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Structural study of two *N*(4)-substituted thiosemicarbazones prepared from 1-phenyl-1,2-propanedione-2-oxime and their binuclear nickel(II) complexes

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Abstract

The crystal structures of the oxime/thiosemicarbazones 1-phenyl-1-{*N*(4)-methyl- and 1-phenyl-1-{*N*(4)-ethylthiosemicarbazone}-2-oximepropane, H_2Po4M and H_2Po4E, were found to have the oxime and thiosemicarbazone moieties on opposite sides of the carbon–carbon backbone. Intermolecular hydrogen bonding involves the oxime function forming a symmetrical dimer for both compounds. The structures of the binuclear nickel(II) complexes, [Ni(Po4M)]$_2$ and [Ni(Po4E)]$_2$, show that bridging by the oximato N–O results in a centrosymmetric arrangement of the two planar nickel centers in each complex. The coordinated thiosemicarbazonato moieties undergo the expected changes in bond distances and angles compared to H_2Po4M and H_2Po4E. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Oxime; Thiosemicarbazone; Binuclear nickel; Oximato bridge

1. Introduction

Although thiosemicarbazones [1] and oximes [2], as well as their metal complexes, have been studied extensively, there have been few reports concerning the structures of molecules and metal complexes containing both a thiosemicarbazone and oxime group. The structure of 2-oxime-3-thiosemicarbazonebutane, H_2Bo4DH, shows the oxime and thiosemicarbazone moieties to be on opposite sides of the carbon–carbon backbone [3]. The same arrangement of the two moieties was found for 1-phenyl-1-(3-piperidylthiosemicarbazone)-2-oximepropane, H_2Popip [4]. Included in that report was a 6-coordinate nickel(II) complex with the two monoanionic ligands (i.e. loss of a thiosemicarbazone proton) coordinated via the thiosemicarbazonato imine nitrogen and thiolato sulfur, as well as the oxime nitrogen. Oximes and thiosemicarbazones can both function as neutral or anionic ligands, and both are capable of being bridging ligands between metal centers in binuclear (or polynuclear) complexes. Binuclear copper(II) and nickel(II) complexes with oximato N–O bridges have been investigated crystallographically and magnetically [5]. Anionic thiosemicarbazone moieties have been shown to bridge metal centers in two different ways: (1) the thiolato sulfur in trinuclear palladium(II) complexes [6,7] and (2) chelation of imine nitrogen and thiolato sulfur to one metal

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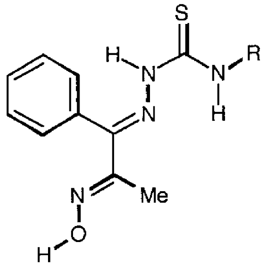

H_2Po4M, R = Me

H_2Po4E, R = Et

Fig. 1. Representation of H_2Po4M and H_2Po4E.

center and coordination of the hydrazinic nitrogen to a second metal center [8]. If both the thiosemicarbazone and oxime functions become anionic, one or the other must bridge in order for the nickel(II) center(s) to be 4-coordinate; determining which function provides the bridge is the basis of this study. Fig. 1 shows the representations of 1-phenyl-1-(*N*(4)-methyl- and 1-phenyl-1-(*N*(4)-ethylthiosemicarbazone)-2-oximepropane, H_2Po4M and H_2Po4E.

2. Experimental

2.1. Syntheses and spectroscopic characterization

Five millimoles (0.815 g) of 1-phenylpropane-1,2-dione-2-oxime (Aldrich) was combined with 5 mmol

Table 1
Crystal data and structure refinement for H_2Po4M, H_2Po4E, $[Ni(Po4M)]_2\cdot 2CHCl_3$ and $[Ni(Po4E)]_2$

