

Synthesis and crystal structure of nickel(II) complexes with bis(5-methyl-2-thiophenemethyl)(2-pyridylmethyl)amine

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ABSTRACT

A series of nickel(II) complexes having the (Me-Tp)₂PMA ligand ((Me-Tp)₂PMA = bis(5-methyl-2-thiophenemethyl)(2-pyridylmethyl)amine) with nitrates (**1**), chlorides (**2**), and perchlorates (**3**) as anions were synthesized and isolated. All these complexes were successfully characterized by physicochemical methods including X-ray crystallographic analysis. In complex **1**, the ligand binds in a bidentate N₂ fashion, whereas in the cases of **2** and **3** the ligand binds in the tridentate N₂S form. The coordination geometry around the nickel(II) atoms in these complexes is distorted octahedral.

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1. Introduction

Chelating ligands with mixed donors that differ in their coordination abilities have become a popular topic of research [1,2]. Such ligands, so-called hemilabile ligands, are known to provide powerful platforms for small molecule functionalization [3] where the relatively labile group can be displaced from the metal center, although the chances for recoordination remain [4]. Thus, the metal complexes bearing hemilabile ligands have been found to be active catalysts in various catalytic processes [5–7].

Hemilabile ligands combining nitrogen and sulfur donor sites produce stable metal complexes and show different modes of bonding, depending on anions, solvent molecules, and the chemical nature of the sulfur atom [8–10]. Recent interest has been directed towards the synthesis of the nickel(II) complexes containing N,S-donor sets due to biological relevance [11–14]. Herein, we describe the synthesis and structure of a series of nickel(II) complexes having the new N,S-donor ligand, bis(5-methyl-2-thiophenemethyl)(2-pyridylmethyl)amine ((Me-Tp)₂-PMA), with nitrates (**1**), chlorides (**2**), and perchlorates (**3**) as anions. The complexes **1** and **3** are hexacoordinated mononuclear complexes, while the complex **2** is dimer through the chloride bridging. The nickel complexes obtained were characterized by UV–Vis, ESI–MS, ¹H NMR and X-ray analysis.

2. Experimental

2.1. Materials and physical measurements

All chemicals were obtained from commercial sources and were used without further purification. Solvents were dried according to published procedures and distilled under Ar prior to use [15].

UV–Vis spectra were measured with a Hewlett–Packard 8453 diode array spectrophotometer equipped with a circulating water bath. Electrospray ionization mass spectra (ESI–MS) were collected on a Thermo Finnigan (San Jose, CA, USA) LCQTM Advantage MAX quadrupole ion trap instrument, by infusing samples directly into the source at 20 μL/min using syringe pump. The spray voltage was set at 4 kV and the capillary temperature at 80 °C. ¹H NMR spectra were measured with Bruker DPX-250 spectrometer. The C, H, N elemental analyses for the crystals **1–3** were carried out by using a Carlo Erba Instruments EA-1108 Elemental Analyzer at the Korean Basic Science Institute. The effective magnetic moments (μ_{eff} , BM) of the complexes **1–3** were determined using the modified ¹H NMR method of Evans at room temperature [16–18]. A WILMAD[®] coaxial insert (sealed capillary) tubes containing the blank acetonitrile-*d*₃ solvent (with 1.0% TMS) only was inserted into the normal NMR tubes containing the complexes (8 mM) dissolved in acetonitrile-*d*₃ (with 0.05% TMS). The chemical shift of the TMS peak (and/or solvent peak) in the presence of the paramagnetic metal complexes was compared to that of the TMS peak (and/or solvent peak) in the inner coaxial insert tube. The effective magnetic moment was calculated using the equation, $\mu = 0.0618 (\Delta\nu T/2fM)^{1/2}$, where *f* is the oscillator frequency (MHz) of the superconducting spectrometer, *T* is the absolute temperature, *M* is the molar concentration of the metal ion, and $\Delta\nu$ is the

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difference in frequency (Hz) between the two reference signals [18].

