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Synthesis, Characterization, and X-ray Crystal Structures of (Diphosphine)Ni(dmit) and (Diphosphine)Ni(dmio) (Diphosphine = dppv, dppb) Complexes

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Keywords: dmit; dmio; Nickel; Diphosphine; X-ray diffraction

Abstract. Four complexes with the ligands dmit and dmio were synthesized. Reaction of $(PhCO)_2$(dmit) and $(PhCO)_2$(dmio) with MeONa afforded the intermediates 2-thioxo-1,3-dithiole-4,5-dithiolate dianion and 2-oxo-1,3-dithiole-4,5-dithiolate dianion, respectively. Reaction of the two dianions with (diphosphine)$NiCl_2$ [diphosphine = (*Z*)-1,2-bis(diphenylphosphanyl)ethane (dppv), 1,2-bis(diphenylphosphanyl)-benzene (dppb)] gave (dppv)Ni(dmit) (**1**), (dppb)Ni(dmit) (**2**), (dppv)Ni(dmio) (**3**), and (dppb)Ni(dmio) (**4**). This synthesis route was found to be an efficient pathway to prepare dmit and dmio ligand complexes. Complexes, **1**–**4** were fully characterized by elemental analysis and IR, ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectroscopy. In addition, the molecular structures of **1**, **3** and **4** were established by X-ray diffraction.

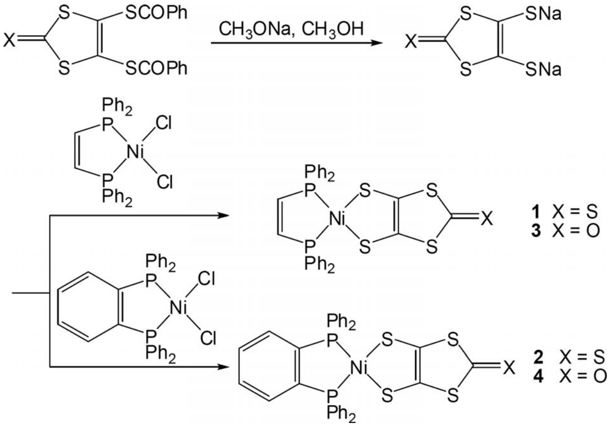
Introduction

Over the past 30 years, complexes with the ligand dmit and their oxygen substituted analogs have received considerable attention because of their high conductivities and in some cases superconductivities.[1–5] Especially, the 2-thioxo-1,3-dithiole-4,5-dithiolate dianion ($dmit^{2-}$) has been used extensively for the preparation of mononuclear bis-dmit and tris-dmit complexes of transition group metals.[6–8] Although a series of $(phosphine)_2M$(dithiolate) complexes have been reported,[9–16] the complex (dppe)Ni(pdt), which was synthesized by *Schmidt* by reaction of (dppe)$NiCl_2$ with $HSCH_2CH_2CH_2SH$ and which has been used to synthesize the [NiFe] hydrogenase model complex (dppe)Ni(μ-pdt)$Fe(CO)_3$ was of particular interest.[17–19] Complexes (diphosphine)Ni(dmit) (diphosphine = dppv, dppb) have not been prepared to date.

As a continuation of our studies on (diphosphine)$NiCl_2$,[20] herein we report the synthesis of four new (diphosphine)Ni(dithiolate) (diphosphine = dppv, dppb) complexes, where dithiolate ligands are 2-thioxo-1,3-dithiole-4,5-dithiolate (dmit) and 2-oxo-1,3-dithiole-4,5-dithiolate (dmio). In the end, complexes (dppv)Ni(dmit) (**1**), (dppb)Ni(dmit) (**2**), (dppv)Ni(dmio) (**3**), and (dppb)Ni(dmio) (**4**) were prepared in high yields and fully characterized by various spectroscopy, as well as **1**, **3**, and **4** were established by X-ray crystallography. We expect the complexes to be used to synthesize [NiFe] hydrogenase model compounds.

Results and Discussion

As indicated in Scheme 1, reaction of $(PhCO)_2$(dmit) and $(PhCO)_2$(dmio) with MeONa affords the intermediates 2-thioxo-1,3-dithiole-4,5-dithiolate dianion and 2-oxo-1,3-dithiole-4,5-dithiolate dianion, respectively. Reaction of the two dianions with (diphosphine)$NiCl_2$ (diphosphine = dppv, dppb) produces (dppv)Ni(dmit) (**1**), (dppb)Ni(dmit) (**2**), (dppv)Ni(dmio), (**3**) and (dppb)Ni(dmio) (**4**) in satisfactory yields. In addition, this synthesis route is found to be an efficient pathway to prepare those complexes.