Empirical formula	$C_{11}H_{14}N_4OS$	$C_{12}H_{16}N_4OS$	$C_{24}H_{26}Cl_6N_8Ni_2O_2S_2$	$C_{24}H_{28}N_8Ni_2O_2S_2$
Color, habit	Colorless, rod	Colorless, rod	Brown, rod	Brown, rod
Crystal size (mm^3)	$0.20 \times 0.20 \times 0.60$	$0.25 \times 0.17 \times 0.10$	$0.60 \times 0.12 \times 0.09$	$0.19 \times 0.10 \times 0.03$
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1/n$ (#14)	$P2_1/n$ (#14)	*Pbca* (#61)	*P*-1 (#2)
Unit cell dimensions				
a (Å)	5.588(6)	5.6690(4)	16.7130(2)	7.0920(8)
b (Å)	10.522(4)	10.4070(4)	7.0280(6)	9.1340(11)
c (Å)	21.656(5)	23.1520(15)	28.9740(10)	10.6660(15)
α (°)	90(0)	90(0)	90(0)	88.681(7)
β (°)	96.29(5)	91.273(3)	90(0)	86.901(7)
γ (°)	90(0)	90(0)	90(0)	86.572(8)
Volume (Å^3)	1266(1)	1365.57(14)	3403.3(3)	688.55(15)
Z	4	4	4	1
Formula weight	250.32	264.35	852.76	642.08
Density(calc.) (mg/m^3)	1.314	1.286	1.664	1.548
Absorption coefficient (mm^{-1})	0.246	0.232	1.738	1.557
F(000)	528	560	1728	332
θ Range for data collection (°)	2.10–27.48	2.15–24.67	2.44–24.70	1.91–24.69
Index ranges	$0 \le h \le 7$	$-6 \le h \le 6$	$-19 \le h \le 19$	$-8 \le h \le 8$
	$0 \le k \le 13$	$-12 \le k \le 11$	$-8 \le k \le 8$	$-10 \le k \le 10$
	$-27 \le l \le 27$	$-26 \le l \le 27$	$-33 \le l \le 34$	$-11 \le 1 \le 12$
Total reflections	3377	4438[a]	5332[a]	3995[a]
Unique reflections (R_{int})	2901 (0.075)	2314 (0.0432)	2873 (0.0579)	2304 (0.0515)
Absorption correction	None	HKL-Scalepack	HKL-Scalepack	HKL-Scalepack
Max./min. transmission	1.000/0.959	0.9772/0.9444	0.8593/0.4220	0.9621/0.7563
Final *R* indices [$I > 2.0\sigma(I)$]	$R_1 = 0.066$	$R_1 = 0.0401$	$R_1 = 0.0423$	$R_1 = 0.0393$
	$wR_2 = 0.273$	$wR_2 = 0.0902$	$wR_2 = 0.0955$	$wR_2 = 0.0745$
R indices (all data)	$R_1 = 0.208$	$R_1 = 0.0829$	$R_1 = 0.0835$	$R_1 = 0.0715$
	$wR_2 = 0.273$	$wR_2 = 0.1060$	$wR_2 = 0.1081$	$wR_2 = 0.0838$
Goodness-of-fit on F^2	1.342	0.956	0.960	0.962
Largest diff. peak/hole (eÅ^{-3})	0.47/−0.55	0.152/−0.153	0.393/−0.430	0.286/−0.281

[a] After merging (Nonius CCD diffractometer).

Table 2
Selected bond distances (Å) for H_2Po4M, H_2Po4E, [Ni(Po4M)]$_2$ and [Ni(Po4E)]$_2$

