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Crystallographic studies of 2-picolyl substituted naphthalene diimide and bis-phthalimide ligands and their supramolecular coordination chemistry

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Here we report the synthesis of two *N*-(2-picolyl) substituted bis-imide ligands, *N,N’*-di(2-picolyl)-1,4,5,8-naphthalenetetracarboxylic diimide **L1** and *N,N’*-di(2-picolyl)-4,4′-oxybisphthalimide **L2**, and describe their coordination chemistry in the crystalline state with late *d*-block metals, with the intention of probing the applicability of the recently reported N,O-chelating mode observed in *N*-(2-picolyl) substituted 1,8-naphthalimides. Four new crystalline coordination compounds have been prepared and structurally characterised; *poly*-[Zn(L1)Cl2]·3(C3H6O) **1** and *poly*-[ZnCl2(**L1**)]·MeCN **2** are structurally related one-dimensional coordination polymers whose extended structure contains well-defined solvent channels, the nature of which is coupled to the ability of the lattice solvent molecules to undergo n···π interactions with the 1,4,5,8-napthaletetracarboxylic diimide (NDI) core. [H2**L1**][ZnCl4]·2H2O **3** is a hydrogen-bonded structure of tetrachlorozincate anions bound by the doubly protonated **H2L1**cation, while repeating this reaction in the presence of copper(II) ions gave the ligand dihydrochloride salt (**H2L1**)2Cl **4**. Finally, reaction of **L1** with AgSbF6 gave the one-dimensional polymer *poly*-[Ag**L1**]SbF6 **5**, in which weak but notable carbonyl coordination was observed in addition to stronger coordination from the pyridyl groups. Conversely, compound **L2** failed to convincingly show any reaction or coordination with transition metals, and only the crystalline ligand itself could be isolated. Analysis of these results, as well as studies into the solution state coordination chemistry of these compounds, suggests an underlying barrier to coordination in these species compared to the 1,8-naphthalimides, but provides interesting avenues for crystal engineering.

Introduction

Naphthalenediimide (NDI) derivatives are versatile building blocks which have been extensively studied in supramolecular coordination chemistry.1 Their large conjugated planar structure and ease of functionalisation has made them attractive tectons in crystal engineering studies,2 while their functionality as dyes and light harvesting chromophores has also led to advances in advanced optical materials and semiconductors.3 Like the related 1,8-naphthalimide fluorophore,4 substituted NDIs also present attractive prospects in chemical sensor design based on both their colorimetric and electrochemical properties.5 In their structural chemistry, NDIs are well known to form extended structures dominated by packing forces involving their conjugated π systems, where offset face-to-face (OFF) and anion···π interactions are both reliable synthons.6

As well as the chemistry of the purely organic derivatives, the coordination chemistry of NDIs is also a popular subject for exploration.7 Most commonly, NDI-based ligands are prepared by functionalisation of the diimide nitrogen site with pyridyl or benzoic acid substituents, enabling coordination to *d*-metal

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**Scheme 1:** Structure of compounds **L1** and **L2** (top), and comparison to the previously reported *N*-(2-picolyl)-1,8-naphthalimide chelators (bottom).

Ions, forming metal organic frameworks (MOFs) and coordination polymers.8 Rigid 4-pyridyl, 4-carboxyphenyl and 3,5-dicarboxyphenyl substitution has been particularly successful in generating functional MOFs with interesting properties, including photochromism, electrical conductivity, lithium storage and charge transfer behaviour.9

While introducing flexible linkers tends to reduce the available pore volume in such systems,10 various NDI systems containing *sp*3 linkages between the core and ligand groups have been prepared.11 For example, Turner and co-workers have reported several examples of chiral NDI ligands leading to homochiral coordination polymers exhibiting interesting topologies and with chiral separation properties.12 While several reports have emerged of flexibly-linked pyridyl or picolyl-substituted NDIs, such investigations almost exclusively focus on the divergent 3- and 4-isomers.13

We have recently reported a family of coordination compounds of late 3*d* metal ions in which an unusual (N,O) chelating coordination mode is observed from 2-picolyl substituted 1,8-naphthalimide ligands.14 Here, we extend our study into the coordination chemistry of 2-picolylimides with the synthesis of two new *N*-(2-picolyl)diimide ligands, *N,N’*-di(2-picolyl)-1,4,5,8-naphthalenetetracarboxylic diimide and *N,N’*-di(2-picolyl)-4,4′-oxybisphthalimide, **L1** and **L2**, respectively, and study their coordination chemistry and supramolecular properties in the crystalline phase and in solution.

