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Nickel(II) and zinc(II) complexes of *N*-substituted di(2-picolyl)amine derivatives: Synthetic and structural studies

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ABSTRACT

The interaction of di(2-picolyl)amine (1) and its secondary N-substituted derivatives, N-(4-pyridylmethyl)di(2-picolyl)amine (2), N-(4-carboxymethyl-benzyl)-di(2-picolyl)amine (3), N-(4-carboxybenzyl)-di(2-picolyl)amine (3), N-(4-carboxybenzyl)amine (3), N-(4-carb picolyl)amine (4), N-(1-naphthylmethyl)-di(2-picolyl)amine (5), N-(9-anthracenylmethyl)-di(2-picolyl)amine (6), 1,4-bis[di(2-picolyl)aminomethyl]benzene (7), 1,3-bis[di(2-picolyl)aminomethyl]benzene (8) and 2,4,6-tris[di(2-picolyl)amino]triazine (9) with Ni(II) and/or Zn(II) nitrate has resulted in the isolation of $[Ni(1)(NO_3)_2]$, $[Ni(2)(NO_3)_2]$, $[Ni(3)(NO_3)_2]$, $[Ni(4)(NO_3)_2] \cdot CH_3CN$, $[Ni(5)(NO_3)_2]$, $[Ni(6)(NO_3)_2]$, $[Ni(6)(NO_3)_$ $(NO_3)_2$, $[Zn(8)(NO_3)_2]$ and $[Zn_2(9)(NO_3)_4] \cdot 0.5H_2O$. X-ray structures of $[Ni(4)(NO_3)_2] \cdot CH_3CN$, $[Ni(6)(NO_3)_2] \cdot (NO_3)_2$ and $[Zn(5)(NO_3)_2]$ have been obtained. Both nickel complexes exhibit related distorted octahedral coordination geometries in which 4 and 6 are tridentate and bound meridionally via their respective N₃-donor sets, with the remaining coordination positions in each complex occupied by a monodentate and a bidentate nitrato ligand. For [Ni(4)(NO₃)₂]-CH₃CN, intramolecular hydrogen bond interactions are present between the carboxylic OH group on one complex and the oxygen of a monodentate nitrate on an adjacent complex such that the complexes are linked in chains which are in turn crosslinked by intermolecular offset π - π stacking between pyridyl rings in adjacent chains. In the case of $[Ni(6)(NO_3)_2]$, two weak CH...O hydrogen bonds are present between the axial methylene hydrogen atoms on one complex and the oxygen of a monodentate nitrate ligand on a second unit such that four hydrogen bonds link pairs of complexes; in addition, an extensive series of $\pi - \pi$ stacking interactions link individual complex units throughout the crystal lattice. The X-ray structure of $[Zn(5)(NO_3)_2]$ shows that the metal centre once again has a distorted six-coordinated geometry, with the N_3 -donor set of N-(1-naphthylmethyl)-di(2-picolyl)amine (5) coordinating in a meridional fashion and the remaining coordination positions occupied by a monodentate and a bidentate nitrato ligand. The crystal lattice is stabilized by weak intermolecular interactions between oxygens on the bound nitrato ligands and aromatic CH hydrogens on adjacent complexes; intermolecular $\pi - \pi$ stacking between aromatic rings is also present.

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1. Introduction

The interaction of transition and post-transition metal ions with di- and polypyridyl ligands continues to receive much attention, in part reflecting the coordination versatility of such ligands and their importance in a number of biological, catalytic, photoactive and sensor applications [1,2]. For example, the 'classical' di(2-picolyl)amine ligand (dipic, 1), as well as its secondary nitrogen substituted derivatives, yield strong complexes with a wide range of metal ions. In particular, reports of the interaction of the parent dipic moiety and its (uncharged) *N*-substituted derivatives with Ni(II) [3–7] and Zn(II)

[8–18] have appeared, although the *N*-substituted derivatives have received less attention than those of dipic itself. Even so, individual *N*-substituted ligand complexes of both metals have been employed in a number of applied investigations – including for carbon dioxide fixation [19] as well as for a range of studies focused on biological and/or sensor applications [10,20–31,17,32–40].

