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# The reaction of nickel(II) xanthates with tetraphenyldiphosphinoethane (dppe) revisited. Formation and crystal structures of $Ni_3S_2(S_2COR)_2(dppe)$ ($R = Me, Et$; dppe = $Ph_2PCH_2CH_2PPh_2$) at room temperature and of $Ni(S_2CO)(dppe)$ at 150 K

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## Abstract

The reaction between nickel(II) xanthates with tetraphenyldiphosphinoethane in molar ratio Ni:dppe 2:1 gives trinuclear complexes, $[Ni_3(\mu_2\text{-}S)_2(S_2COR)_2(dppe)]$ ($R = Me, Et$), whose crystal structures were investigated by single crystal X-ray diffraction. These complexes contain a trigonal bipyramidal central $Ni_3S_2$ core, with sulfur atoms in axial positions and nickel atoms in equatorial positions. One of the nickel(II) sites is coordinated by a chelating dppe ligand, the other two nickel atoms are chelated by two xanthate ligands. The crystal structure of $[Ni(S_2CO)(dppe)]$, which is formed in reactions of nickel(II) xanthates with excess dppe, was reinvestigated at low temperature (150 K) and more accurate parameters were obtained.

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*Keywords:* Nickel(II) xanthates; Trinuclear nickel-sulfur cluster; Nickel(II) dithiocarbonate complexes; Tetraphenyldiphosphinoethane; X-ray structures

## 1. Introduction

The reaction between nickel(II) xanthates and tetraphenyldiphosphinoethane, $Ph_2CH_2CH_2PPh_2$ (dppe) has been studied in several laboratories, with differing results. The products seem to be very sensitive to the reaction conditions. Red and orange compounds of composition $Ni(S_2COR)_2(dppe)_2$ with $R = Me$, Et, $^n$Pr, $^n$Bu, Cy were reported to form in $CHCl_3$ solution from xanthate and dppe, regardless of the combination ratio (excess dppe); on the basis of elemental analysis, electronic, IR and $^1$H NMR spectra and conductivity measurements; the compounds were described as square-planar complexes, in which both dppe and xanthate ligands are believed to be monodentate [1]. Other authors [2] reported paramagnetic, five-coordinate reddish-brown $[Ni(S_2COR)_2(dppe)]$ ($R = Et$, Cy), green six-coordinate $[Ni(S_2COR)_2(dppe)]$ ($R = Cy$), and a red–orange square-planar, four-coordinate, dithiocarbonate dealkylation product $[Ni(S_2CO)(dppe)]$ formed from $[Ni(S_2COR)_2]$ ($R = Me$, Et, Cy) with an excess of dppe in acetone–$CHCl_3$. Dealkylation of the xanthate complexes occurs on heating or by using long reaction times. The formation of the dithiocarbonato complex was confirmed by an X-ray crystal structure determination (at room temperature) of $[Ni(S_2CO)(dppe)]$ obtained from $[Ni(S_2CO^iPr)_2]$ and dppe in $CHCl_3$ (1:1 ratio) [3]. A tetra(isopropyl)diphosphinoethane analogue, $[Ni(S_2CO)(^iPr_2PCH_2CH_2P^iPr_2)]$, has also been reported and structurally characterized [4].

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Table 1
Crystal data and structure refinement for complexes **1**, **2** and **3**