Experimental

**Materials and Methods**

All reagents and solvents were purchased from Sigma-Aldrich, Merck or Fisher Scientific, were of reagent grade or better and used without further purification.

All NMR spectra were recorded using a Bruker Spectrospin DPX-400 instrument operating at 400 MHz, for 1H and 100 MHz for 13C or a Bruker AV-600 instrument operating at 600.1 MHz for 1H NMR and 150.9 MHz for 13C NMR. Chemical shifts are reported in ppm with the residual solvent as the internal reference. All NMR spectra were carried out at 293 K.

Mass spectra were required using a Micromass time of flight spectrometer (tof), interfaced to a Waters 2690 HPLC. The instrument was operated in positive or negative mode as required. Leucine Enkephalin was used as an internal lock mass. Masses were recorded over the range 100-1000 m/z.

Melting points were determined using an Electrothermal IA9000 digital melting point apparatus and are uncorrected.

Infrared spectra were recorded on a PerkinElmer Spectrum One FTIR spectrometer in the range 4000 - 650 cm-1.

Phase purity of all crystalline materials was confirmed with X-ray powder diffraction patterns measured with a Bruker D2 Phaser instrument using Cu-Kα (λ = 1.5405 Å) radiation. Samples were finely ground and applied to a quartz sample holder. Raw data were compared with the simulated patterns from the single crystal data collections carried out at 100 K.

Thermogravimetric analysis of **L1**, **L2** and compounds **1-4** was performed on Perkin Elmer Pyrus 1 TGA equipped with an ultra-micro balance with a sensitivity of 0.1 microgram. The temperature range is from 25 – 900 °C with a scan rate 5 °C min-1, under a N2 purge flow of 20 mL.min-1.

**X-ray Crystallography**

Structural and refinement parameters are presented in Table 1. All diffraction data were measured using a Bruker APEX-II Duo dual-source instrument using graphite-monochromated Mo Kα (λ = 0.71073 Å) or microfocus Cu Kα (1.5405 Å) radiation as specified. Datasets were collected using ω and φ scans with the samples immersed in NVH immersion oil and maintained at a constant temperature of 100 K using a Cobra cryostream. The data were reduced and processed using the Bruker APEX-3 suite of programs.15 Multi-scan absorption corrections were applied using SADABS.16 The diffraction data were solved using SHELXT and refined by full-matrix least squares procedures using SHELXL-2015 within the OLEX-2 GUI.17 All non-hydrogen atoms were refined with anisotropic displacement parameters. All carbon-bound hydrogen atoms were placed in calculated positions and refined with a riding model, with isotropic displacement parameters equal to either 1.2 or 1.5 times the isotropic equivalent of their carrier atoms. Compounds **L2**, **1-3** and **5** provided good quality diffraction data and their models could be refined to convergence with only minimal restraints, mostly involving disordered lattice solvent molecules. Compound **4** exhibited poor diffraction characteristics with generally low intensity scattering and no useful reflections beyond 1.0 Å resolution. For this reason, the structure model presented for compound **4** is purely a connectivity model presented only to support the conclusions drawn from supporting characterisation methods. Particular refinement strategies for each structure, including the specific use of restraints, are provided in the combined crystallographic information files: CCDC 1872943-1872948

**Photophysical Measurements**

Unless otherwise stated, all measurements were performed at 298 K in acetonitrile (spectroscopic grade, Aldrich) solutions. UV-Vis absorption spectra were measured in 1 cm quartz cuvettes (Hellma) on a Varian Cary 50 spectrophotometer. Baseline correction was applied for all spectra.