Bond	H_2Po4M	H_2Po4E	[Ni(Po4M)]$_2$	[Ni(Po4E)]$_2$
S1–C3	1.669(6)	1.673(2)	1.744(4)	1.743(3)
C3–N4	1.327(7)	1.321(3)	1.329(5)	1.342(4)
C3–N3	1.364(6)	1.367(3)	1.314(5)	1.319(4)
N3–N2	1.372(6)	1.361(3)	1.387(4)	1.377(4)
N2–C2	1.293(6)	1.293(3)	1.302(5)	1.310(4)
C2–C1	1.483(7)	1.467(3)	1.452(5)	1.460(5)
C1–N1	1.290(6)	1.279(3)	1.307(5)	1.314(4)
N1–O1	1.397(5)	1.403(2)	1.349(4)	1.336(3)
Ni–N1			1.885(3)	1.876(3)
Ni–N2			1.846(3)	1.844(3)
Ni–S1			2.172(1)	2.164(1)
Ni–O1a			1.827(3)	1.842(2)

of either 3-methyl-(0.520 g) or 3-ethylthiosemicarbazide (0.590 g, Aldrich) in 40 ml of 95% EtOH and refluxed for 3 h. The volume of the mixtures was slowly reduced at 35 °C, filtered in vacuo and dried. H_2Po4M, yield = 67.7%, m.p. = 195–196 °C (dec); H_2Po4E, yield = 68.5%, m.p. = 192–193 °C (dec). The binuclear nickel(II) complexes were prepared by reacting 0.001 mol of either H_2Po4M (0.250 g) or H_2Po4E (0.264 g) with 0.001 mol, 0.249 g, of [Ni($C_2H_3O_2$)$_2$]·4H_2O in 50 ml of 95% EtOH. The mixtures were refluxed for 2 h, their volumes reduced, and filtered in vacuo. ^{1}H NMR spectra were recorded on a 300 MHz Bruker Spectrometer in $[_2H^6]$-acetone.

Table 3
Selected bond angles (°) for H_2Po4M, H_2Po4E, [Ni(Po4M)]$_2$ and [Ni(Po4E)]$_2$

Angle	H_2Po4M	H_2Po4E	[Ni(Po4M)]$_2$	[Ni(Po4E)]$_2$
O1–N1–C1	112.5(4)	111.9(2)	114.9(3)	114.6(2)
N1–C1–C2	114.8(4)	113.7(2)	112.5(3)	112.9(3)
C1–C2–N2	115.6(5)	116.6(2)	113.2(3)	112.2(3)
C2–N2–N3	116.0(5)	116.9(2)	119.6(3)	119.1(3)
N2–N3–C3	120.7(5)	121.5(2)	110.7(3)	111.0(3)
N3–C3–S1	119.1(4)	118.0(2)	123.3(3)	122.8(3)
N3–C3–N4	115.4(5)	115.5(2)	117.9(4)	119.1(3)
S1–C3–N4	125.5(4)	126.5(2)	118.8(3)	118.1(3)
C1–N1–Ni1			115.0(3)	114.8(2)
O1–N1–Ni1			129.7(2)	130.1(2)
C2–N2–Ni1			116.1(3)	116.4(2)
N3–N2–Ni1			124.1(2)	124.2(2)
C3–S1–Ni1			95.1(1)	95.3(1)
N1–Ni1–S1			169.4(1)	169.80(8)
N1–Ni1–N2			82.8(1)	83.2(1)
N1–Ni1–O1a			102.5(1)	102.7(1)
N2–Ni1–S1			86.7(1)	86.70(9)
N2–Ni1–O1a			172.9(1)	172.4(1)
S1–Ni1–O1a			85.06(9)	87.46(8)