In a recent paper we presented the results of an investigation of the interaction of Cu(II) with both di(2-picolyl)amine (dipic, **1**) and a range of its *N*-substituted derivatives (including **2**, **3** and **6–9** shown in Scheme 1) [41]. In parallel studies, we have also investigated aspects of the metal ion chemistry of a number of related *N*-substituted derivatives of 2,2-dipyridylamine with Cu(II) [42], Pd(II) [42] and Ag(I) [43,44]. We now report the results of an extension of these studies that involve the interaction of the *N*-substituted



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Scheme 1.

di(2-picolyl)amine derivatives **2–9** with Ni(II) and **2**, **3**, **5**, **6**, **8** and **9** with Zn(II).

2. Experimental

2.1. Physical methods

NMR spectra were determined on a DRX-500 Bruker or Varian 300 MHz spectrometer. Column chromatography was performed on silica gel 60 (0.040–0.063 mm Merck) or neutral Al₂O₃ (FH 300 mm, HNS 29 Por.0). ESI-MS were determined on a Micromass LCT-TOF mass spectrometer.

2.2. Ligand synthesis

Di(2-picolyl)amine (1) was obtained commercially. The syntheses of **2** [41], **3** [36,45], **4** [46], **6** [33], **7** [47], **8** [47] and **9** [48] have been reported previously. A preparation for **5** has also been reported [49] but the modified procedure given below was employed in the present study.

2.2.1. N-(1-naphthylmethyl)-di(2-picolyl)amine (5, Scheme 2)

1-(Chloromethyl)naphthalene (0.883 g, 5.00 mmol) in acetone (20 mL) was added dropwise to di(2-picolyl)amine (1.003 g, 5.03 mmol) and a suspension of K₂CO₃ (0.967 g, 7.00 mmol). After 25 h of heating under reflux, the solvent was removed on a rotary evaporator. The residue was washed well with water and then extracted several times with chloroform. The combined chloroform phases were washed three times with water then dried over MgSO₄ and the solvent was removed on a rotary evaporator. The orange oil that remained was purified by chromatography on an alumina column [eluent: ethylacetate/heptane (1:1), R_f = 0.43]. The purified product was obtained as a yellow oil. Yield: 1.37 g (80%). ESI-MS m/z = 340.1 [M+H]⁺. ¹H NMR (500 MHz, CDCl₃, 300 K): δ (ppm) 3.87 (4H, s, 12-H); 4.14 (2H, s, 11-H); 7.12 (2H,





t, 16-H); 7.39 (1H, t, 8-H); 7.45 (4H, m, 1/2/14-H); 7.60 (3H, m, 9/15-H); 7.72 (1H, d, 7-H); 7.80 (1H, d, 3-H); 8.12 (1H, d, 6-H); 8.52 (2H, d, 17-H). ¹³C NMR (CDCl₃, 300 K): δ (ppm) 57.06 (11-C); 60.46 (12-C); 121.97 (16-C); 123.19 (14-C); 124.50 (6-C); 125.20 (8-C); 125.48 (1-C); 125.52 (2-C); 127.36 (9-C); 127.86 (7-C); 128.38 (3-C); 132.28 (10-C); 133.76 (5-C); 134.53 (4-C); 136.37 (15-C); 148.77 (17-C); 159.50 (13-C).

2.3. Synthesis of Ni(II) and Zn(II) complexes

The metal complexes were washed with ether and dried under vacuum before microanalysis. Crystals for X-ray analysis were removed from the reaction solution and used directly for the X-ray study. The synthesis and characterisation of $[Ni(1)(NO_3)_2]$, $[Ni(2)(NO_3)_2]$, $[Ni(3)(NO_3)_2]$, $[Ni(5)(NO_3)_2]$, $[Ni_2(7)(NO_3)_4]$, $[Ni_2(8)(NO_3)_4]$, and $[Ni_3(9)(NO_3)_6]$ ·3H₂O, $[Zn(3)(NO_3)_2]$ ·0.5CH₃OH, $[Zn(6)(NO_3)_2]$, $[Zn(8)(NO_3)_2]$ and $[Zn_2(9)(NO_3)_4]$ ·0.5H₂O, all of which were not employed for X-ray diffraction studies, are presented in the Supplementary data.