Synthesis and characterisation of *N,N’*-di(2-picolyl)-1,4,5,8-naphthalenetetracarboxylic diimide (L1)

The synthesis of L1 was carried out according to modified literature procedures.14 To a suspension of 1,4,5,8-tetracarboxylic naphthalic dianhydride (250 mg, 0.93 mmol) and AcOH (8 mL), 2-picolylamine (0.40 mL, 4 mmol, 4 eq) was added and the mixture was heated under reflux for six hours. After cooling to room temperature, the reaction mixture was poured into H2O (100 mL), which produced a yellow precipitate. The mixture was then taken to pH 6 with aqueous KOH to aid precipitation. The resulting precipitate was filtered and washed with MeOH and Et2O and dried in air. Yield (338 mg, 93 %), mp > 300 °C. Found C 69.38, H 3.51, N 12.25. Anal. Calc. for C26H16N4O4 C 69.64, H 3.60, N 12.49% δH (600 MHz, d6- DMSO) δ 8.74 (s, 4H, H5), 8.42 (d, 3J=4.2 Hz, 2H, H4), 7.78 (t, 3J1 = 7.7Hz, 2H, H2), 7.49 (d, 3J=7.8 Hz, 2H, H1), 7.29 – 7.25 (m, 2H, H3), 5.40 (s, 4H, H7); δC (151 MHz, d6-DMSO): 163.15, 155.90, 149.50 (C4), 137.25 (C2), 131.29 (C5), 126.87, 122.75 (C3), 121.62 (C1), 80.32, 45.80 (C6); νmax (ATR) cm-1: 2995w, 1704s, 1667s, 1581s, 1455s, 1412m, 1375m, 1285m, 1347s, 1331s, 1247s, 1188m, 1152m, 1051m, 1005s, 812m, 765s; LRMS *(m/z)* (ESI+): 449.1 (M+H)+ calculated for C18H12N3O4 *m/z =* 449.1. UV-vis (CH3CN) λmax/nm (×103 εmax/L.mol-1.cm-1): 237 (34.5±0.5), 357 (19.9±0.2), 378 (25.0±0.2).

**Synthesis and characterisation of *N,N’*-di(2-picolyl)-4,4′-oxybisphthalimide (L2)**

To a suspension of 4,4’-oxybis-phthalic anhydride (300 mg, 0.97 mmol) and AcOH (5 mL), 2-picolylamine (0.40 mL, 4 mmol, 4 eq) was added and the mixture was heated under reflux for six hours. After cooling to room temperature, the reaction mixture was poured into H2O (100 mL), which produced a yellow precipitate. The mixture was then taken to pH 6 with aqueous KOH to aid precipitation. The resulting precipitate was filtered and washed with MeOH and Et2O and dried in air. Yield (462 mg, 97 %), mp > 300 °C Found C 68.41, H 3.59, N 11.41. Anal. Calc. for C28H18N4O5 C 68.57, H 3.70, N 11.42% δH (400 MHz, d6- DMSO) δ 8.45 (d, 2H, H8), 8.00 (d, 3J=8.2 Hz, 2H, H1), 7.78 (td, 3J1 = 7.7Hz, 1.8Hz, 2H, H6), 7.61(dt, 3J=8.0 Hz, 4H, H5,H7), 7.42 (d, 3J=7.9 Hz 2H, H2), 4.92 (s, 4H, H4); δC (151 MHz, d6-DMSO): 166.75, 166.57, 160.52, 154.75, 148.83, 136.39, 134.31, 127.06, 125.55, 124.42, 122.30, 120.97, 113.39, 113.52; νmax (ATR) cm-1: 3077w, 1768m, 1702s, 1604m, 1570w, 1422s, 1394s, 1326w, 1268m, 1237s, 1154w, 1114s, 995w, 953m, 919m, 850w, 751s, 672m, 641m, 600m. LRMS *(m/z)* (ESI+): 490.5 (M+H)+ calculated for C18H12N3O4 *m/z =* 490.5. UV-vis (CH3CN) λmax/nm (×103 εmax/L.mol-1.cm-1): 235 (50.3±0.5).