2.2. Synthesis of the new ligand (Me-Tp)₂PMA

A THF solution (50 mL) of 5-methylthiophene-2-aldehyde (5.047 g, 40 mmol) was added to a THF solution (50 mL) of 2-(aminomethyl)pyridine (4.806 g, 44 mmol). To the resulting solution was slowly added NaBH(CH₃CO₂)₃ (9.613 g, 44 mmol) with stirring at room temperature. After the solution was stirred for a day, a THF solution (50 mL) of 5-methylthiophene-2-aldehyde (5.047 g, 40 mmol) was added to the resulting mixture. NaBH(CH₃CO₂)₃ (9.613 g, 44 mmol) was slowly added to the solution. After the solution was stirred for a day, HCl was added to make the solution pH 1 in order to decompose remained NaBH(CH₃CO₂)₃. An aqueous solution of NaOH was added to make the solution basic, and the solution was concentrated under reduced pressure. The resulting was extracted with Et₂O (3 times × 100 mL). The combined extracts were dried over Na₂SO₄, and Et₂O was removed by evaporation under reduced pressure to give a brown oil of (Me-Tp)₂PMA. Yield: 11.54 g, 87%. ¹H NMR (CD₃CN, 250 MHz): δ 2.42 (6H, s, CH₃), 3.73 (6H, s, CH₂), 6.60 (2H, t, thiopheneH), 6.73 (2H, t, thiopheneH), 7.22 (H, t, pyH), 7.61 (H, d, pyH), 7.75 (H, t, pyH), 8.49 (H, d, pyH). ESI-MS (CH₃CN): *m/z* 329 ([M + H]⁺).

2.3. Synthesis of [Ni{(Me-Tp)₂PMA}(NO₃)₂] (1)

(Me-Tp)₂PMA (0.33 g, 1 mmol) was added to a THF solution (50 mL) of Ni(NO₃)₂·6H₂O (0.29 g, 1 mmol). The resulting solution was stirred for 3 h, affording a green solution. The mixture was dried over Na₂SO₄. The solvent was removed under vacuum to yield a green oil, which was recrystallized from CH₂Cl₂/pentane solution as a green crystalline product. Yield of the crystalline product was 0.37 g (72%). Anal. Calc. for C₁₈H₂₀N₄NiO₆S₂: C, 42.29; H, 3.94; N, 10.96. Found: C, 41.91; H, 3.90; N, 10.87%. UV-Vis (λ_{max}/nm (ε/M⁻¹ cm⁻¹); CH₃CN solution): 609 (20), 993 (11). ESI-MS (CH₃CN): *m/z* 448.1 ([Ni{(Me-Tp)₂PMA}(NO₃)₂]⁺). μ_{eff} = 3.3 BM. X-ray crystallographically suitable crystals were obtained by slow diffusion of pentane into concentrated CH₂Cl₂ solutions of **1**.

2.4. Synthesis of [Ni{(Me-Tp)₂PMA}Cl₂]₂ (2)

(Me-Tp)₂PMA (0.33 g, 1 mmol) was added to a THF solution (50 mL) of NiCl₂·6H₂O (0.24 g, 1 mmol). The resulting solution was stirred overnight, giving **2** as a yellow powder, which was recrystallized from CH₂Cl₂/pentane solution as a yellow-green crystalline product. Yield of the crystalline product was 0.29 g (52%). Anal. Calc. for C₃₇H₄₂Cl₆N₄Ni₂S₄: C, 44.39; H, 4.23; N, 5.60. Found: C, 44.12; H, 4.19; N, 5.83%. UV-Vis (λ_{max}/nm (ε/M⁻¹ cm⁻¹); CH₂Cl₂ solution): 443 (239), 768 (92), 961 (62). ESI-MS (CH₂Cl₂/CH₃CN): *m/z* 878.8 ([Ni₂{(Me-Tp)₂PMA}₂Cl₃]⁺), 420.9 ([Ni{(Me-Tp)₂PMA}(Cl)]⁺). μ_{eff} = 4.6 BM. X-ray crystallographically suitable crystals were obtained by slow diffusion of pentane into concentrated CH₂Cl₂ solutions of **2**.