2.3.1. [Ni(4)(NO3)2]·CH3CN

Nickel nitrate hexahydrate (0.022 g, 0.076 mmol) in warm acetonitrile (2 mL) was added to 4 (0.025 g, 0.075 mmol) in warm acetonitrile (2 mL). The solution was let stand at 4 °C under an

Table 1

Crystal data and structure refinement for [Ni(4)(NO₃)₂]·CH₃CN, [Ni(6)(NO₃)₂] and [Zn(5)(NO₃)₂].

Empirical formula $C_{22}H_{22}N_6NiO_8$ $C_{27}H_{23}N_5NiO_6$ $C_{23}H_{21}N_5O_6Zn$ Formula weight557.17572.21528.84Temperature (K)198(2)198(2)120Wavelength (Å)0.710730.710730.71073Crystal systemmonoclinictriclinictriclinicSpace group P_1 P_1 (No. 2)
Formula weight 557.17 572.21 528.84 Temperature (K) 198(2) 198(2) 120 Wavelength (Å) 0.71073 0.71073 0.71073 Crystal system monoclinic triclinic triclinic Space group P21 P1 P1 (No. 2)
Temperature (K) 198(2) 198(2) 120 Wavelength (Å) 0.71073 0.71073 0.71073 Crystal system monoclinic triclinic triclinic Space group P_1 P_1 P_1 (No. 2) Unit cell dimensions Unit cell dimensions P_1 P_2
Wavelength (Å)0.710730.710730.71073Crystal systemmonoclinictriclinictriclinicSpace group $P2_1$ $P\overline{1}$ $P\overline{1}$ (No. 2)Unit cell dimensions
Crystal systemmonoclinictriclinictriclinicSpace group $P2_1$ $P\overline{1}$ $P\overline{1}$ (No. 2)Unit cell dimensions
Space group $P2_1$ $P\overline{1}$ $P\overline{1}$ (No. 2)Unit cell dimensions
Unit cell dimensions
a (Å) 8.583(2) 9.402(1) 8.3038(3)
b (Å) 13.871(3) 10.133(1) 8.6756(3)
c (Å) 10.635(2) 14.225(2) 16.6453(7)
α (°) 90 103.62(1) 78.638(1)
β (°) 110.33(3) 103.33(1) 83.272(2)
γ (°) 90 107.96(1) 70.568(1)
Volume (Å ³) 1187.3(4) 1183.6(2) 1106.94(7)
Z 2 2 2
$D_{calc} (mg/m^3)$ 1.559 1.606 1.587
Absorption coefficient (mm ⁻¹) 0.878 0.877 1.162
Crystal size (mm ³) $0.51 \times 0.27 \times 0.09$ $0.30 \times 0.13 \times 0.13$ $0.32 \times 0.15 \times 0.12$
Reflections collected 3392 55652 20511
Independent reflections $6714 [R_{int} = 0.1046]$ $6886 [R_{int} = 0.0594]$ $6912 [R_{int} = 0.029]$
Data/restraints/parameters 4481/1/336 5238/7/353 5528/0/316
Goodness-of-fit on F^2 1.043 1.017 1.020
Final R indices $[I > 2\sigma(I)]$ $R_1 = 0.0514, wR_2 = 0.0766$ $R_1 = 0.0487, wR_2 = 0.1157$ $R_1 = 0.0377, wR_2 = 0.0884$
R indices (all data) $R_1 = 0.1035$, $wR_2 = 0.0886$ $R_1 = 0.0731$, $wR_2 = 0.1267$ $R_1 = 0.0531$, $wR_2 = 0.0957$
Largest differences in peak and hole (e $Å^{-3}$)0.539 and -0.3871.352 and -1.0991.00 and -0.52