Scheme 1. Preparation of complexes **1**–**4**.

Complexes **1**–**4** are all air-stable solids. They were fully characterized by elemental analysis and IR, ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectroscopy. For example, the IR spectra of **1** and **2** displayed a absorption bands in the region 1014–1015 cm^{-1} for their ν(C=S) groups, whereas the IR spectra of **3** and **4** displayed a absorption bands in the region 1615–1623 cm^{-1} for their ν(C=O) groups, respectively. The ^{1}H NMR spectra of **1**–**4** displayed signals in the range of 7.10–7.92 ppm

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for their Ph groups. In addition the ^{31}P NMR spectra of **1**–**4** in DMSO or $CDCl_3$ solutions gave peaks at $\delta = 70.64$ ppm for **1**, 58.34 ppm for **2**, 69.44 ppm for **3**, and 58.73 ppm for **4**, which can be assigned to the diphosphine (dppv, dppb) ligands.

Crystals of complexes **1**, **3**, and **4** suitable for X-ray diffraction analysis were grown from the CH_2Cl_2/*n*-hexane mixture after slow evaporation at –20 °C. Their molecular structures are presented in Figure 1, Figure 2, and Figure 3. Their selected bond lengths and angles are listed in Table 1, and details of crystal data and structure refinements are summarized in Table 2.

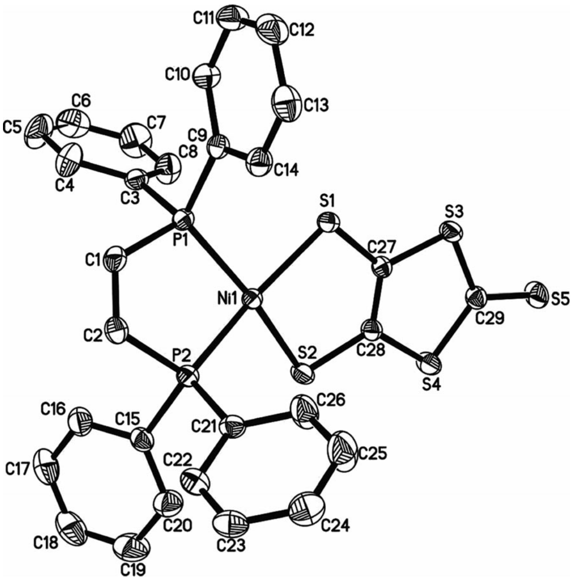

Figure 1. ORTEP view of **1** with 30 % probability level ellipsoids.

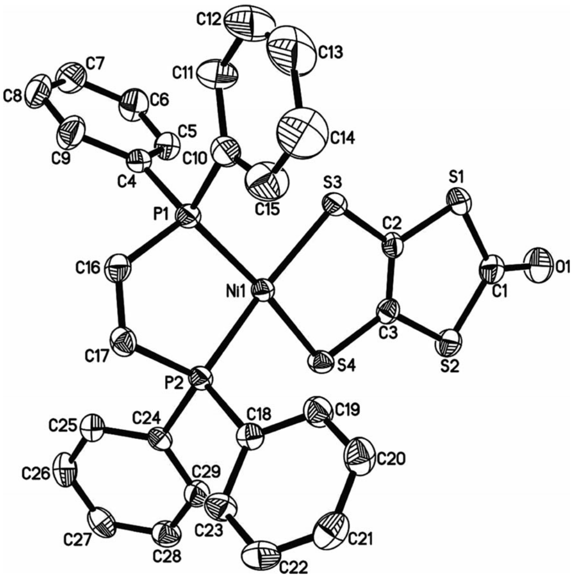

Figure 2. ORTEP view of **3** with 30 % probability level ellipsoids.

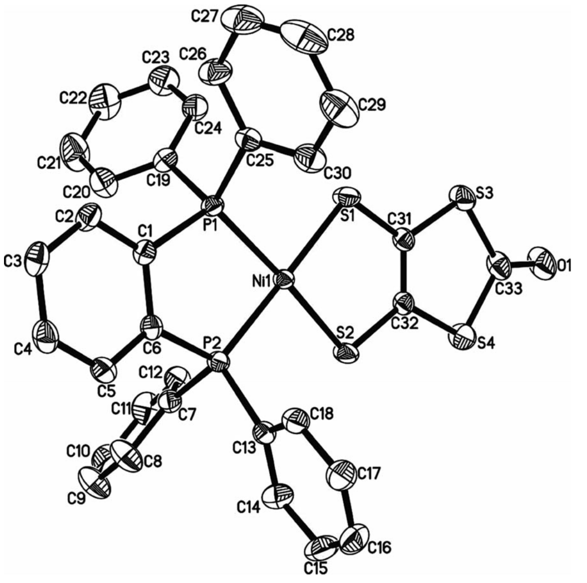

Figure 3. ORTEP view of **4** with 30 % probability level ellipsoids.