2.5. Synthesis of [Ni{(Me-Tp)₂PMA}(CH₃CN)₃](ClO₄)₂ (3)

(Me-Tp)₂PMA (0.33 g, 1 mmol) was added to a THF solution (50 mL) of Ni(ClO₄)₂·6H₂O (0.37 g, 1 mmol). The resulting solution was stirred for several hours, affording a olive-green solution. The mixture was dried over Na₂SO₄. The solvent was removed under vacuum yielding a green oil, which was recrystallized from CH₃CN/Et₂O solution as an olive-green crystalline product. Yield of the crystalline product was 0.41 g (58%). Anal. Calc. for C₂₄H₂₉Cl₂N₅NiO₈S₂: C, 40.64; H, 4.12; N, 9.87. Found: C, 40.43; H, 4.15; N, 9.95%. UV-Vis (λ_{max}/nm (ε/M⁻¹ cm⁻¹); CH₃CN solution):

567 (11), 929 (9). ESI-MS (CH₃CN): *m/z* 484.9 ([Ni{(Me-Tp)₂PMA}(ClO₄)₂]⁺). μ_{eff} = 3.2 BM. X-ray crystallographically suitable crystals were obtained by slow diffusion of Et₂O into concentrated CH₃CN solutions of **3**.

Caution! Perchlorate salts are explosive and should be handled with care in small amounts.

2.6. X-ray crystal structure analysis

Single crystals were selected and mounted with viscous oil on glass fibers. Data collections were carried out on a Bruker SMART AXS diffractometer equipped with a monochromator in the Mo Kα (λ = 0.71073 Å) incident beam. The CCD data were integrated and scaled using the Bruker-S SAINT software package, and the structure was solved and refined using SHELXL V 6.12 [19]. Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were positioned at the calculated positions. Relevant crystal data are given in Table 1.

3. Results and discussion

3.1. Syntheses

The N,S-donor ligand, bis(5-methyl-2-thiophene-methyl)(2-pyridylmethyl)amine ((Me-Tp)₂PMA), was prepared by the reaction of 5-methylthiophene-2-aldehyde with 2-(aminomethyl)pyridine in the presence of NaBH(CH₃CO₂)₃. The (Me-Tp)₂PMA ligand was characterized by ESI-MS and ¹H NMR spectroscopic methods.

Synthetic procedures for a series of nickel(II) complexes having (Me-Tp)₂PMA are summarized in Scheme 1. The reaction of (Me-Tp)₂PMA with equimolar amount of Ni(NO₃)₂·6H₂O in THF caused a color change to greenish blue. From the reaction mixture, [Ni{(Me-Tp)₂PMA}(NO₃)₂] (**1**) was isolated at room temperature. UV-Vis spectrum of **1** in CH₃CN exhibits two absorption bands at 609 and 993 nm. The band maxima in the region of 400–1100 nm can be attributed to two possible d-d transitions ³A_{2g} → ³T_{1g}(F), ³A_{2g} → ³T_{1g}(P) for the nickel(II) ion in a distorted octahedral environment [20]. The ESI-MS of **1** showed a parent cation signal at *m/z* 448.1, whose mass and observed isotope distribution pattern were consistent with those of [Ni{(Me-Tp)₂PMA}(NO₃)₂]⁺.