| Complex | **1** | **2** | **3** |
|---|---|---|---|
| Empirical formula | $C_{30}H_{31}Ni_3O_2P_2S_6$ | $C_{32}H_{34}Ni_3O_2P_2S_6$ | $C_{27}H_{24}NiOP_2S_2$ |
| Formula weight | 853.98 | 881.02 | 549.23 |
| Crystal color | black | black | orange |
| Temperature (K) | 293(2) | 293(2) | 150(1) |
| Wavelength (Å) | 0.71073 | 0.71073 | 0.71073 |
| Crystal size (mm) | 0.50 × 0.25 × 0.25 | 0.25 × 0.25 × 0.20 | 0.45 × 0.35 × 0.10 |
| Crystal system | monoclinic | orthorhombic | monoclinic |
| Space group | *Cc* | $Pna2_1$ | *Pn* |
| $a$ (Å) | 11.8334(4) | 18.0676(10) | 10.5948(1) |
| $b$ (Å) | 18.6505(6) | 37.6894(3) | 15.9900(1) |
| $c$ (Å) | 16.3068(7) | 22.0596(2) | 15.5434(1) |
| $\beta$ (°) | 102.108(1) | 90 | 105.9606(4) |
| $V$ (Å$^3$) | 3518.8(2) | 15021.6(2) | 2531.71(3) |
| $Z$ | 4 | 16 | 4 |
| $D_{calc}$(Mg m$^{-3}$) | 1.612 | 1.558 | 1.441 |
| Absorption coefficient (mm$^{-1}$) | 2.063 | 1.936 | 1.076 |
| $F$(0 0 0) | 1748 | 7232 | 1136 |
| $\theta$ Range for data collection (°) | 2.53–27.46 | 1.08–25.62 | 1.27–30.00 |
| Limiting indices | $0 \leq h \leq 15$,<br>$0 \leq k \leq 24$,<br>$-21 \leq l \leq 20$ | $0 \leq h \leq 21$,<br>$0 \leq k \leq 45$,<br>$0 \leq l \leq 26$ | $-14 \leq h \leq 14$,<br>$-22 \leq k \leq 22$,<br>$-21 \leq l \leq 21$ |
| Reflections collected/unique | 8305/3987<br>[$R_{int} = 0.035$] | 15 758/14 356<br>[$R_{int} = 0.040$] | 28 729/14 730<br>[$R_{int} = 0.034$] |
| Data/restraints/parameters | 3987/2/391 | 14528/172/1622 | 14730/2/595 |
| Goodness-of-fit on $F^2$ | 1.043 | 0.996 | 1.054 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0334$, $wR_2 = 0.0659$ | $R_1 = 0.0643$, $wR_2 = 0.1248$ | $R_1 = 0.0381$, $wR_2 = 0.0855$ |
| $R$ indices (all data) | $R_1 = 0.0490$, $wR_2 = 0.0693$ | $R_1 = 0.1408$, $wR_2 = 0.1425$ | $R_1 = 0.0497$, $wR_2 = 0.0897$ |
| Largest difference peak and hole (e Å$^{-3}$) | 0.338 and −0.342 | 1.117 and −0.523 | 0.950 and −0.392 |

We report here the formation of trinuclear $[Ni_3(\mu_3\text{-}S)_2(S_2COR)_2(dppe)]$ complexes (R = Me, Et) and their crystal structures. A low-temperature (150 K) X-ray crystal structure reinvestigation of $[Ni(S_2CO)(dppe)]$ (obtained from $[Ni(S_2COEt)_2]$ and dppe in methylethylketone in 1:1 molar ratio) is also reported.

## 2. Experimental

### 2.1. Synthesis

### 2.1.1. $[Ni_3S_2(S_2COMe)_2(dppe)]$ (1)

A solution of $Ni(S_2COMe)_2$ (0.544 g, 0.002 mol) in 150 ml methylethylketone was treated with a solution of dppe (0.384 g, 0.001 mol) in 25 ml methylethylketone. The colour of the solution changed to dark red. Slow evaporation of the solvent produced black crystals, which were filtered, washed with a little solvent and dried in vacuo. M.p. 280 °C. *Anal*. Calc. for $C_{30}H_{30}Ni_3O_2P_2S_6$: Ni, 20.64; S, 22.55%. Found: Ni, 21.03; S, 23.11%.

### 2.1.2. $[Ni_3S_2(S_2COEt)_2(dppe)]$ (2)

A solution of $Ni(S_2COEt)_2$ (0.600 g, 0.002 mol) in 60 ml methylethylketone was treated with a solution of dppe (0.384 g, 0.001 mol) in 25 ml methylethylketone. The colour of the solution changed to dark red. Slow evaporation of the solvent produces black crystals, which were filtered, washed with a little solvent and dried in vacuo. M.p. 260 °C. *Anal.* Calc. for $C_{34}H_{34}Ni_3O_2P_2S_6$: Ni, 19.99; S, 21.83%. Found: Ni, 19.42; S, 21.31%.