Table 1. Selected bond lengths /Å and angles /° for **1**, **3** and **4**.

1			
Ni(1)–P(1)	2.1507(6)	S(1)–C(27)	1.733(2)
Ni(1)–P(2)	2.1520(6)	S(5)–C(29)	1.647(2)
Ni(1)–S(1)	2.1601(6)	P(1)–C(1)	1.809(2)
Ni(1)–S(2)	2.1693(6)	P(2)–C(2)	1.813(2)
P(1)–Ni(1)–P(2)	88.43(2)	S(1)–Ni(1)–S(2)	94.71(2)
P(1)–Ni(1)–S(1)	89.13(2)	C(27)–S(1)–Ni(1)	100.58(7)
P(2)–Ni(1)–S(1)	160.48(2)	C(28)–S(2)–Ni(1)	100.43(7)
P(1)–Ni(1)–S(2)	165.85(3)	C(1)–P(1)–Ni(1)	108.44(7)
P(2)–Ni(1)–S(2)	92.34(2)	C(3)–P(1)–Ni(1)	114.76(7)
3			
Ni(1)–P(1)	2.1570(7)	S(1)–C(1)	1.768(3)
Ni(1)–P(2)	2.1606(7)	O(1)–C(1)	1.217(3)
Ni(1)–S(3)	2.1681(7)	P(1)–C(16)	1.812(3)
Ni(1)–S(4)	2.1642(7)	P(2)–C(17)	1.806(3)
P(1)–Ni(1)–P(2)	88.07(3)	S(4)–Ni(1)–S(3)	94.20(3)
P(1)–Ni(1)–S(3)	89.67(3)	C(3)–S(4)–Ni(1)	101.01(9)
P(1)–Ni(1)–S(4)	170.99(3)	C(16)–P(1)–Ni(1)	108.19(9)
P(2)–Ni(1)–S(3)	165.55(3)	C(2)–S(3)–Ni(1)	100.96(9)
P(2)–Ni(1)–S(4)	90.15(3)	C(24)–P(2)–S(1)	120.71(8)
4			
Ni(1)–P(1)	2.1612(8)	S(1)–C(31)	1.733(3)
Ni(1)–P(2)	2.1640(8)	O(1)–C(33)	1.206(3)
Ni(1)–S(2)	2.1707(9)	P(1)–C(1)	1.829(3)
Ni(1)–S(1)	2.1744(8)	P(2)–C(6)	1.819(3)
P(1)–Ni(1)–P(2)	87.72(3)	S(2)–Ni(1)–S(1)	93.30(3)
P(1)–Ni(1)–S(2)	176.19(3)	C(31)–S(1)–Ni(1)	101.38(10)
P(1)–Ni(1)–S(1)	89.92(3)	C(1)–P(1)–Ni(1)	109.58(9)
P(2)–Ni(1)–S(1)	176.49(3)	C(32)–S(2)–Ni(1)	101.46(9)
P(2)–Ni(1)–S(2)	89.16(3)	C(6)–P(2)–Ni(1)	109.42(9)

As shown in Figure 1, Figure 2, and Figure 3, the arrangement at the central nickel atom in each of the complexes is square-planar with the NiP_2S_2 chromophore. The nickel atom is coordinated by two phosphorus atoms from diphosphine (diphosphine = dppv, dppb) ligands and two sulfur atoms from dmit or dmio ligand.

The crystallographic study of **1**, **3**, and **4** show that each nickel atom is coordinated by two phosphorus atoms from diphosphine ligand (dppv or dppb), which is consistent with the results of the ^{31}P NMR spectra. The Ni–P and Ni–S bond

Table 2. Crystallographic data and structure refinements results for **1**, **3**, and **4**.