2.2. X-ray data collection, structure solution and refinement

Rod-like crystals were grown by slow evaporation of 1:1 by volume MeOH–MeCN (H_2Po4M and H_2Po4E), 1:1 by volume MeCN–$CHCl_3$ for [Ni(Po4M)]$_2$ and MeCN ([Ni(Po4E)]$_2$) solutions at room temperature. Crystals were mounted on glass fibers and used for data collection at 293 K on a Rigaku AFC6S (H_2Po4M) or Nonius CCD (H_2Po4E, [Ni(Po4M)]$_2$ and [Ni(Po4E)]$_2$) automatic diffractometer, Mo Kα ($\lambda = 0.71073$ Å). Cell constants and an orientation matrix for data collections were obtained by least squares refinements of the diffraction data from 25 reflections for H_2Po4M, 153 reflections for H_2Po4E, 219 reflections for [Ni(Po4M)]$_2$·2CH_2Cl_2 and 154 reflections for [Ni(Po4E)]$_2$. The structures were solved with direct methods and missing atoms were found by difference-Fourier synthesis. All non-hydrogen atoms were refined with anisotropic temperature factors and hydrogens attached to nitrogens and oxygens were found on the difference map and refined isotropically. The CH hydrogens were fixed at $d = 0.96$ Å, allowed to ride on the C atoms and assigned fixed isotropic temperature factor, $U = 0.05$ Å^2. Refinement of the structures was made by full-matrix least-squares on F^2. Scattering factors are from Waasmaier and Kirfel [9], calculations were done by maXus, version 2.0 [10], and graphics are Platon for Windows [11]. Table 1 has summaries of crystal data collection, data reduction, and structure refinement for the four compounds.

3. Results and discussion

The bond distances for the compounds are given in Table 2 and their bond angles in Table 3. Table 4 has the mean plane data, atoms with the greatest deviation from the mean plane and angles between planes. Figs. 2 and 3 show the ORTEP diagrams of H_2Po4E and [Ni(Po4E]$_2$ and are representative of H_2Po4M and [Ni(Po4M)]$_2$, respectively.

Table 4
Mean plane deviations (Å) and angles (°) between planes for H$_2$Po4M, H$_2$Po4E, [Ni(Po4M)]$_2$ and [Ni(Po4E)]$_2$

Compound	Plane	rms dev.	Largest dev.	∠ (°)[a]
H$_2$Po4M	C7–C8–C9–C10–C11–C12	0.0039	C9, 0.008(5)	
	C2–C1–N1–O1	0.0088	C1, 0.012(4)	72.5(3)
	C2–N2–N3–C3–N4–S1	0.0155	C2, 0.034(4)	10.7(4)
H$_2$Po4E	C7–C8–C9–C10–C11–C12	0.0001	C9, 0.004(4)	
	C2–C1–N1–O1	0.0000	C1, 0.003(3)	76.5(3)
	C2–N2–N3–C3–N4–S1	0.0019	N3, 0.016(3)	10.9(4)
[Ni(Po4M)]$_2$	N1–C1–C2–N2–N3–C3–S1	0.0010	C1, 0.045(4)	
	O1–N1–C1–C2	0.0004	C2, 0.012(4)	6.2(3)
	C2–C3–N2–N3–N4–S1	0.0012	N2, 0.019(3)	6.8(3)
	C7–C8–C9–C10–C11–C12	0.0002	C11, 0.013(5)	50(2)
[Ni(Po4E)]$_2$	N1–C1–C2–N2–N3–C3–S1	0.0002	N1, 0.056(4)	
	O1–N1–C1–C2	0.0006	C2, 0.023(5)	4.9(2)
	C2–C3–N2–N3–N4–S1	0.0018	C2, 0.036(5)	5.4(2)
	C7–C8–C9–C10–C11–C12	0.0001	C10, 0.009(7)	46(2)

[a] Angle with previous plane.