### 2.1.3. $[Ni(S_2CO)(dppe)]$ (3)

A solution of $Ni(S_2CO^iPr)_2$ (0.329 g, 0.001 mol) in 50 ml methylethylketone was treated with a solution of dppe (0.384 g, 0.001 mol) in 25 ml methylethylketone. The colour of the solution became red–brown. Slow evaporation produced orange crystals, which were filtered, washed with a small amount of solvent and dried in vacuo. M.p. 190 °C. *Anal.* Calc. for $C_{27}H_{24}NiOP_2S_2$: Ni, 10.69; S, 11.67%. Found: Ni, 10.23; S, 10.54%.

The same compound was similarly obtained when other nickel(II) xanthates, $[Ni(S_2COR)_2]$ (R = Me, Et), were reacted with dppe in a 1:1 molar ratio.

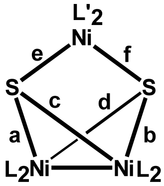
### 2.2. X-ray structure determination

A summary of the crystal data of **1**, **2** and **3** is given in Table 1. Selected bond lengths and bond angles are given in Table 2 for **1** and **2**, and in Table 3 for compound **3**. The measurements have been performed

Table 2
Selected interatomic distances (Å) and bond angles (°) for compounds **1** and **2**

| | **1** | **2a** | **2b** | **2c** | **2d** |
|---|---|---|---|---|---|
| *Bond lengths* | | | | | |
| Ni(1)–S(1) | 2.231(1) | 2.247(6) | 2.246(4) | 2.233(4) | 2.204(6) |
| Ni(1)–S(2) | 2.235(1) | 2.198(5) | 2.224(4) | 2.226(5) | 2.222(5) |
| Ni(1)–S(5) | 2.177(1) | 2.168(4) | 2.164(4) | 2.172(4) | 2.163(4) |
| Ni(1)–S(6) | 2.170(1) | 2.186(4) | 2.182(4) | 2.170(3) | 2.177(5) |
| Ni(2)–S(3) | 2.232(2) | 2.232(5) | 2.257(5) | 2.224(4) | 2.245(4) |
| Ni(2)–S(4) | 2.231(2) | 2.237(4) | 2.226(4) | 2.248(4) | 2.244(6) |
| Ni(2)–S(5) | 2.171(1) | 2.152(4) | 2.153(4) | 2.177(4) | 2.176(5) |
| Ni(2)–S(6) | 2.174(1) | 2.151(4) | 2.165(4) | 2.170(4) | 2.162(4) |
| Ni(3)–P(1) | 2.170(1) | 2.159(3) | 2.150(3) | 2.176(3) | 2.162(3) |
| Ni(3)–P(2) | 2.168(1) | 2.160(3) | 2.160(4) | 2.164(3) | 2.164(4) |
| Ni(3)–S(5) | 2.194(1) | 2.197(3) | 2.194(3) | 2.203(3) | 2.193(4) |
| Ni(3)–S(6) | 2.199(1) | 2.189(3) | 2.203(3) | 2.200(3) | 2.197(3) |
| Ni(1)···Ni(2) | 2.8990(8) | 2.905(3) | 2.911(3) | 2.929(3) | 2.909(3) |
| Ni(1)···Ni(3) | 2.7243(7) | 2.792(2) | 2.771(2) | 2.825(3) | 2.783(3) |
| Ni(2)···Ni(3) | 2.8693(8) | 2.782(2) | 2.801(2) | 2.765(2) | 2.783(3) |
| S(5)···S(6) | 2.883(2) | 2.867(4) | 2.875(4) | 2.874(4) | 2.882(5) |
| *Bond angles* | | | | | |
| S(1)–Ni(1)–S(2) | 78.59(6) | 78.1(2) | 78.6(2) | 78.9(2) | 77.9(3) |
| S(1)–Ni(1)–S(5) | 99.12(5) | 98.1(2) | 98.0(1) | 99.3(1) | 99.0(2) |
| S(2)–Ni(1)–S(6) | 99.22(5) | 101.2(2) | 100.6(2) | 98.9(1) | 99.9(2) |
| S(5)–Ni(1)–S(6) | 83.08(5) | 82.4(2) | 82.8(2) | 82.9(2) | 83.2(2) |
| S(3)–Ni(2)–S(4) | 78.65(6) | 78.3(2) | 78.8(2) | 78.5(2) | 78.6(2) |
| S(3)–Ni(2)–S(5) | 98.26(5) | 98.3(1) | 96.9(2) | 99.3(1) | 100.2(2) |
| S(4)–Ni(2)–S(6) | 99.94(5) | 99.8(1) | 100.9(2) | 99.4(1) | 97.8(2) |
| S(5)–Ni(2)–S(6) | 83.11(5) | 83.6(2) | 83.5(2) | 82.8(1) | 83.3(2) |
| P(1)–Ni(3)–P(2) | 88.60(5) | 88.9(1) | 89.1(1) | 88.4(1) | 89.2(1) |
| P(1)–Ni(3)–S(5) | 95.90(5) | 93.7(1) | 94.1(1) | 96.3(1) | 94.3(1) |
| P(2)–Ni(3)–S(6) | 93.25(4) | 95.7(1) | 95.1(1) | 93.8(1) | 94.4(1) |
| S(5)–Ni(3)–S(6) | 82.03(5) | 81.7(1) | 81.7(1) | 81.5(1) | 82.1(1) |