Synthesis and characterization of *poly*-[Zn(L1)Cl2]·3(C3H6O) (1)

*N*-(2-Picolyl)-naphthalene diimide (20 mg, 1 eq, 4.44x10-5 mol)

and ZnCl2 (2 eq, 12 mg) were dissolved in acetone (5 mL). The resulting solution was colourless, forming orange crystals after 24 hours which gradually lost lattice solvent and hydrated on standing in air. Yield (16 mg, 49 %); m.p. >300 °C. Found C 52.68, H 3.26, N 8.31. Anal. Calc. for C29H24N4O6Cl2Zn ([Zn(L1)Cl2]·C3H6O·H2O C 52.71, H 3.66, N 8.48%; νmax (ATR) cm‑1 1707s, 1664s, 1510m, 1581m, 1489m, 1441m, 1333s, 1289s, 1245s, 1184m, 1005m, 889w, 812w, 767s, 642m, 579m.

Synthesis and characterization of *poly*‑[ZnCl2(L1)]·MeCN (2)

*N*-(2-Picolyl)-naphthalene diimide (20 mg, 1 eq, 4.44x10-5 mol) and ZnCl2 (4 eq, 24 mg) were dissolved in MeCN (5 mL). The resulting solution was colourless, forming orange crystals after 24 hours which gradually lost lattice solvent and hydrated on drying in air. Yield (16 mg, 58 %); m.p. >300 °C. Found C 50.98, H 2.57, N 9.24. Anal. Calc. for C26H16N4O4Cl2Zn·1.5H2O ([ZnCl2(L1)]·1.5H2O)C 51.05, H 3.13, N 9.16% νmax (ATR) cm-1 2986w, 2252m, 1706s, 1655s, 1610s, 1580s, 1486m, 1441s, 1411m, 1373s, 1328s, 1244s, 1176s, 1119w, 1066w, 1026m, 1004s, 917m, 895m, 807w, 758s, 700m, 636m, 610w, 568w, 557w.

Synthesis and characterization of [H2L1][ZnCl4]·2H2O (3) and (H2L1)2Cl (4)

Due to the similar conditions required for each phase, the two pyridinium compounds were inevitably formed as mixtures under all conditions screened. The methods used to obtain the highest fraction of each individual phase are reported here.

Compound 3: *N*-(2-Picolyl)-naphthalene diimide (20 mg, 1 eq, 4.44x10-5 mol) and ZnCl2 (2 eq, 12 mg) were added to MeCN:EtOAc (1:1, 5 mL) and hydrochloric acid (0.1 mL, 100 µM) was added to the suspension. The resulting beige suspension precipitated yellow crystalline material after 24 hours which was analysed for a mixture of the tetrahalozincate and hydrochloride salts. Yield (12 mg, 40 %); m.p. >300 °C. Found C 50.21, H 2.86, N 8.91. Anal. Calc. for C26H22N4O6Cl4Zn (3) C, 45.02; H, 3.20; N, 8.08%; Anal. Calc. for the mixture (C26H22N4O6Cl4Zn)0.65(C26H18Cl2N4O4)0.35 C 50.21, H 3.29, N 9.00. νmax (ATR) cm-1 IR 3077w, 1704s, 1655s, 1606w, 1581m, 1445m, 1431w, 1375w, 1347s, 1332s, 1248s, 1183s, 1002m, 925w, 905w, 824w, 810w, 767s, 751s, 711w, 637w, 571w.