Fig. 1. ORTEP representation of $[Ni(4)(NO_3)_2]$ -CH₃CN (50% thermal ellipsoids). Selected bond lengths [Å] and angles [°]: Ni–N1 2.086(3), Ni–N4 2.023(2), Ni–N11 2.030(2), Ni–O1 2.157(2), Ni–O2 2.120(3), Ni–O4 2.070(2); N1–Ni–N4 82.7(1), Ni–Ni–N1 82.7(1), N1–Ni–O1 92.2(1), N1–Ni–O4 96.32(9), N4–Ni–O1 87.4(1), N4–Ni–O2 94.0(1), N4–Ni–O4 91.5(1), N4–Ni–O1 91.5(1), N4–Ni–O2 98.1(1), N11–Ni–O4 91.7(1), O1–Ni–O2 59.6(1), O2–Ni–O4 111.8(1).

atmosphere of diethyl ether to yield dark blue crystals. A crystal from this batch was used directly for the X-ray structure analysis. *Anal.* Calc. for $C_{22}H_{22}N_6NiO_8$: C, 47.43; H, 3.98; N, 15.08. Found: C, 47.60; H, 3.89; N, 15.14%. ESI-MS $m/z = 255.0 [4+2Ni+NO_3-H]^{2+}$; 390.1 $[4+Ni-H]^+$.



Fig. 3. Offset π - π stacking in the crystal lattice of [Ni(**4**)(NO₃)₂]·CH₃CN; C_g-C_g 3.752(2) Å, aromatic planes are not parallel (α = 5.5(2)°), β = 17.1°/22.5° [58], symmetry operation: 1 + *x*, *y*, *z*.

2.3.2. [Ni(6)(NO₃)₂]

Nickel nitrate hexahydrate (0.037 g, 0.128 mmol) in warm acetonitrile (3 mL) was added to **6** (0.050 g, 0.128 mmol) in warm acetonitrile (3 mL). Diethyl ether (2 mL) was added and the solution was let stand at 4 °C under an atmosphere of diethyl ether to yield grey-blue crystals. A crystal from this batch was used directly for the X-ray structure analysis. *Anal.* Calc. for C₂₇H₂₃N₅NiO₆: C, 56.67; H, 4.05; N, 12.24. Found: C, 56.41; H, 4.12; N, 12.57%. ESI-MS m/z = 446.1 [**6**+Ni–H]⁺; 1080.1 [2(**6**)+2Ni+3NO₃]⁺. UV–Vis (CH₃CN): λ_{max} in nm (ε in L mol⁻¹ cm⁻¹) = 572 (19.9), 943 (14.7) (the spectrum is in accord with a pseudo octahedral ligand field; it also contained the 'tail' of an intense charge transfer absorption



Fig. 2. Hydrogen bonding interactions present in the crystal lattice of $[Ni(4)(NO_3)_2]$ ·CH₃CN; OH₂4···O6 1.94 Å (O24–H24···O6 150°), symmetry operation: $x_r - 1 + y_r z$; CH₂A···N101 2.59 Å (C2–H2A···N101 151°); CH₃B···N101 2.62 Å (C9H₃B···N101 153°), symmetry operation: $2 - x_r - 0.5 + y_r 1 - z_r$.



Fig. 4. ORTEP representation of the X-ray structure of [Ni(**6**)(NO₃)₂] showing selected atom labels (50% thermal ellipsoids); disorder in the monodentate nitrate ligand not shown. Selected bond lengths [Å] and angles [°]: Ni–N1 2.099(3), Ni–N4 2.046(2), Ni–N11 2.032(2), Ni–O1 2.139(2), Ni–O3 2.114(3), Ni–O4A 2.032(7); N1–Ni–N4 81.69(8), N1–N11 82.26(8), N1–Ni–O1 102.03(7), N1–Ni–O3 162.71(8), N1–Ni–O4A 95.3(2), N4–Ni–N11 163.93(8), N4–Ni–O1 92.39(8), N4–Ni–O3 97.10(8), N4–Ni–O4 82.4(2), N11–Ni–O191.77(8), N11–Ni–O3 98.48(8), N11–Ni–O4A 94.98.2(2), O1–Ni–O3 60.71(7), O1–Ni–O4A 161.0(2).