Table 3
Comparison of molecular parameters of $Ni_3S_2$ clusters in compounds **1**, **2** and related phosphine complexes



| Compound | a | b | c | d | e | f | Reference |
|---|---|---|---|---|---|---|---|
| $[Ni_3S_2(dppe)(S_2COMe)]$ | 2.177(1) | 2.174(1) | 2.170(1) | 2.171(1) | 2.194(1) | 2.199(1) | this work |
| $[Ni_3S_2(dppe)(S_2COMe)]$ [a] A | 2.168(4) | 2.151(4) | 2.186(4) | 2.152(4) | 2.197(3) | 2.189(3) | this work |
| B | 2.164(4) | 2.165(4) | 2.182(4) | 2.153(4) | 2.194(3) | 2.203(3) | this work |
| C | 2.172(4) | 2.170(4) | 2.170(3) | 2.177(3) | 2.203(3) | 2.200(3) | this work |
| D | 2.163(4) | 2.162(4) | 2.177(5) | 2.176(5) | 2.193(4) | 2.197(3) | this work |
| $[Ni_3S_2(dppe)(S_2C\text{-}NEt_2)_2]$ | 2.168(3) | 2.168(3) | 2.161(4) | 2.161(4) | 2.213(3) | 2.213(3) | [8] |
| $[Ni_3S_2(dppe)_3][PF_6]_2 \cdot MeCN$ | 2.190(3) | 2.190(3) | 2.190(3) | 2.190(3) | 2.195(4) | 1.195(4) | [9] |
| $[Ni_3S_2(dppe)(2,2'\text{-}C_6H_4C_6H_4)][PF_6]_2$ | 2.191(2) | 2.194(2) | 2.201(2) | 2.192(2) | 2.233(2) | 2.238(2) | [10] |
| $[Ni_3S_2(PEt_3)_6][BPh_4]_2$ | 2.20(3) | 2.11(3) | 2.11(3) | 2.11(3) | 2.16(3) | 2.23(3) | [11] |
| $[Ni_3S_2(PEt_3)_5Cl][BPh_4]$ | 2.199(4) | 2.195(4) | 2.194(4) | 2.197(4) | 2.135(4) | 2.200(5) | [12] |
| $[Ni_3S_2(PEt_3)_5(SH)][BPh_4]$ | 2.190(5) | 2.193(5) | 2.201(5) | 2.199(5) | 2.168(5) | 2.194(5) | [13] |
| $[Ni_3S_2(PEt_3)_5(H_2O)][PF_6]$ | 2.16(1) | 2.20(2) | 2.23(2) | 2.16(2) | 2.14(2) | 2.10(2) | [14] |
| $[Ni_3S_2(PPh_3)_4Cl_2]$ | 2.200(2) | 2.193(2) | 2.138(2) | 2.146(2) | 2.192(2) | 2.180(2) | [15] |