Compound 4: *N*-(2-Picolyl)-naphthalene diimide (20 mg, 1 eq, 4.44x10-5 mol) and CuCl2 (2 eq, 12 mg) were dissolved in MeCN:EtOAc (1:1) (5 mL), an acid spike (HCl, (0.1 mL, 0.0001M) was added to the suspension. The resulting beige suspension precipitated yellow crystals after 24 hours. This phase was predominantly the dihydrochloride salt, though elemental analysis of multiple batches consistently indicated the presence (*ca.* 5%) of a denser phase with a larger inorganic fraction. This phase could not be isolated, but based on the structure of 3 we suggest a tetrachlorocuprate species is feasible. Yield (15 mg, 52 %); m.p. >300 °C. Found C 59.01, H 3.32, N 10.46; Anal. Calc. for C26H18N4O4Cl2 (4) C, 59.90; H, 3.48; N, 10.75%; Anal. Calc. for the mixture (C26H18N4O4Cl2)0.95 (C26H22N4O6Cl4Cu)0.05 C 59.01, H 3.46, N 10.59. νmax (ATR) cm-1 1997w, 1703s, 1654s, 1580s, 1535w, 1453m, 1375m, 1334s, 1245s, 1182m, 1001m, 903w, 824w, 766s, 637m, 617m, 576w.

Synthesis and characterization of *poly*-[AgL1]SbF6 (5)

*N*-(2-Picolyl)-naphthalene diimide (20 mg, 1 eq, 4.44x10-5 mol) and AgSbF6 (2 eq, 60 mg) were dissolved in acetone (5 mL). The resulting solution was colourless, forming yellow crystals after 24 hours. Yield (17 mg, 48 %); m.p. >300 °C. Found C 39.48, H 1.98, N 6.77. Anal. Calc. for C26H16N4O4AgSbF6 C 39.43, H 2.03, N 7.07% νmax (ATR) cm-1 3082w, 2958w, 1691s, 1654s, 1604s, 1578s, 1488m, 1446s, 1366s, 1330s, 1297s, 1250s, 1176m, 1094m, 1017m, 997m, 876m, 841s, 765s.

Results and discussion

**Synthesis and characterization of L1 and L2**

The ligands *N,N’*-di(2-picolyl)-1,4,5,8-naphthalene tetracarboxylic diimide **L1** and *N,N’*-di(2-picolyl)-4,4′-oxybisphthalimide **L2** were prepared based on modified literature procedures,14 by the reaction of 2-picolylamine with the appropriate dianhydride in acetic acid, and characterized by standard analytical methods. In both cases, we envisaged analogous coordination chemistry to that previously observed for the *N*-(2-picolyl)-1,8-naphthalimide analogues, involving either N,O-chelation or monodentate coordination through the pyridine nitrogen atom, depending on the availability of the imide oxygen atom lone pairs as illustrated in Scheme 1. The structure of **L1** especially would also be expected to lend itself to structure-directing crystal packing forces involving the π backbone.

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**Figure 1:** Structure of **L2** with heteroatom labelling scheme. Hydrogen atoms are omitted for clarity.

Single crystals of **L1** itself suitable for X-ray diffraction were not obtained, despite screening a range of solvent systems (toluene, hexane, chloroform, dichloromethane, ethyl acetate, acetonitrile, acetone, THF, methanol and mixtures of these solvents), and exploring a variety of standard crystallization techniques. However, single crystals of **L2** were regularly obtained from mixtures of **L2** and metal ions; indeed, the ready crystallization of **L2** as the free base seemed to hinder the generation of any crystalline coordination compounds containing this ligand.

Analysis of the colourless crystals of **L2** by X-ray diffraction provided a structural model in the orthorhombic space group *Pccn*. The complete molecule is present in the asymmetric unit and exhibits a twisted, near-helical conformation as illustrated in Figure 1. The two imide rings exhibit a mean interplanar angle of 111.11(4)° manifested by twisting about the central oxo spacer, while the two picolyl nitrogen atoms are separated by 11.6571(18) Å. No solvent molecules or other guests were located within the lattice.

Due to the relatively small size of the individual aromatic domains in **L2**, the extended structure shows relatively few strong intermolecular π-π or related contacts of any significance. Adjacent phthalimide groups facilitate offset symmetric face-to-face interactions with interplanar distances of 3.32 Å and 3.41 Å, albeit with slipped distances of 1.73 Å and 1.22 Å, respectively, between the phenyl centroids for the two unique interactions. These interactions are supported by C-H···O hydrogen bonds between the aromatic C-H group at the phthalimide 3-position and an adjacent imide oxygen atom (distance C···O 3.3522(16) Å).