3.1. Crystal structure of H$_2$Po4M and H$_2$Po4E

Like H$_2$Bo4DH [3] and H$_2$Popip [4], H$_2$Po4M and H$_2$Po4E have the thiosemicarbazone and oxime moieties on the opposite side of the C1–C2 backbone. When the two moieties are on the same side of the C1–C2 backbone, as found for some bis(thiosemicarbazones), intramolecular hydrogen bonding between the thiosemicarbazone moieties occurs [12,13]. Intermolecular hydrogen bonding for H$_2$Po4M and H$_2$Po4E involves only the oxime function forming a symmetrical dimer, as was found for H$_2$Bo4DH [3] and H$_2$Popip [4]. For H$_2$Po4M: *d*(O1–H10) = 0.863(4) Å, *d*(H10···N1) = 2.211(3) Å, *d*(O1···N1) = 2.874(4) Å and ∠(O1–H10···N1) = 154(3)° and for H$_2$Po4E *d*(O1–H10) = 0.88(4) Å, *d*(H10···N1) = 2.06(4) Å, *d*(O1···N1) = 2.845(3) Å and ∠(O1–H10···N1) = 153(4)°. Both interactions are somewhat weaker than found for H$_2$Popip [4], *d*(O1–H10) = 0.88(3) Å, *d*(H10···N1) = 1.96(3) Å, *d*(O1···N1) = 2.790(2) Å and ∠(O1–H10···N1) = 156(3)°.

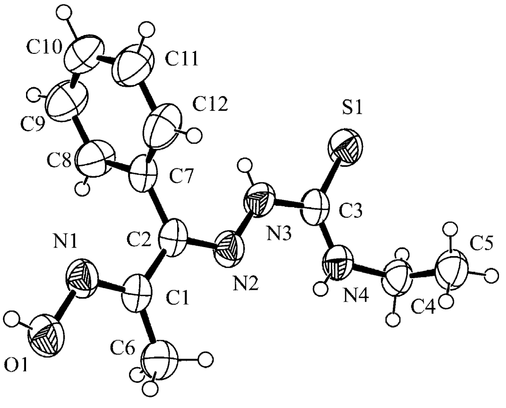

Fig. 2. ORTEP diagram of H$_2$Po4E with atom numbering scheme and displacement ellipsoids at 50% probability level.

The C1–N1 and N1–O1 bond distances of the oxime function of H$_2$Po4M and H$_2$Po4E are virtually the same as found for H$_2$Bo4DH [3] and H$_2$Popip [4]. The largest differences in bond distances of the thiosemicarbazone moieties of H$_2$Popip and H$_2$Bo4DH are C3–N3, 1.376(2) and 1.357(3) Å, and C3–N4, 1.335(2) and 1.312(4) Å and the analogous bonds in H$_2$Po4M and H$_2$Po4E are in the middle of the two ranges, Table 2. The C1–N1–O1 angles of the oxime function in the four compounds are similar, but there are differences in some of the angles of the thiosemicarbazone moieties [3,4]. For example, in H$_2$Po4M the angles N3–C3–S1, N3–C3–N4 and N2–N3–C3 are 119.1(4), 115.4(5), and 120.7(2)° compared to 118.0(2), 115.5(2), and 121.5(2)° for H$_2$Po4E, 115.0(1), 120.3(2) and 124.0(2)° for H$_2$Popip [4] and 119(2), 117(2) and 119(2)° for H$_2$Bo4DH [3]. These variations result from the different functional groups

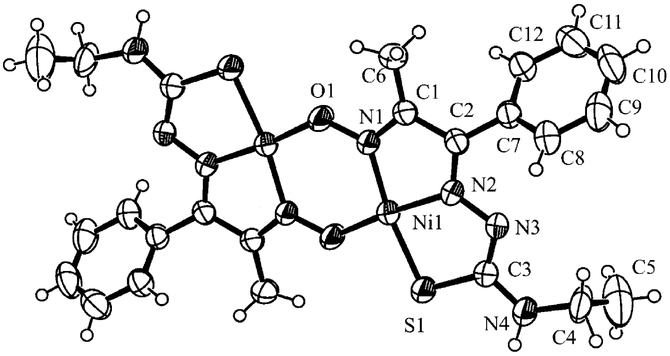

Fig. 3. ORTEP diagram of $[Ni(Po4E)]_2$ with numbering scheme and displacement ellipsoids at 50% probability level.

attached to N4 and the N4–C3–S1 angles also differ significantly as expected.