	1	**3**	**4**
Mol. formula	$C_{29}H_{22}NiP_2S_5$	$C_{29}H_{22}NiOP_2S_4$	$C_{33}H_{24}NiOP_2S_4$
Mol weight	651.42	635.36	685.41
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a /Å	9.6598(12)	14.7078(4)	13.435(3)
b /Å	12.8619(17)	11.1060(3)	12.965(2)
c /Å	12.9484(17)	19.3128(5)	22.341(4)
α /°	101.493(2)	90	90
β /°	101.101(2)	92.397(2)	106.436(3)
γ /°	108.649(2)	90	90
V /Å^3	1435.7(3)	3151.89(14)	3732.3(12)
Z	2	4	4
Dc /g•cm^{-3}	1.507	1.339	1.220
Abs. coeff. /mm^{-1}	1.170	1.002	0.851
F(000)	668	1304	1408
$2\theta_{max}$ /°	50.06	52.74	50.06
Index ranges	$-10 \le h \le 11$; $-15 \le k \le 15$. $-11 \le l \le 15$	$-18 \le h \le 12$; $-13 \le k \le 13$. $-24 \le l \le 24$	$-15 \le h \le 15$; $-15 \le k \le 15$. $-26 \le l \le 20$
No. of reflection	7398	6409	18621
No. of independent reflection	5033	4803	6580
Goodness of fit	1.033	1.012	1.105
R	0.0260	0.0399	0.0357
Rw	0.0634	0.0954	0.1071
Largest different peak and hole /e•Å^{-3}	0.339 / –0.234	0.332 / –0.289	0.339 / –0.230

lengths of **1**, **3**, and **4** (Table 1) are shorter than the corresponding bonds of complex (tp)Ni(dmit).[21] The selected bond angels P(1)–Ni(1)–P(2) 88.43°, P(1)–Ni(1)–S(1) 89.13°, S(1)–Ni(1)–S(2) 94.71°, and P(2)–Ni(1)–S(2) 92.34° for **1** and the corresponding bonds for **3** and **4** indicated that the coordination arrangements around nickel are distorted from an ideal arrangement.

Conclusions

Four complexes with the ligands dmit and dmio were prepared in high yields by reaction of the 2-thioxo-1,3-dithiole-4,5-dithiolate and 2-oxo-1,3-dithiole-4,5-dithiolate dianions with (diphosphine)$NiCl_2$ (diphosphine = dppv, dppb). This synthesis route can also be used to prepare other analogs. All the four complexes were fully characterized by elemental analysis and IR, ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectroscopy. Furthermore, the molecular structures of **1**, **3**, and **4** were determined by X-ray diffraction. The complexes have potential to be used in the synthesis of [NiFe] hydrogenase model compounds.

Experimental Section

General: All reactions were carried out in a nitrogen atmosphere using standard Schlenk techniques. All solvents were dried using standard procedures and distilled in a nitrogen atmosphere. $(PhCO)_2$(dmit), $(PhCO)_2$(dmio),[22] Ni(dppv)Cl_2 (dppv = $Ph_2PCH{=}CHPPh_2$),[23] and Ni(dppb)Cl_2 [dppb = 1,2-$(Ph_2P)_2C_6H_4$][24] were prepared according to literature procedures. Some other materials were available commercially. Preparative TLC was carried out on glass plates (26 × 20 × 0.25 cm) coated with silica gel H (10–40 μm). IR spectra were recorded at room temperature with a Bruker Vector 22 infrared spectrophotometer. ^{1}H (^{13}C, ^{31}P) NMR spectra were obtained with a Varian Mercury Plus 400 NMR spectrometer. Elemental analyses were performed with an Elementar Vario EL analyzer. Melting points were determined with a SGW X-4 microscopic melting point apparatus and were uncorrected.

(dppv)Ni(dmit) (1): MeONa (0.054 g, 1.0 mmol) was slowly added to a solution of $(PhCO)_2$(dmit) (0.203 g, 0.5 mmol) in 20 mL MeOH. The mixture was stirred for 0.5 h at room temperature to give a red solution. Afterwards Ni(dppv)Cl_2 (0.263 g, 0.5 mmol) was added, and the resulting mixture was stirred for 2 h at room temperature. Volatiles were removed under vacuum and the residue was subjected to TLC using CH_2Cl_2/THF (v/v = 4:1) as eluent. From the main green band, complex **1** (0.290 g) was obtained as a green solid. Yield: 89 %. Mp 276–278 °C. $C_{29}H_{22}NiP_2S_5$: calcd. C 53.47; H 3.40 %; found: C 53.36; H 3.58 %. **IR** (KBr): ν(C=S) 1014 (m) cm^{-1}. **^{1}H NMR** (400 MHz, DMSO): δ = 7.57–8.04 (m, 22 H, 4C_6H_5, CH=CH) ppm. **^{13}C NMR** (100.6 MHz, DMSO): δ = 129.72, 132.37, 133.34, 138.64, 138.72, 138.80 (C_6H_5, $S_2C{=}CS_2$), 147.30 (PCH=CHP), 219.16 (C=S) ppm. **^{31}P NMR** (162 MHz, DMSO, 85 % H_3PO_4): δ = 70.64 (s) ppm.