For **L2**, the comparatively electron rich backbone would lead one to expect more favourable coordination through the carbonyl groups compared to the naphthalimide or naphthalene diimide congeners. One factor influencing the lack of observed coordination may be the deviation in imide ring geometry between **L1** and naphthalimide derivatives, where the 5-membered imide ring in **L2** imparts a smaller N‑C=O angle with geometric ramifications for any chelate ring involving this site. Nonetheless, the very poor solubility of **L2** in weakly competitive solvents and ready crystallization of the free base seems the most likely factor behind the lack of observed coordination of **L2** in the crystalline phase.

The thermal stabilities of both **L1** and **L2** were probed through thermogravimetric analysis. Both ligands had high melting points (>300 °C) and maintained stable mass in TGA until above this temperature. A rapid single step decomposition of the ligands was then observed; for **L1**, decomposition was observed above 340 °C, and for **L2** above 360 °C. This further corroborates that both ligands have high thermal stabilities. (Figures S10 and S11, ESI)

Solution Studies of L1 and L2

We initially attempted to discern coordination of the 2-picolylimide motifs in solution, focusing on Zn(II) ions for the purposes of NMR compatibility and expecting to monitor coordination through changes in the pyridyl π-π\*/n-π\* UV-Vis absorbances. **L1** itself shows several absorbances in the UV region, with λmax = 234 nm, 356 nm and 376 nm (ε = 34.5 ± 0.5**,** 19.9 ± 0.2, and 25.0 ± 0.2 ×103 L·mol-1·cm-1, respectively), while the absorption profile of the free **L2** is more simple due to its limited conjugation (λmax = 235 nm (ε = 50.3± 0.5 ×103 L·mol-1·cm-1). (Figure S18, ESI) The addition of Zn(II) chloride in acetonitrile to these solutions led to only minor variations in the global intensity with no significant local changes to indicate any significant coordination in solution at these concentrations.

The absorption spectra of re-dissolved compound **2** also closely agreed with the absorption spectrum of free **L1**. Similarly, no [ML] adducts were observed by electrospray mass spectrometry. NMR spectroscopy was hampered by the poor solubility of pure **L1** in CD3CN. Ligand **L2** shows better solubility in CD3CN and exhibits a minor and monotonic downfield shift of most resonances following addition of ZnCl2 aliquots by NMR. However, given the apparent lack of a strongly preferred binding mode in solution, these observations are difficult to delineate from the concurrent reduction in pH of the solution also caused by addition of ZnCl2, and so we are hesitant to definitively ascribe these findings to metal coordination. These findings are in contrast to our findings with *N*-(2-picolyl)-1,8-naphthalimide, which showed clear interaction with ZnCl2 by NMR with an inflection corresponding to the [ML] species,14 and imply a variation in solution state binding properties in switching from the monoimide to the diimide compounds. (Figure S19, ESI).

**Synthesis of Zn(II) coordination polymers of L1**

To probe the coordination behaviour of **L1** and **L2** in the absence of convincing solution-state evidence of metal coordination, we redirected our attention to generating crystalline coordination compounds, reasoning that any metal binding tendencies would be enhanced at higher concentrations and that the lower solubility of a chelated MCl2 species might drive an otherwise unfavourable equilibrium. Divalent first row transition metal chlorides (cobalt, manganese, nickel, zinc and copper) and silver(I) salts in a range of organic solvents were screened for evidence of coordination by **L1** and **L2**. Of these experiments, crystalline material was obtained from zinc(II), copper(II) and silver(I), while only unreacted ligand was recovered from manganese(II), cobalt(II) and nickel(II) as their chloride salts, immediately indicating a difference in binding affinity between **L1/L2** and the previously reported naphthalimides. A summary of the relevant structural parameters for these compounds is provided in Table 1. The composition and purity of each material was determined through powder X-ray diffraction, IR and elemental analysis.