The angle between the thiosemicarbazone mean plane, C2–N2–N3–C3–N4–S1, and the O1–N1–C1–C2 mean plane is 10.7(4)° for H_2Po4M and 10.9(4)° for H_2Po4E showing that the oxime and thiosemicarbazone functions are close to coplanar. The mean plane of the phenyl ring forms an angle with the mean plane of the thiosemicarbazone function of 72.5(5)° for H_2Po4M and 76.5(3)° for H_2Po4E, compared to 66.3(1)° for H_2Popip. Therefore, the phenyl ring is substantially turned out of the plane of the rest of the molecule, and to the greatest extent for H_2Po4E.

3.2. Crystal structure of $[Ni(Po4M)]_2 \cdot 2CHCl_3$ and $[Ni(Po4E)]_2$

As indicated earlier, the thiosemicarbazone moiety loses a proton in $[Ni(HPohexim)_2]$, where HPohexim is the anion of 1-phenyl-1-(3-hexamethyleneiminylthiosemicarbazone)-2-oximepropane, and the two ligands coordinate via their N1, N2, and S1 atoms in this 6-coordinate nickel(II) complex [4]. This is the same mode of coordination found earlier for $[Ni(HBo4DH)_2]$ [3]. Using nickel(II) acetate allows hydrogens from both moieties to be displaced and results in formation of binuclear nickel(II) complexes. Fig. 3 shows that the two nickel(II) centers in $[Ni(Po4M)]_2$ and $[Ni(Po4E)]_2$ are bridged by oximato functions to form six-membered rings with the ring's center being the center of symmetry for each molecule.

The bond distances for the thiosemicarbazonato and oximato moieties of $[Ni(Po4M)]_2$ and $[Ni(Po4E)]_2$ are not significantly different: they are within twice their combined e.s.d. values. Similarly, the two Ni–N bonds do not significantly differ in the two complexes, but Ni–S in $[Ni(Po4M)]_2$, 2.172(1) Å, is longer, and Ni–O1a, 1.827(3) Å, shorter than 2.164(1) and 1.842(2) Å, respectively, for $[Ni(Po4E)]_2$. $[Ni(Po4M)]_2$ and $[Ni(Po4E)]_2$ have shorter Ni–N1 and Ni–S1 bond distances than in the 6-coordinate $[Ni(HPohexim)_2]$ [4], but Ni–N2, the bond involving the imine nitrogen of the thiosemicarbazone moiety, is similar.

The bridging in $[Ni(Po4M)]_2$ and $[Ni(Po4E)]_2$ is identical to a binuclear nickel(II) dication having an NNN tridentate ligand with a bridging NO function (i.e. anion of *N*-(6-amino-4-aza-3,3,6-trimethyl-2-heptylidenyl)hydroxylamine) [14]. The six-membered Ni1–N1–O1–N2–N1a–O1a ring has a center of symmetry and each nickel(II) is in a nearly square-planar coordination site. The Ni–N1 and Ni–O1 distances for the oximato bridged ligands are 1.861(2) and 1.836(2) Å, respectively [14], both somewhat shorter than found for $[Ni(Po4M)]_2$ and $[Ni(Po4E)]_2$, Table 2. The Ni–Ni distance is 3.661(1) and 3.646(1) Å in $[Ni(Po4M)]_2$ and $[Ni(Po4E)]_2$, respectively, which are marginally longer than found for the above-mentioned cation, 3.631(2) Å [14]. The N1–Ni–O1a angles of the present complexes are essentially the same as found previously, but the Ni–N1–O1 angles, 129.7(2) and 130.1(2)° are somewhat larger than 127.8(1)° [14].