Fig. 5. Hydrogen bonding between pairs of complex units in $[Ni(6)(NO_3)_2]$; CH9A···O5A 2.53 Å (C9–H9A–O5A 137°); CH2B···O5A 2.54 Å (C2–H2B–O5A 133°); symmetry operation: 2 - x, -y, -z.

band that extended into the visible region and obscured the highest energy d-d transition expected for this geometry).



Fig. 7. ORTEP representation of the structure of $[Zn(5)(NO_3)_2]$ showing selected atom labels (50% thermal ellipsoids). Selected bond lengths [Å] and angles [°]: Zn1–N1 2.059(1), Zn1–N2 2.281(1), Zn1–N3 2.053(2), Zn1–O3 2.079(1), Zn1–O5 2.114(1), Zn1–O4 2.471(2), Zn1–O1 2.728(2); N(1)–Zn1–N(2) 78.01(6), N(1)–Zn1–N(3) 155.95(6), N(1)–Zn1–O(3) 101.01(6), N(1)–Zn1–O(4) 84.47(5), N(1)–Zn1–O(5) 94.82(6), N(2)–Zn1–N(3) 78.28(6), N(2)–Zn1–O(3) 138.39(6), N(2)–Zn1–O(4) 85.91(5), N(2)–Zn1–O(5) 141.19(5), N(3)–Zn1–O(3) 99.34(6), N(3)–Zn1–O(4) 89.89(5), N(3)–Zn1–O(5) 101.13(6), O(3)–Zn1–O(5) 80.36(5), O(4)–Zn1–O(5) 55.32(5).

2.3.3. $[Zn(5)(NO_3)_2]$

Zinc nitrate hexahydrate (0.033 g, 0.112 mmol) in methanol (1 mL) was added to **5** (0.038 g, 0.112 mmol) in methanol (2 mL) and the solution was let stand for several days under an atmosphere of ether to yield the product as a white precipitate. *Anal.* Calc. for $C_{23}H_{21}N_5O_6Zn$: C, 52.24; H, 4.00; N, 13.24. Found: C, 51.99; H, 4.02; N, 13.26%. ESI-MS m/z = 340.2 [**5**+H]⁺; 402.2 [**5**+Zn-H]⁺; 465.1 [**5**+Zn+NO₃]⁺. ¹H NMR (500 MHz, DMSO-d₆, 300 K): δ [ppm] = 3.73 (2H, d, 12a-H); 4.26 (4H, m, 11/12b-H); 7.52 (2H, d, 14-H); 7.59 (2H, m, 2/8-H); 7.68 (5H, m, 1/7/9/16-H); 8.06 (2H, m, 3/6-H); 8.14 (2H, t, 15-H); 8.72 (2H, d, 17-H).

2.4. Crystallography

X-ray structures of $[Ni(4)(NO_3)_2]$ ·CH₃CN and $[Ni(6)(NO_3)_2]$ were determined on a Bruker Nonius Kappa CCD with ω and φ scans at 198(2) K. Data collections were undertaken with collect [50], cell



Fig. 6. Intermolecular $\pi - \pi$ stacking present in the crystal lattice of [Ni(6)(NO₃)₂]; C_g(1)-C_g(2) 3.795(2) Å, aromatic planes are not parallel ($\alpha = 12.2(1)^{\circ}$), $\beta = 27.6^{\circ}/15.5^{\circ}$, symmetry operation: 3 - x, 1 - y, 1 - z; C_g(1)-C_g(3) 3.905(2) Å, aromatic planes are not parallel ($\alpha = 14.6(1)^{\circ}$), $\beta = 21.1^{\circ}/24.2^{\circ}$; symmetry operation: x, -1 + y, z [58].