Synthesis and structure of *poly*-[Zn(L1)Cl2]·3(C3H6O) 1

Combining acetone solutions of **L1** and ZnCl2 in a 1:2 stoichiometry afforded orange crystals after standing at room temperature for 48 hours, which were isolated by filtration. Analysis by single crystal X-ray diffraction provided a structural model in the monoclinic *P*2/*c* space group, revealing a polymeric structure with the formula *poly*-[Zn(**L1**)Cl2]·3(C3H6O), shown in Figure 2. The asymmetric unit contains half of one molecule of **L1**, and a zinc ion occupying a special position, exhibiting a regular tetrahedral geometry (τ4 = 0.89)18 with a coordination sphere occupied by two equivalent pyridyl nitrogen atoms and two chlorido ligands. The N-Zn and Cl-Zn bond lengths of 2.0765(7) and 2.2321(2) Å, respectively, conform to the expected values. There are also two acetone sites within the asymmetric unit, with a total occupancy of 3 molecules per zinc site. The coordination mode exhibited in this structure contrasts the analogous naphthalimide derivative, as coordination occurs in a purely monodentate fashion through the pyridyl nitrogen atom rather than in a chelating (N,O) coordination mode as previously observed. Expanding the structure through crystallographic symmetry reveals a one-dimensional coordination polymer oriented parallel to the [201] vector.

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**Figure 2** Structure of compound **1**, showing repeat unit with labelling scheme for coordinating heteroatoms (top) and extended structure of a single chain of **1** (bottom). All hydrogen atoms and lattice solvent molecules are omitted for clarity. Symmetry codes used to generate equivalent atoms: (i) 2-x, +y, 3/2-z.

Concerning the weak intermolecular forces governing the extended structure of **1,** the most significant consist of reciprocated C-H···O interactions between adjacent coplanar NDI moieties, and n-π interactions between the lattice solvent molecules and the aromatic faces as illustrated in Figure 3. These interactions involve the imide oxygen atom and nearest NDI C-H group and exhibit a relatively short C···O distance of 3.246(1) Å and a C-H···O angle of 152°. While naphthalene and perylene-diimide species in general are well-known for their aggregation through parallel offset face-to-face (OFF) π-π interactions, surprisingly no such contacts are observed in the structure of **1**. Rather, both equivalent aromatic faces of the **L1** group undergo n-π interactions with the lattice acetone

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**Figure 3** (Top)The interactions between lattice acetone molecules and the π-surface of **L1** within the structure of **1**. A single disordered contributor is represented for clarity. (Bottom) Extended structure of compound **1** viewed parallel to the primary solvent channels. All hydrogen atoms are omitted for clarity.

molecules, largely centered on the imide rings; the minimum O···mean plane distances of 2.77 and 3.13 Å for the ordered and disordered acetone molecules, respectively, are indicative of a substantial attractive force. The clustering of the lattice acetone molecules towards both faces of the NDI core serves to align the lattice acetone molecules into one-dimensional stacks parallel to the chain propagation axis (Figure 3, bottom).

Thermogravimetric analysis of an air-dried sample of **1** reveals a two-step thermal decomposition pathway. An initial mass loss of 10 % occurs with initiation at room temperature, representing rapid desolvation within the structure. Above 300 °C, decomposition of the organic fraction of the material is observed (Figure S12, ESI). The rapid mass loss near room temperature is consistent with the findings from elemental analysis of a partially hydrated phase for an air-dried sample, which suggested a formula of *poly*-[Zn(**L1**)Cl2]·(C3H6O)·H2O (calculated volatile mass 11 %). To confirm this finding, thermogravimetric analysis was repeated with a sample that had been heated to the desolvation temperature (120 °C, which caused a visible loss of crystallinity) and left to dry in air overnight. An initial mass loss of 11 % occurred from room temperature, suggesting rehydration occurs at ambient conditions. This is followed by a further 4 % mass loss until 200 °C. As with the pristine material, decomposition of the organic fraction of the material is observed above 300 C. (Figure S13, ESI)