[a] Four independent molecules in the crystal.

on a Nonius Kappa CCD diffractometer using Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å) at room temperature for **1** and **2** and at 150 K for **3**. The unit cell parameters are based on 7304 reflections with $2.53° \leq \theta \leq 27.46°$ for **1**, on 32334 reflections with $1.08° \leq \theta \leq 25.50°$ for **2** and on 17600 reflections with $1.27° \leq \theta \leq 30.00°$ for **3**. The data were processed using software described in Ref. [5]. The structures **1** and **2** were solved by direct methods and refined by the full-matrix least-squares method on $F^2$ using the SHELX-97 program package [6]. The non-hydrogen atoms have been refined anisotropically. The H-atoms were placed in calculated positions and refined isotropically with a riding model.

The structure of compound **3** has been reported in Ref. [3], but the data were collected from a twinned crystal. To obtain more reliable geometric parameters, we redetermined this structure using a monocrystal without traces of twining at a low temperature (150 K). The structure determination of compound **3** at low temperature is more accurate ($R = 0.0381$) than the one that previously reported in the literature ($R = 0.0673$) [3].

## 3. Results and discussion

### 3.1. Synthesis

We found that when a deficit of dppe is used in the reactions with nickel(II) xanthates (Ni:dppe = 2:1) in methylethylketone, after concentration of the solution, black crystals are formed. These were identified as trinuclear complexes containing the $Ni_3(\mu_3\text{-}S)_2$ cluster and have the composition $[Ni_3(\mu_3\text{-}S)_2(S_2COR)_2(dppe)]$ [R = Me (**1**), Et (**2**)]. The crystal structures of the methyl and ethyl derivatives were determined by single crystal X-ray diffraction and the results are discussed below.

The trinuclear $Ni_3(\mu_3\text{-}S)_2$ cluster was first identified by X-ray diffraction in a cyclopentadienylnickel derivative $[(\eta^5\text{-}C_5H_5)_3Ni_3(\mu_3\text{-}S)_2]$ [7], then in several other compounds, most of which three are phosphine complexes, i.e. $[Ni_3(\mu_3\text{-}S)_2(PEt_3)_2(S_2CNEt_2)_2]$ [8], $[Ni_3(\mu_3\text{-}S)_2(dppe)_3][PF_6]_2\cdot MeCN$ [9], $[Ni_3(\mu_3\text{-}S)_2(dppe)_3(2,2'\text{-}C_6H_4C_6H_4)]$ [10], $[Ni_3(\mu_3\text{-}S)_2(PEt_3)_6][BPh_4]_2$ [11], $[Ni_3(\mu_3\text{-}S)_2(PEt_3)_5Cl][BPh_4]$ [12], $[Ni_3(\mu_3\text{-}S)_2(PEt_3)_5(SH)][BPh_4]$ [13], $[Ni_3(\mu_3\text{-}S)_2(PEt_3)_5(H_2O)][PF_6]$ [14], $[Ni_3(\mu_3\text{-}S)_2(PPh_3)_4Cl_2]$ [15] and $[NBu_4][Ni_3(\mu_3\text{-}S)_2(S_3N)_3]$ [16]. The compound $[Ni_3(\mu_2\text{-}S)_2(PEt_3)_6][BPh_4]_2$ was obtained from $Ni[BF_4]_2$, $PEt_3$ and $H_2S$ in ethanol [11]; whereas the compound $[Ni_3(\mu_2\text{-}S)_2(PPh_3)_4Cl_2]$ was formed in the reaction of $[NiCl_2(PPh_3)_2]$ with $S(SiMe_3)_2$ [15]. The dithiocarbamato derivative $[Ni_3(\mu_3\text{-}S)_2(PEt_3)_2(S_2CNEt_2)_2]$ was prepared by a substitution reaction, from $[Ni_3(\mu_2\text{-}S)_2(PEt_3)_6][BPh_4]_2$ and $NaS_2CNEt_2\cdot 3H_2O$ in ethanol/acetone [8].

