(2)S(11) | 172.16 (17) |
| Ni(3)S(12)Ni(2) | 78.39 (6) | P(22*A*)Ni(2)S(12) | 98.92 (16) |
| P(11*A*)Ni(1)S(11) | 92.08 (8) | P(31*B*)Ni(3)S(11) | 176.8 (2) |
| P(11*A*)Ni(1)S(12) | 177.97 (8) | P(31*B*)Ni(3)S(12) | 92.2 (2) |
| P(12*B*)Ni(1)S(11) | 171.82 (19) | P(31*A*)Ni(3)S(11) | 176.7 (2) |
| P(12*B*)Ni(1)S(12) | 96.85 (18) | P(31*A*)Ni(3)S(12) | 93.21 (19) |
| P(12*A*)Ni(1)S(11) | 179.5 (2) | P(32*B*)Ni(3)S(11) | 95.86 (18) |
| P(12*A*)Ni(1)S(12) | 93.36 (19) | P(32*B*)Ni(3)S(12) | 173.26 (19) |
| P(21*B*)Ni(2)S(11) | 97.18 (19) | P(32*A*)Ni(3)S(11) | 94.83 (18) |
| P(21*B*)Ni(2)S(12) | 175.58 (19) | P(32*A*)Ni(3)S(12) | 178.45 (18) |

* Symmetry codes: $^{i} -x+1, -, -z$; $^{ii} -x, -y, -z+1$.

{*P*,*P*-$PCH_2O\underline{P}$}, respectively. Some decomposition also takes place, liberating paramagnetic $Ni^{2+}$, which causes peak broadening and prevents determination of J constants. Formation of $[P(CH_2OH)_4]^+$ can be explained by disproportionation:

$$2P(CH_2OH)_3 + H^+ = [P(CH_2OH)_4]^+ + HP(CH_2OH)_2,$$

which furnishes necessary secondary phosphine for condensation.

Condensation of two THP molecules into $(HOCH_2)_2PCH_2OP(CH_2OH)_2$ can be explained by intermediate formation of $HP(CH_2OH)_2$, either via $CH_2OH$ elimination or by disproportionation reaction 1, followed by oxidation of $HP(CH_2OH)_2$ into $HOP(CH_2OH)_2$, followed by its condensation with THP into $(HOCH_2)_2PCH_2OP(CH_2OH)_2$. Alternatively, addition of strong acid $(H_7O)_3[Mo_6Cl_{14}]$ causes elimination of methanol from protonated THP, fol-

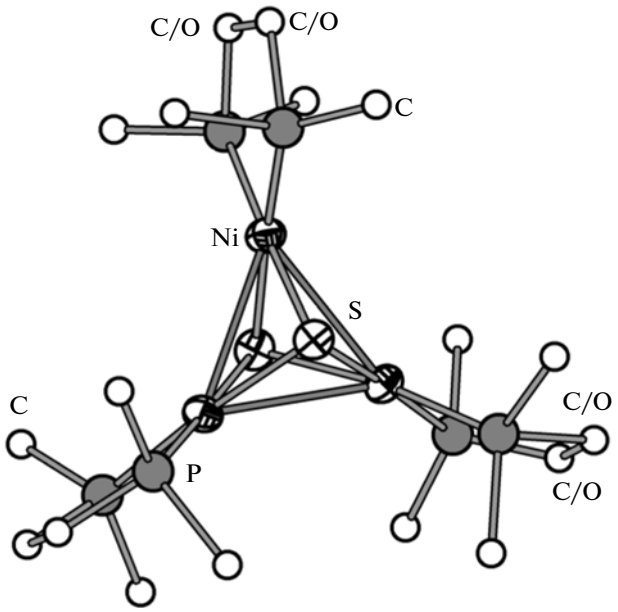


**Fig. 1.** View of $[Ni_3S_2\{(HOCH_2)_2PCH_2OP(CH_2OH)_2\}_3]^{2+}$. Hydrogen-atoms and OH groups of the ligand are omitted for clarity.

lowed by condensation of $HOP(CH_3OH)_2$ with another THP molecule. Ligand condensation of coordinated THP with itself or with $PPh_3$ into $\{P,P\text{-}PCH_2OP\}$-type ligands was reported for Pt, Pd [20] and Rh [21] complexes. Reaction of $[MCl_2(P(CH_2OH)_3)_2]$ (M = Pd, Pt) with excess $P(CH_2OH)_3$ produced $[M\{(CH_2OH)_2PCH_2OP(CH_2OH)_2\}_2]^{2+}$, but attempts to isolate free $\{P,P\text{-}PCH_2OP\}$ ligand failed because of its rapid decomposition into $P(CH_2OH)_3$ and $HP(O)(CH_2OH)_2$ [7].