Admixture of solutions of (Me-Tp)₂PMA and NiCl₂·6H₂O in THF afforded a green solution and a yellow precipitate in several hours. The precipitate was identified as the binuclear complex, [Ni{(Me-Tp)₂PMA}Cl₂]₂ (**2**). The UV-Vis spectrum of **2** in CH₂Cl₂ shows three absorption bands at 443, 768 and 961 nm. These are the characteristic spectra expected for a high-spin d⁸ nickel(II) ion in a distorted octahedral environment, and can be attributed to ²A_{2g} → ³T_{2g}, ³A_{2g} → ³T_{1g}(F), ³A_{2g} → ³T_{1g}(P) transitions, respectively [20]. The ESI-MS of **2** in CH₂Cl₂/CH₃CN (1:1) exhibits a prominent ion peak at *m/z* 878.8, whose mass and isotope distribution pattern correspond to [Ni₂{(Me-Tp)₂PMA}₂Cl₃]⁺.

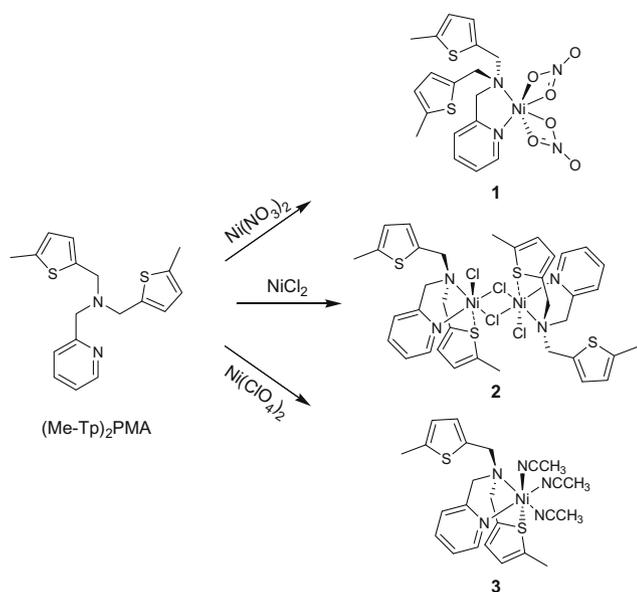
[Ni{(Me-Tp)₂PMA}(CH₃CN)₃](ClO₄)₂ (**3**) was obtained by a method similar to that for **1** with the corresponding nickel salt, Ni(ClO₄)₂·6H₂O, in THF. The UV-Vis spectrum of **3** in CH₃CN shows two absorption bands at 567 and 929 nm, which are comparable to those of **1**. These are attributable to two possible d-d transitions ³A_{2g} → ³T_{1g}(F), ³A_{2g} → ³T_{1g}(P) for the nickel(II) ion in a distorted octahedral environment [20]. The ESI-MS of **3** shows a parent cation signal at *m/z* 484.9, whose mass and observed isotope distribution pattern were consistent with those of [Ni{(Me-Tp)₂PMA}(ClO₄)₂]⁺.

3.2. Crystal structures

Complexes **1–3** were successfully characterized by X-ray crystallography. The molecular structures of **1** and **2**, and the cationic

Table 1
Crystallographic data and structure refinements for **1**, **2**·CH₂Cl₂ and **3**.

	1	2 ·CH ₂ Cl ₂	3
Empirical formula	C ₁₈ H ₂₀ N ₄ NiO ₆ S ₂	C ₃₈ H ₄₄ Cl ₈ N ₄ Ni ₂ S ₄	C ₂₄ H ₂₉ Cl ₂ N ₅ NiO ₈ S ₂
Formula weight	511.21	1086.03	709.25
Temperature (K)	273(2)	170(2)	170(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>Unit cell dimensions</i>			
<i>a</i> (Å)	10.1213(8)	9.4450(8)	10.617(5)
<i>b</i> (Å)	17.1576(14)	11.7339(9)	11.785(6)
<i>c</i> (Å)	13.2544(10)	11.7587(9)	12.362(6)
α	90.00	71.282(1)	85.458(9)
β	107.343(1)	78.150(2)	86.993(9)
γ	90.00	88.390(1)	89.782(8)
Volume (Å ³)	2197.1(3)	1206.94(17)	1539.7(13)
<i>Z</i>	4	1	2
<i>d</i> _{calcd} (g/cm ⁻³)	1.545	1.494	1.530
μ (mm ⁻¹)	1.115	1.428	0.993
Reflections collected	13584	6782	8683
Independent reflections [<i>R</i> _{int}]	5105 [0.0588]	4630 [0.0230]	5927 [0.1007]
Restraints	0	0	0
Parameters	283	255	384
Goodness-of-fit on <i>F</i> ²	0.749	0.976	0.900
Final <i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.0350	0.0484	0.0633
Final <i>wR</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.0652	0.1411	0.1623