(dppb)Ni(dmit) (2): MeONa (0.054 g, 1.0 mmol) was slowly added to a solution of $(PhCO)_2$(dmit) (0.203 g, 0.5 mmol) in 20 mL MeOH. The mixture was stirred for 0.5 h at room temperature to give a red solution. Afterwards Ni(dppb)Cl_2 (0.288 g, 0.5 mmol) was added, and the resulting mixture was stirred for 6 h at room temperature. After removing the solvent, column chromatography of the crude reaction mixture on silica gel with CH_2Cl_2 afforded **2** (0.268) as a green solid. Yield: 76 %. Mp >300 °C. $C_{33}H_{24}NiP_2S_5$: calcd.C 56.50; H 3.45 %; found: C 56.61; H 3.50 %. **IR** (KBr): ν(C=S) 1015 (m) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.35–7.88 (m, 22 H, 4C_6H_5, CH=CH) ppm. **^{31}P NMR** (162 MHz, $CDCl_3$, 85 % H_3PO_4): δ = 58.34 (s) ppm.

(dppv)Ni(dmio) (3): The same procedure as that for **1** was followed, but $(PhCO)_2$(dmio) (0.195 g, 0.5 mmol) was used instead of $(PhCO)_2$(dmit). From the main band, complex **3** (0.278 g) was obtained as a dark solid. Yield: 87 %. Mp 238–240 °C. $C_{29}H_{22}NiOP_2S_4$: calcd. C 54.82; H 3.49 %; found: C 54.67; H 3.60 %. **IR** (KBr): ν(C=O) 1623 (m) cm^{-1}. **^{1}H NMR** (400 MHz, DMSO): δ = 7.56–8.04 (m, 22 H, 4C_6H_5, CH=CH) ppm. **^{13}C NMR** (100.6 MHz, DMSO): δ = 123.53, 123.62, 129.65, 129.88, 130.07, 130.27, 132.25, 133.33 (C_6H_5, $S_2C{=}CS_2$), 147.41 (PCH=CHP), 198.98 (C=O) ppm. **^{31}P NMR** (162 MHz, DMSO, 85 % H_3PO_4): δ = 69.44 (s) ppm.

(dppb)Ni(dmio) (4): The same procedure as that for **2** was followed, but $(PhCO)_2$(dmio) (0.195 g, 0.5 mmol) was used in place of $(PhCO)_2$(dmit). From the main band, complex **4** (0.285 g) was obtained as a dark solid. Yield: 83 %. Mp 281–283 °C. $C_{33}H_{24}NiOP_2S_4$: calcd. C 57.82; H 3.53 %; found: C 57.65; H 3.80 %. **IR** (KBr): ν(C=O) 1615 (m) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.36–7.64 (m, 24 H, 4C_6H_5, C_6H_4) ppm. **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ = 124.37, 124.45, 128.70, 128.79, 131.40, 132.57, 133.08, 133.71, 142.18 (C_6H_5, C_6H_4, $S_2C{=}CS_2$), 201.07 (C=O) ppm. **^{31}P NMR** (162 MHz, $CDCl_3$, 85 % H_3PO_4): δ = 58.73 (s) ppm.

X-ray Crystallographic Analysis: The single crystals of **1**, **3**, and **4** suitable for X-ray diffraction analyses were grown by slow evaporation of the CH_2Cl_2/*n*-hexane solutions at about –20 °C. The single crystals were mounted on a Rigaku MM-007 (rotating anode) diffractometer equipped with Saturn 70CCD. Data were collected at 293 K by using a graphite monochromator with Mo-K_α radiation (λ = 0.71073) in the ω-ϕ scanning mode. Absorption correction was performed by the CRYSTALCLEAR program.[25] The structure was solved by direct methods using the SHELXS-97 program[26] and refined by full-matrix least-squares techniques (SHELXL-97)[27] on F^2. Hydrogen atoms were located by using the geometric method. Details of crystal data, data collections, and structure refinements are summarized in Table 2.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-914956, CCDC-907972, and CCDC-918231 (for **1**, **3**, and **4**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

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