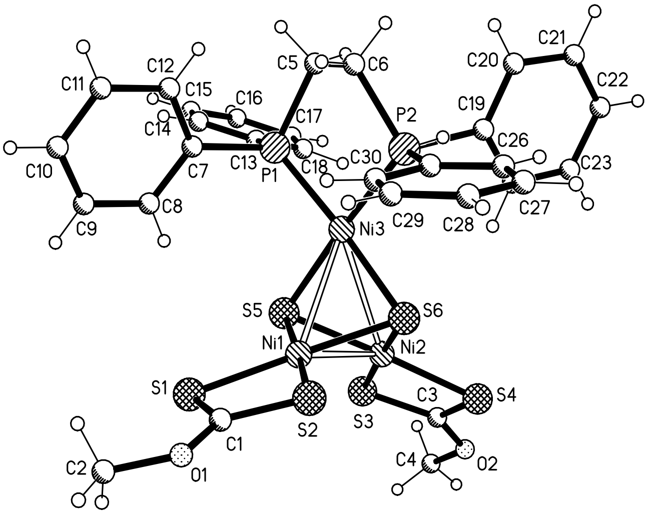


Fig. 1. View of complex **1**.

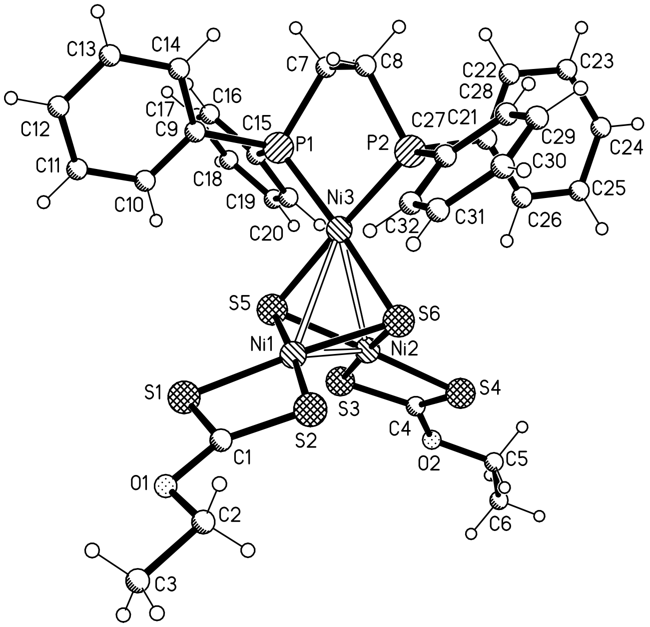


Fig. 2. The general view of one of the independent molecules (**a**) in the crystal structure of complex **2**.

The red–orange dithiocarbonato complex $[Ni(S_2CO)(dppe)]$ (**3**) was obtained whenever nickel(II) xanthates, $[Ni(S_2COR)_2]$ (R = Me, Et, Pr, $CH_2CH_2OMe$), were mixed with dppe in methylethylketone in a 1:1 molar ratio and the solution was allowed to concentrate by evaporation at room temperature. We selected a crystal obtained from the ethylxanthate and investigated the crystal structure at low temperature (150 K). Similar compounds with the dithiocarbonato ligand are also known for other Group 10 metals, e.g. $[Pd(S_2CO)(PR_2Ph)_2]$ where R = Me, Ph [17], $[Pt(S_2CO)(dppe)]$ [18] and $[Pt(S_2CO)(PR_2Ph)_2]$ where R = Ph, OMe [18,19]. In all these, the dithiocarbonato ligand is bidentate chelating. Only in the dinuclear iron