Scheme 1. Synthetic procedures for complexes.

part of **3** are depicted Figs. 1, 3 and 4, with selected bond distances and angles listed in Tables 2–4.

As shown in Fig. 1, complex **1** has a six-coordinate nickel(II) with the (Me-Tp)₂PMA ligand and two symmetrically coordinated bidentate nitrate anions. None of the sulfur atoms of the two thienopyridine units in (Me-Tp)₂PMA bind to the nickel ion. The center to center inter-ring distance of 3.9 Å between the pyridine ring and thiophene ring containing S1 indicates that there is inter-ring interaction, although it is very weak. The symmetrically coordinated bidentate nitrates could prevent formation of the Ni–S bond, whose closest contact distance is 3.8744(8) Å (Ni1⋯S1). It is interesting to note that the intermolecular distance between the two parallel thiophene rings S2/C8–C11 and S2ⁱ/C8ⁱ–C11ⁱ [Symmetry code: (i) $-x, -y + 1, -z + 1$] of the (Me-Tp)₂PMA ligand in the packing structure of **1** is 3.5 Å, indicating the existence of significant

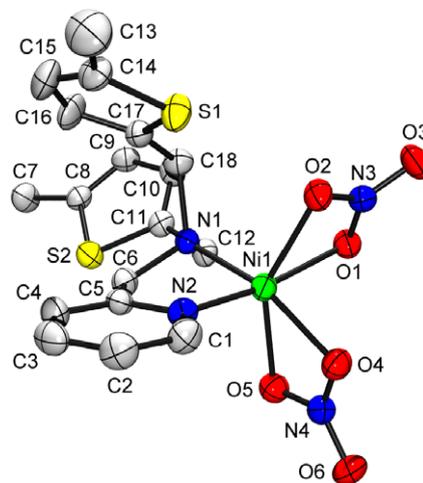


Fig. 1. ORTEP view of [Ni((Me-Tp)₂PMA)(NO₃)₂] (**1**) showing 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

intermolecular π – π stacking interaction between S2/C8–C11 and of S2ⁱ/C8ⁱ–C11ⁱ rings (see Fig. 2). The geometry around nickel(II) center is best described as distorted octahedral with two nitrogens of (Me-Tp)₂PMA and four oxygens of two nitrates.

Complex **2** has a centro-symmetric Ni(μ-Cl)₂Ni core with terminal chlorides and the (Me-Tp)₂PMA ligands in which 2-pyridyl-methyl side arms are in the equatorial positions (see Fig. 3). The Ni–Cl bond distance of the terminal chloride (2.3332(12) Å) is shorter than those of bridging chlorides (2.3665(10) and 2.4122(10) Å). The Ni–Cl–Ni bridge is formed by atoms Ni1, Cl1, Cl1ⁱⁱ and Ni1ⁱⁱ [Symmetry code: (ii) $-x + 1, -y + 1, -z + 2$] and the bridging Ni(μ-Cl)₂Ni core, which has Cl–Ni–Cl angles of 86.87(4)° and Ni–Cl–Ni angles of 93.13(4)°, is planar with a crystallographic inversion center, which is located in the center of the two nickel(II) atoms. Each one of the sulfur atoms of the two thiophene units in (Me-Tp)₂PMA is weakly bound to the nickel(II) centers with Ni–S bond distances of 2.8673(13) Å. To the best of our knowledge, only one example of structurally characterized nickel(II) thiophene