Fig. 8. Three views of the lattice structure of $[Zn(5)(NO_3)_2]$ showing the intermolecular CH···O interactions as dotted lines; CH3···O1 2.44 Å (C3–H3···O1 132°), symmetry operation: x, 1 + y, z; CH16···O1 2.57 Å (C16–H16···O1 148°), symmetry operation: -1 + x, y, z; CH6A···O6 2.70 Å (C6–H6A···O6 145°), symmetry operation: -x, 1 – y, 2 – z; CH7B···O6 2.62 Å (C7–H7B···O6 144°), symmetry operation: -x, 1 – y, 2 – z; CH9···O3 2.48 Å (C9–H9···O3 164°), symmetry operation: -1 + x, y, z; CH10···O4 2.57 Å (C10–H10···O4 2.57 Å (C10–H10···O4 155°), symmetry operation: -x, -y, 2 - z; CH2···O5 2.47 Å (C12–H12···O5 124°), symmetry operation: 1 - x, -y, 2 - z.



Fig. 9. The three $\pi - \pi$ interaction types present in the crystal lattice of $[2n(5)(NO_3)_2]$: $\pi - \pi$ stacking interactions along the crystallographic *b*-axis ($C_g(1) - C_g(2) 3.747(1)$ Å, aromatic planes are not parallel ($\alpha = 3.9(1)^\circ$), $\beta = 22.1^\circ/25.6^\circ$, symmetry operation: *x*, 1 + *y*, *z*); intermolecular stacking between adjacent pyridyl rings ($C_g(2) - C_g(2) 3.711(1)$ Å, aromatic planes parallel, $\beta = 24.2^\circ$, symmetry operation: *-x*, *-y*, 2 - *z*) and two intermolecular $\pi - \pi$ stacking interactions between naphthalene rings to form a dimer ($C_g(3) - C_g(4) 3.812(2)$ Å, aromatic planes not parallel ($\alpha = 4.2(1)^\circ$), $\beta = 22.92^\circ/26.55^\circ$, symmetry operation: *-x*, 1 - *y*, 1 - *z*) [58].

refinement with Dirax/Isq [51] and data reduction with EvalCCD [52]. The X-ray-data for structure $[Zn(\mathbf{5})(NO_3)_2]$ were collected on a Bruker-AXS Kappa Apex II CCD diffractometer at 120 K. Programs used: APEXII [53], SAINT [54], and DIAMOND3.1 [55].

Both diffractometers employed graphite-monochromated Mo K α radiation generated from a sealed tube (0.71073 Å). Multi-scan empirical absorption corrections were applied to all data sets using the program sADABS [56]. All structures were refined and extended with shelxL-97 [57].

3. Results and discussion

3.1. Complex synthesis

During attempts to obtain crystalline products suitable for X-ray analysis, interaction of **1–9** with nickel nitrate hexahydrate in acetonitrile and/or zinc nitrate hexahydrate in methanol, acetonitrile or methanol/ethyl acetate led to isolation of the range of 1:1 (metal nitrate:N-substituted di(2-picolyl)amine derivative) complexes listed above (also see Supplementary data). The ¹H NMR spectra of the Zn(II) complexes in DMSO-d₆ confirmed complexation of the respective substituted di(2-picolyl)amine ligands in each case with, as expected, the majority of the ligand proton signals occurring at lower field for the complexes relative to those for the corresponding free ligand (see Supplementary data). Mass spectral and microanalysis data for all complexes were in accord with their respective formulations. In our hands only [Ni(4) $(NO_3)_2$]·CH₃CN, $[Ni(6)(NO_3)_2]$ and $[Zn(5)(NO_3)_2]$ yielded suitable crystals for X-ray structure determinations and only these are now discussed (Table 1). Further details for the remaining complexes are presented in the Supplementary data.