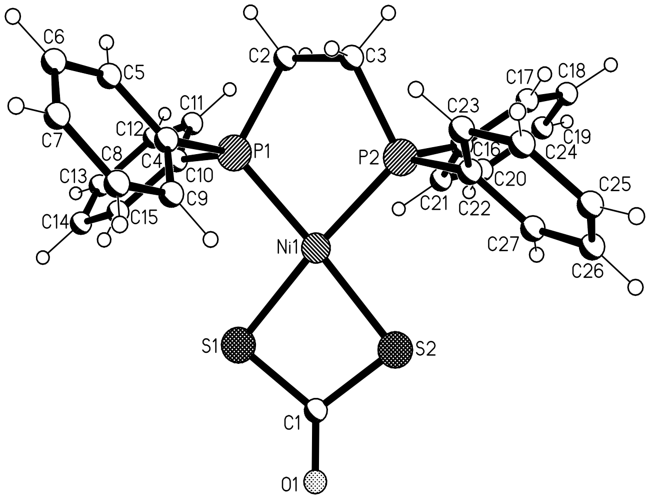


Fig. 3. View of the molecule **3a** in the crystal structure of complex **3**.

complex $[Fe_2(S_2CO)(CO)_6]$ does the dithio ligand display a different pattern, i.e. bimetallic tetraconnective coordination mode [20].

### 3.2. X-ray structure determination

The X-ray structure analysis showed that the crystal structures of **1** and **2** consist of discrete trinuclear $[Ni_3(\mu_3\text{-}S)_2(S_2COMe)_2(dppe)]$ and $[Ni_3(\mu_3\text{-}S)_2(S_2COEt)_2(dppe)]$ complexes, with no significant intermolecular interactions.

The crystal structure of **2** contains four similar crystallographically independent units (**a**, **b**, **c** and **d**) slightly differing in the mutual orientation of the phenyl groups of dppe. The view of the complex **1** and one of the independent molecules **2(a)**, with the atom numbering schemes, are depicted in Fig. 1 and Fig. 2, respectively. Selected bond lengths and angles are given in Table 2. In both structures, the central $Ni_3S_2$ core consists of a triangle of nickel atoms capped by two $\mu_3$-sulfur atoms, thus forming an almost regular trigonal bipyramid. The average $Ni–S_{bridge}$ distances are 2.185 Å, Ni–S–Ni bond angles 80.96(4)° and S···S 2.876(2) Å. All these parameters of the $Ni_3S_2$ core are similar to those reported in the previous references cited (Table 3). Furthermore, two of the nickel atoms coordinate additionally a bidentate xanthate ligand each, and the third nickel atom is coordinated by a chelating tetraphenyldiphosphinoethane molecule. As a result, every metal atom has a square-planar environment determined by neighbouring donor S and P atoms. Thus, the overall geometry may be regarded as built of two square-planar $Ni(II)S_4$ [av. $Ni–S_{xant}$ 2.232(1) Å] and one $Ni(II)S_2P_2$ [av. Ni–P 2.169(1) Å] moieties sharing two sulfur atoms. The dihedral angles between these coordination planes and the plane of the nickel triangle are very close to orthogonal, with the maximum deviation less than 1.2°. The Ni···Ni separations in the metal clusters are in the range of 2.724–2.927 Å and the longest (2.899–2.927 Å) in the triangle correspond invariably to Ni1···Ni2 distance (metal atoms coordinated by xanthato groups).

Table 4
Selected bond lengths (Å) and bond angles (°) for compound **3**

| | **3a** | **3b** |
|---|---|---|
| *Bond length* | | |
| Ni(1)–S(1) | 2.1853(8) | 2.1897(8) |
| Ni(1)–S(2) | 2.1933(8) | 2.1970(8) |
| Ni(1)–P(1) | 2.1602(8) | 2.1562(8) |
| Ni(1)–P(2) | 2.1453(8) | 2.1497(8) |
| S(1)–C(1) | 1.768(3) | 1.763(3) |
| S(2)–C(1) | 1.762(3) | 1.764(3) |
| O(1)–C(1) | 1.206(4) | 1.221(4) |
| P(1)–C(2) | 1.836(3) | 1.835(3) |
| P(1)–C(4) | 1.818(3) | 1.814(3) |
| P(1)–C(10) | 1.813(3) | 1.816(3) |
| P(2)–C(3) | 1.847(3) | 1.834(3) |
| P(2)–C(16) | 1.817(3) | 1.812(3) |
| P(2)–C(22) | 1.813(3) | 1.823(3) |
| *Bond angles* | | |
| S(1)–Ni(1)–S(2) | 80.15(3) | 80.46(3) |
| S(1)–Ni(1)–P(1) | 96.83(3) | 96.70(3) |
| S(1)–Ni(1)–P(2) | 175.27(3) | 172.62(3) |
| S(2)–Ni(1)–P(1) | 176.92(3) | 174.64(3) |
| S(2)–Ni(1)–P(2) | 95.27(3) | 95.77(3) |
| P(1)–Ni(1)–P(2) | 87.76(3) | 87.55(3) |
| C(2)–P(1)–Ni(1) | 108.68(10) | 108.52(10) |
| C(3)–P(2)–Ni(1) | 108.97(10) | 109.42(10) |
| S(1)–C(1)–S(2) | 105.95(17) | 106.90(16) |