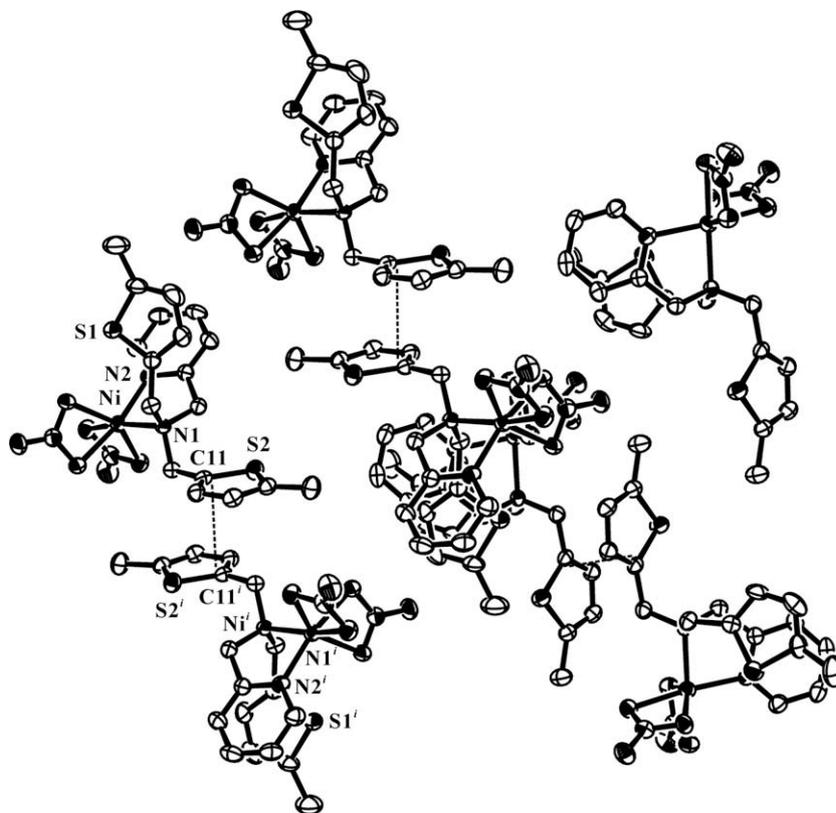


Fig. 2. π - π Interaction (dashed line) between the two parallel thiophene rings S2/C8-C11 and S2'/C8'-C11ⁱ with symmetry code (i) $-x, -y + 1, -z + 1$ in the packing structure of **1**. Hydrogen atoms are omitted for clarity.

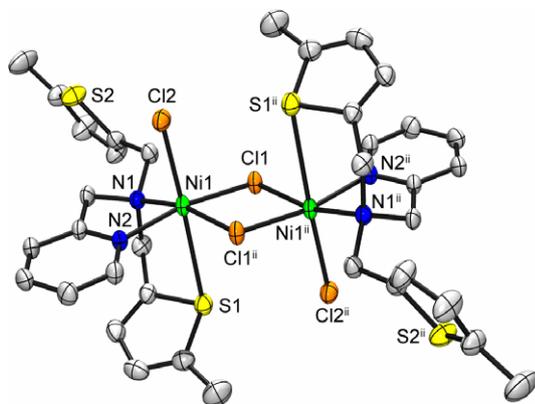


Fig. 3. ORTEP view of $[\text{Ni}\{(\text{Me-Tp})_2\text{PMA}\}\text{Cl}_2]_2$ (**2**) showing 30% probability thermal ellipsoids with symmetry code (ii) $-x + 1, -y + 1, -z + 2$. Hydrogen atoms are omitted for clarity.

interactions have been reported so far [21,22]. The torsional angle of N1–N2–C11ⁱⁱ–C11 is $0.55(10)^\circ$, indicating all four atoms (N1, N2, C11ⁱⁱ and C11) are coplanar. The deviation of the Ni1 atom from the N1–N2–C11ⁱⁱ–C11 plane is only 0.24 Å towards atom Cl2. The center to center inter-ring distance of 3.7 Å between the pyridine ring and thiophene ring containing S1 in **2** is shorter than that in **1** (3.9 Å).