3.2. Discussion of the X-ray structures

The structure of the dark blue crystalline complex, $[Ni(4) (NO_3)_2]$ -CH₃CN, formed from reaction of *N*-(4-carboxybenzyl)-di(2-picolyl)amine (4) with nickel nitrate in acetonitrile, shows

that the Ni(II) centre exhibits a distorted octahedral coordination geometry with **4** acting as a tridentate ligand, bound meridionally (mer) via its N₃-donor set (Fig. 1). The remaining three coordination sites are occupied by a monodentate and a bidentate nitrato ligand. The acetonitrile molecule is not bound to the nickel but occupies a void in the lattice structure; there is a bifurcated hydrogen bond to N101 of the acetonitrile from the methylene protons CH2a and CH9b (Fig. 2). In part, the large distortion from O_h symmetry present in this complex is a consequence of the small bite angle associated with the four-membered chelate ring formed on coordination of the bidentate nitrato ligand. It is interesting to compare this structure with those recently reported for two nickel nitrate complexes of the related di(2-picolyl)amine derivative incorporating a *t*-butyl *N*-substituent. This latter ligand forms 1:1 metal:ligand complexes which crystallize with both facial and meridional conformations in the same unit cell [3]. In the case of the mer derivative the coordination geometry is quite similar to that observed in $[Ni(4)(NO_3)_2] \cdot CH_3CN$.

The non-coordinated carboxylic –OH of **4** in each complex unit is intermolecularly hydrogen bonded to an O-atom of a monodentate nitrate ligand in an adjacent complex unit such that individual complexes are linked in chains that are directed along the crystallographic *b*-axis (Fig. 2). Adjacent pairs of pyridine rings are also involved in intermolecular offset π – π stacking to produce a further chain-like arrangement that is orientated along the crystallographic *a*-axis (Fig. 3).

The X-ray structure of the dark blue crystalline complex, $[Ni(6)(NO_3)_2]$, obtained by reaction of *N*-(9-anthracenylmethyl)di(2-picolyl)amine (6) with nickel nitrate in acetonitrile, shows that the Ni(II) centre once again exhibits a distorted octahedral coordination geometry, with 6 being bound meridionally *via* its N₃-donor set (Fig. 4). The remaining three coordination sites are filled by a (disordered) monodentate and a bidentate nitrato ligand, with the coordination sphere in [Ni(6)(NO₃)₂] being thus quite similar to that in [Ni(4)(NO₃)₂]·CH₃CN.

Two weak hydrogen bonds are present between the axial methylene hydrogen atoms on one complex unit and an O-atom of the non-chelating NO_3^- ligand on a second unit such that four hydrogen bonds link pairs of complexes as shown in Fig. 5.

Weak intermolecular π - π stacking interactions are also present between the anthracene and pyridine rings such that one such interaction type links complex units to form a chain orientated along the crystallographic *b*-axis, while two other interactions link pairs of complexes in different chains in a reciprocal fashion as shown in Fig. 6.

As found for the Ni(II) complexes discussed above, the Zn(II) centre in $[Zn(5)(NO_3)_2]$ also has a distorted six-coordinate environment with the N₃-donor set of **5** once again coordinating in a meridional fashion with the remaining coordination positions occupied by a monodentate and a bidentate nitrato ligand (Fig. 7). The six coordinate geometry is thus broadly similar to those in the related $[Ni(4)(NO_3)_2]$ ·CH₃CN and $[Ni(6)(NO_3)_2]$ complexes discussed above.

There are no classical hydrogen bonds present in the zinc complex structure, although a number of weak intermolecular interactions between oxygens on the bound nitrato ligands and CH hydrogens on adjacent complex units are present that help stabilize the lattice arrangement (Fig. 8). Three types of intermolecular π - π stacking also occur between complex units in the structure; these are illustrated in Fig. 9.

4. Concluding remarks

The synthesis of the Ni(II) and Zn(II) nitrate complexes of di(2picolyl)amine and selected *N*-substituted derivatives chosen from $\mathbf{2}$ to $\mathbf{9}$ are described and the crystal structures of [Ni(4)

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Appendix A. Supplementary data

CCDC 798320, 798321 and 798322 contains the supplementary crystallographic data for ($[Ni(6)(NO_3)_2]$), ($[Ni(4)(NO_3)_2]$ ·CH₃CN) and ($[Zn(5)(NO_3)_2]$). 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.poly.2010.12.005.

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