Loss of the OH hydrogen and coordination of the oxime oxygen results in a significant decrease in the N1–O1 bond distance, 1.349(4) Å for $[Ni(Po4M)]_2$, compared to 1.397(5) Å for H_2Po4M and 1.336(3) and 1.403(2) Å for H_2Po4E and [Ni(Po4E)]$_2$, respectively. The N1–O1 bond, when coordinated as the neutral oxime moiety via N1 to nickel(II) in [Ni(HPohexim)$_2$], is even shorter, 1.262(9) Å [4]. The thiosemicarbazone moiety distances in [Ni(Po4M)]$_2$ and [Ni(Po4E)]$_2$ and the average bond distances in [Ni(HPohexim)$_2$] are within their combined e.s.d. values, except for N2–N3, which are 1.387(4), 1.377(4) and 1.362(9) Å, for [Ni(Po4M)]$_2$, [Ni(Po4E)]$_2$ and [Ni(HPohexim)$_2$], respectively. The usual changes in bond distances that occur for a coordinated thiosemicarbazone anion compared to an uncoordinated thiosemicarbazone [15] occur in [Ni(Po4M)]$_2$ and [Ni(Po4E)]$_2$, i.e. increase in C3–S1, decrease of N3–C3, increase in N2–N3 and a small increase in C2–N2, Table 2.

The N1–Ni1–S1 bond angle in [Ni(Po4M)]$_2$ and [Ni(Po4E)]$_2$, 169.4(1) and 169.80(8)°, is a measure of distortion from regular stereochemistry for complexes with tridentate thiosemicarbazonato ligands. These angles are comparable to those found for 4-coordinate nickel(II) complexes with a heterocyclic tridentate thiosemicarbazonato ligand [15–17]. It is also of interest that tetradentate N_2S_2 bis(thiosemicarbazonato)-nickel(II) complexes have *trans* N–Ni–S angles of ca. 172° [18] and neutral thiosemicarbazones have N–Ni–S angles of ca. 158° [19–21]. The only significant difference in the ligand bond angles between [Ni(Po4M)]$_2$, [Ni(Po4E)]$_2$, and [Ni(HPohexim)$_2$] [4] is the C1–N1–O1 angle which is 114.9(3), 114.6(2) and 126(1)°, respectively. The smaller angle for [Ni(Po4M)]$_2$ and [Ni(Po4E)]$_2$ is due to oximato bridging with formation of the six-membered ring.

The bichelate rings, N1–C1–C2–N2–N3–C3–N4–S1 in [Ni(Po4M)]$_2$ and [Ni(Po4E)]$_2$ have mean plane deviations of almost zero, but individual atoms are as much as 0.056(4) Å out of the plane. In addition, the nickel(II) center is 0.045(2) and 0.041(2) Å from the mean plane of the bichelate rings for [Ni(Po4M)]$_2$ and [Ni(Po4E)]$_2$, respectively. The angle between the phenyl ring mean plane and thiosemicarbazonato mean plane, 50(2)° for [Ni(Po4M)]$_2$ and 46(2)° for [Ni(Po4E]$_2$ are smaller than an average of 65° found for [Ni(HPohexim)$_2$] and considerably less than the >70° found for free ligands, H_2Po4M and H_2Po4E.

3.3. ^{1}H NMR spectral results

The OH resonance appears at 10.66 and 10.94 ppm for H_2Po4M and H_2Po4E, respectively, indicating hydrogen bonding to oxygen of [$^2H_6$]-acetone. The N3*H* and N4*H* resonances can be distinguished because the latter is broadened due to interaction with the N4-alkyl function, and the N3*H* (and O*H*) resonance is absent in the spectra of the binuclear nickel(II) complexes. N3*H* appears at 10.07 and 11.07 ppm in the spectra of H_2Po4M and H_2Po4E while N4*H* is found at 8.60, 8.55, 9.45 and 9.48 ppm in the spectra of H_2Po4M, H_2Po4E, [Ni(Po4M)]$_2$ and [Ni(Po4E)]$_2$. The N4CH_3 resonance appears at 3.12 ppm in H_2Po4M and 3.15 ppm in [Ni(Po4M)]$_2$ and the N4CH_2CH$_3$ at 3.73 and 3.64 ppm in H_2Po4E and [Ni(Po4E)]$_2$, respectively.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no CCDC-156879 for H_2Po4M, CCDC-156365 for H_2Po4E, CCDC-156362 for [Ni(Po4M)]$_2$ and CCDC-156361 for [Ni(Po4E)]$_2$. Copies of available material can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44-0-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

References

[1] M. Gil, E. Bermejo, A. Castiñeiras, H. Beraldo, D.X. West, Z. Anorg. Allg. Chem. 626 (2000) 2353 and references therein.