The room-temperature magnetic moment (μ_{eff}) of **2** determined using the modified ^1H NMR method of Evans [16–18] was 4.6 BM, which is similar to the typical value of 4.5 BM derived from the expression $[(3.2)^2 + (3.2)^2]^{1/2}$ for dimeric nickel(II) complexes, where 3.2 BM is typical value for the six-coordinate high-spin nick-

Table 2
Selected bond distances and angles for **1**.

Bond distances (Å)			
Ni1–N1	2.0929(18)	Ni1–O2	2.0968(15)
Ni1–N2	2.0053(19)	Ni1–O4	2.1071(16)
Ni1–O1	2.1047(15)	Ni1–O5	2.0872(17)
Bond angles (°)			
N1–Ni1–N2	82.90(8)	N2–Ni1–O5	97.35(7)
N1–Ni1–O1	98.62(7)	O1–Ni1–O2	61.72(6)
N1–Ni1–O2	104.53(7)	O1–Ni1–O4	87.37(6)
N1–Ni1–O4	163.80(7)	O1–Ni1–O5	94.02(6)
N1–Ni1–O5	102.53(7)	O2–Ni1–O4	91.57(7)
N2–Ni1–O1	167.93(7)	O2–Ni1–O5	145.87(7)
N2–Ni1–O2	106.26(7)	O4–Ni1–O5	61.86(7)
N2–Ni1–O4	94.41(7)		

Table 3
Selected bond distances and angles for **2**·CH₂Cl₂.

Bond distances (Å)			
Ni1–N1	2.180(3)	Ni1–Cl1	2.3665(10)
Ni1–N2	2.030(3)	Ni1–Cl1 ⁱⁱ	2.4122(10)
Ni1–S1	2.8673(13)	Ni1–Cl2	2.3332(12)
Bond angles (°)			
N1–Ni1–N2	81.22(12)	N2–Ni1–Cl1 ⁱⁱ	94.48(10)
N1–Ni1–S1	81.55(9)	S1–Ni1–Cl1	82.33(4)
N1–Ni1–Cl1	94.91(9)	S1–Ni1–Cl1	175.33(4)
N1–Ni1–Cl2	93.80(9)	S1–Ni1–Cl1	86.43(4)
N1–Ni1–Cl1 ⁱⁱ	167.49(9)	Cl1–Ni1–Cl2	97.67(4)
N1–Ni1–S1	85.60(10)	Cl1–Ni1–Cl1 ⁱⁱ	86.87(4)
N2–Ni1–Cl1	167.75(10)	Cl2–Ni1–Cl1 ⁱⁱ	98.24(4)
N2–Ni1–Cl2	94.19(10)	Ni1–Cl1–Ni1 ⁱⁱ	93.13(4)

Symmetry code: (ii) $-x + 1, -y + 1, -z + 2$.

Table 4
Selected bond distances and angles for **3**.

Bond distances (Å)			
Ni1–N1	2.136(4)	Ni1–N3	2.025(4)
Ni1–N2	2.036(4)	Ni1–N4	2.036(5)
Ni1–S1	2.6274(19)	Ni1–N5	2.043(5)
Bond angles (°)			
N1–Ni1–N2	82.77(16)	N2–Ni1–N5	93.13(16)
N1–Ni1–S1	86.34(11)	S1–Ni1–N3	85.16(12)
N1–Ni1–N3	92.93(15)	S1–Ni1–N4	176.14(12)
N1–Ni1–N4	95.30(16)	S1–Ni1–N5	88.10(13)
N1–Ni1–N5	173.12(16)	N3–Ni1–N4	91.26(16)
N2–Ni1–S1	89.27(11)	N3–Ni1–N5	90.62(16)
N2–Ni1–N3	173.18(15)	N4–Ni1–N5	90.50(17)
N2–Ni1–N3	94.40(15)		