Table 5
Hydrogen bonds for **3**

| D–H···A | d(D···A) (Å) | d(H···A) (Å) | d(D–H) (Å) | Angle (D–H···A) (°) |
|---|---|---|---|---|
| C(25a)–H···O(1a) #1 | 3.373(4) | 2.57 | 0.95 | 142.9 |
| C(3b)–H···O(1a) #2 | 3.407(4) | 2.43 | 0.99 | 169.1 |
| C(2a)–H···O(1b) #3 | 3.260(4) | 2.31 | 0.99 | 160.8 |
| C(25b)–H···O(1b) #4 | 3.312(4) | 2.49 | 0.95 | 144.8 |
| C(11a)–H···O(1b) #3 | 3.505(4) | 2.56 | 0.95 | 174.2 |

Symmetry transformations used to generate equivalent atoms: (#1) $x-1, y, z$; (#2) $x-1/2, -y+1, z-1/2$; (#3) $x+1/2, -y+2, z+1/2$; (#4) $x+1, y, z$.

In the structure of **3** two crystallographically independent (**a** and **b**) molecules are present, having essentially the same geometry and they are shown in Fig. 3. The nickel atom is four-coordinated by two sulfur atoms and two phosphorus atoms in a square-planar arrangement of the donor atoms with a slight tetrahedral distortion. The donor atoms displacement

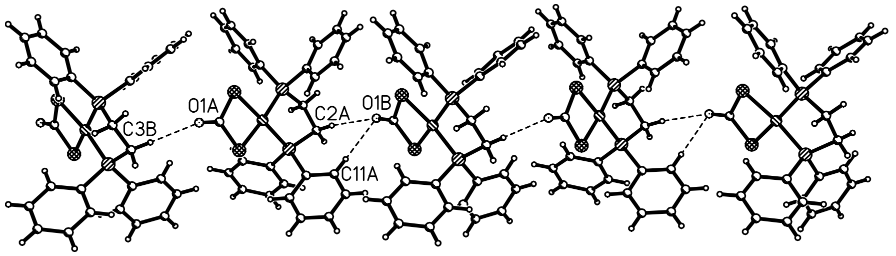


Fig. 4. The supramolecular array of complexes along the *b* axis in the crystal structure of compound **3**.

from the common plane are in the range $-0.1030(4)$–$0.1023(4)$ Å, whereas the metal atom deviation from the best plane is only $-0.0169(5)$ Å.

The bond lengths in the two independent complexes **3a**,**b** are in good agreement (Table 4). The S–C bonds in the dithiocarbonate ligands are completely delocalised and adopt almost the same length 1.764 Å with variation less than 0.005 Å. These values indicate the expected lengthening in comparison with xanthate ligands in the structure of **1** and **2**. The quality of data permits to distinguish between P–C(sp$^2$) and P–C(sp$^3$) bond lengths, which are 1.812–1.823 and 1.834–1.847 Å, respectively. At the same time, the difference in the C=O distances is 0.015 Å and may be due to the intermolecular hydrogen bonds C2(**a**)–H···O1(**b**) (Table 5) ($x+1/2$, $-y+2$, $z+1/2$), which are the shortest intermolecular contacts in the structure. The $C_{methylene}$–H···O hydrogen bonds connect the alternate **a** and **b** molecules in an infinite chain-like supramolecular array along the *b* axis of the unit cell (Fig. 4).

## 4. Supplementary material

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 205048 (**1**), 205049 (**2**) and 205050 (**3**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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