[2] P.S. Reddy, K.H. Reddy, Polyhedron 19 (2000) 1687 and references therein.

[3] K.V. Kattic, P.R. Singh, C.L. Barnes, J. Chem. Soc., Dalton Trans. (1993) 2153.

[4] E. Bermejo, A. Castiñeiras, D.X. West, Z. Naturforsch. 56b (2001) 369.

[5] M. Maekawa, S. Kitagawa, Y. Nakao, S. Sakamoto, A. Yatani, W. Mori, S. Kashino, M. Munakata, Inorg. Chim. Acta 293 (1999) 20 and references therein.

[6] D. Kovala-Demertzi, N. Kourkoumelis, D.X. West, J. Valdés-Martínez, S. Hernández-Ortega, Eur. J. Inorg. Chem. (1998) 861.

[7] D. Kovala-Demertzi, N. Kourkoumelis, M.A. Demertzis, J.R.

Miller, C.S. Frampton, J.K. Swearingen, D.X. West, Eur. J. Inorg. Chem. (2000) 727.
[8] M.L. Durán, A. Sousa, J. Romero, A. Castiñeiras, E. Bermejo, D.X. West, Inorg. Chim. Acta 294 (1999) 79.
[9] D. Waasmaier, A. Kirfel, Acta Crystallogr. A51 (1995) 416.
[10] S. Mackay, C. Edwards, A. Henderson, C. Gilmore, N. Stewart, K. Shankland, A. Donald, Maxus 10, version 2 University of Glasgow, Scotland, 1997.
[11] A.L. Spek, PLATON. A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 1999.
[12] A. Castiñeiras, E. Bermejo, L.J. Ackerman, H. Beraldo, D.X. West, J. Mol. Struct. 477 (1999) 1.
[13] A. Castiñeiras, E. Bermejo, D.X. West, L.J. Ackerman, J. Valdés-Martínez, S. Hernández-Ortega, Polyhedron 18 (1999) 1463.
[14] E.S. Schlemper, R.K. Murmann, Inorg. Chem. 13 (1974) 2424.
[15] D.X. West, G.A. Bain, R.J. Butcher, J.P. Jasinski, Y. Li, R.Y. Pozdniakiv, J. Valdés-Martínez, R.A. Toscano, S. Hernández-Ortega, Polyhedron 15 (1996) 665.
[16] D.X. West, J.K. Swearingen, J. Valdés-Martínez, S. Hernández-Ortega, A.K. El-Sawaf, F. van Meurs, A. Castiñeiras, I. Garcia, E. Bermejo, Polyhedron 18 (1999) 2919.
[17] K.A. Ketcham, I. Garcia, J.K. Swearingen, E. Bermejo, A.K. El-Sawaf, A. Castiñeiras, D.X. West, Polyhedron (2001) in press.
[18] D.X. West, M.A. Lockwood, H. Gebremedhin, A. Castiñeiras, A.E. Liberta, Polyhedron 12 (1993) 1887.
[19] A. Castiñeiras, E. Bermejo, D.X. West, A.K. El-Sawaf, J.K. Swearingen, Polyhedron 17 (1998) 2751.
[20] A. Castiñeiras, E. Bermejo, D.X. West, L.J. Ackerman, J. Valdés-Martínez, S. Hernández-Ortega, Polyhedron 18 (1999) 1463.
[21] M. Gil, E. Bermejo, A. Castiñeiras, H. Beraldo, D.X. West, Z. Anorg. Allg. Chem. 626 (2000) 2353.