Because of high hydrofilicity of $[Ni_3S_2(P(CH_2OH)_3)_6]^{2+}$ attempts to intercept this complex failed, since even addition of $NH_4PF_6$ or $NaBPh_4$ did not bring about crystallization. We decided to substitute relatively small $[PF_6]^-$ with topologically similar, but much larger $[Mo_6Cl_{14}]^{2-}$ which has octahedral $\{Mo_6Cl_8\}^{4+}$ core and can be regarded as "superoctahedral" analogue of $PF_6^-$. Indeed, addition of $[Mo_6Cl_{14}]^{2-}$ gave suitable for X-ray analysis single crystals of **I** after slow crystallization. It is insoluble in common organic solvents and sparingly soluble in

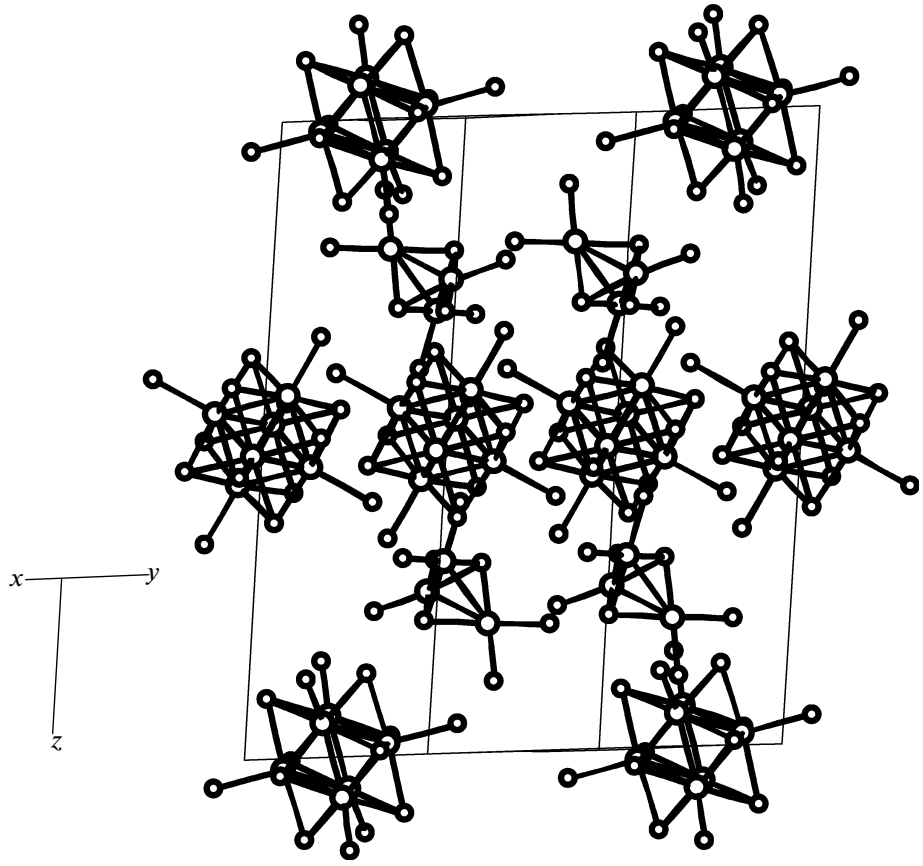


**Fig. 2.** Crystal packing of **I**, only phosphorus atoms at the $\{P,P\text{-}PCH_2OP\}$ ligands are shown. Water molecules are omitted for clarity.

DMSO and DMF. The $[Ni_3S_2(P(CH_2OH)_3)_6]^{2+}$ can also be generated in aqueous solutions (both neutral and in 4 M Hpts). However, these solutions were found to be unstable, especially at high $[H]^+$, decomposing to liberate $H_2S$ and octahedral $Ni^{2+}$.

To conclude, we have succeeded in preparation and full characterization of $[Ni_3S_2(\{P,P\text{-}PCH_2OP\})_3][Mo_6Cl_{14}] \cdot 0.8H_2O$, which contains hydrophilic hydroxyphosphine ligands. This chemistry promises new developments including catalytic reactions in aqueous media, or preparation of dendrimers by functionalization of the OH groups at the phosphine ligands. It is also worth mentioning that complexes containing Ni in mixed *P*, *S*-donor coordination environment have been suggested as functional models of hydrogenases [22].

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