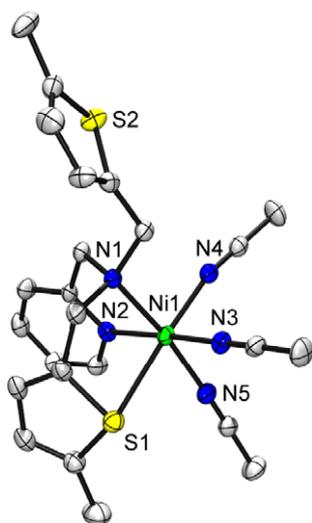


Fig. 4. ORTEP view of the complex cation of $[\text{Ni}((\text{Me-Tp})_2\text{PMA})(\text{CH}_3\text{CN})_3](\text{ClO}_4)_2$ (**3**) showing 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

el(II) complexes [23]. This result indicates that geometry around nickel(II) center in acetonitrile solution is similar to that in solid crystal, but no magnetic exchange or very weak ferromagnetic coupling occurs via Ni–Cl–Ni at room temperature.

Complex **3** has a six-coordinate nickel(II) with the (Me-Tp)₂PMA ligand and three coordinated CH₃CN solvent molecules (see Fig. 4). One of the sulfur atoms of the two thiophene units in (Me-Tp)₂PMA takes part in the coordination. The Ni–S bond distance in **3** (2.6274(19) Å) is shorter than that in **2** (2.8673(13) Å), which is consistent with the increased center to center inter-ring interaction between the pyridine ring and thiophene ring containing S1 in **3** (3.5 Å) compared to those in **1** (3.9 Å) and **2** (3.7 Å). The torsional angle of N1–N2–N5–N3 is $-0.27(16)^\circ$, indicating all four atoms (N1, N2, N5 and N3) are coplanar. The deviation of the Ni1 atom from the N1–N2–N5–N3 plane is only 0.10 Å towards atom N4, indicating that Ni1 atom is located almost in plane of N1–N2–N5–N3. According to these results together with bond angles around nickel(II) center, the geometry around nickel(II) center is best described as a quite symmetrical octahedral structure with two nitrogens and one sulfur of (Me-Tp)₂PMA and three nitrogens of solvent molecules.

It is noteworthy that the Ni–S interaction in the complexes **1–3** is significantly affected by the counter anions. All complexes have the (Me-Tp)₂PMA ligand which gives two nitrogens occupying the equatorial positions and the other coordination sites depend on the

counter anions. In **1**, two bidentate nitrate anions coordinate to nickel(II) occupying four coordination sites, which could prevent the approaching of sulfur atoms in (Me-Tp)₂PMA. In **2**, however, two chloride anions occupy three coordination sites via dimerization, which gives one vacant coordination site on each nickel(II) center. One of the sulfur atoms of the thiophene units in (Me-Tp)₂PMA is positioned to the vacant coordination site, resulting in the weak Ni–S interaction. Complex **3** has three solvent molecules with the non-coordinating perchlorate anions, which gives one coordination site for much stronger Ni–S interaction. A good correlation between the Ni–S interaction and the inter-ring interaction was observed in the order of **1** < **2** < **3**.

In conclusion, a series of nickel(II) complexes bearing (Me-Tp)₂PMA were successfully isolated and characterized by physicochemical methods, including X-ray crystallographic analysis. The changes of anion from nitrate to chloride and perchlorate induce changes in the positioning of the anions around nickel(II) centers. In addition, the non-coordinating nature of the perchlorate anion increases the ability of the nickel to bind sulfur.

Supplementary data

CCDC 728426, 728427 and 728428 contain the supplementary crystallographic data for **1**, **2**·CH₂Cl₂ and **3**, respectively. 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.

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