Synthesis and structure of *poly*‑[ZnCl2(L1)]·MeCN 2

Given the notable interactions between the acetone guests and the NDI backbone of **L1** in compound **1**, the reaction was repeated in acetonitrile to test for any structural dependence on the electron donor properties of the guest solvent. Orange crystals were deposited from the reaction of acetonitrile solutions of **L1** and zinc chloride after 24 hours. Analysis by X-ray diffraction provided a structural model in the orthorhombic space group *Pnna*. The asymmetric unit of *poly*‑[ZnCl2(**L1**)]·MeCN is shown in Figure 4, and contains one

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**Figure 4** The structure of compound **2**, showing the repeat unit with labelling scheme for the coordination sphere (top) and the structure of a single one-dimensional chain (bottom). All hydrogen atoms and lattice solvent molecules are omitted for clarity. Symmetry codes used to generate equivalent atoms: (i) +x, 3/2-y, 1/2-z.

zinc ion occupying a special position and bound in tetrahedral geometry (τ4 = 0.95)18 by two pyridyl nitrogen atoms and two chlorido ligands. This arrangement is strongly reminiscent of the structure of **1**, and the N-Zn and Cl-Zn bonds of 2.061(2) and 2.2260(7) Å are also functionally identical to compound **1**. However, in contrast to **1**, in **2** the two pyridyl groups are oriented on the same face of the central NDI, rather than the *anti* conformation. There is also a considerable bowing evident in the NDI backbone in compound **2**; defining mean planes in the two six-membered imide rings reveals an (interplanar) angle of *ca* 10°. Solvent molecules were also detected within the lattice, although only a single acetonitrile site was located within the asymmetric unit with a total occupancy of one MeCN species per zinc ion. When compared to **1**, the intermolecular interactions in **2** contain similar elements, however the reduced quantity of lattice solvent and desymmetrization of the two faces of the naphthalene diimide plane are related to variations in the longer-range intermolecular contacts and packing modes. On one face, n-π interactions are observed between the acetonitrile molecules and the NDI plane, with N···mean plane distance of 3.21 Å which are considerably longer than that observed in **1** and consistent with the reduced electron donor capacity of the nitrile nitrogen atom.

On the opposing face of the NDI core, adjacent **L1** species engage in offset face-to-face π-π interactions. While the mean interplanar distance of 3.24 Å suggests a substantial interaction, the large slip distance of 5.4 Å between the two naphthyl centroids ensures that direct interaction is only achieved at the periphery of the molecule with overlap between the imide carbonyl groups and the adjacent naphthyl core. The long-range structure of **2** bears some resemblance to **1**; the one-dimensional polymeric strands oriented parallel to the crystallographic *b* axis lie perpendicular to the acetonitrile solvent channels which proceed along the *a* axis, but rather than being flanked on both faces by solvent molecules, a double-layer is evident to the channel walls in the direction of the *c* axis; enforced by the stacking of adjacent imides as illustrated in Figure 5. Thermogravimetric analysis of an air-dried sample of **2** revealed a multistep decomposition (Figure S14, ESI). There is an initial weight loss of approximately 6 % between 30-100 °C, consistent with the solvation of one acetonitrile molecule per zinc ion suggested from the diffraction data (calculated volatile mass 6.5 %). Compound **2** was found by elemental analysis to eventually lose the volatile lattice solvent upon drying in air, however; the best formulation to describe the air-dried sample is *poly*‑[ZnCl2(**L1**)]·1.5H2O (calculated volatile mass 4.5 %). Above 300 °C, thermal decomposition of the material framework occurs (Figure S14, ESI). Thermogravimetric analysis was repeated with a sample that was heated to the desolvation temperature (100 °C) and left to dry in air overnight. Similarly to **1**, this process was accompanied by a loss of crystallinity. For the dried and air-exposed sample, initial mass loss of 7 % occurred from 30-100 °C, followed by a further mass loss of 4 % until 200 °C, again indicating association of atmospheric water with the dried sample. (Figure S15, ESI)

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**Figure 5** (Top) The interactions of lattice acetonitrile, shown as overlapping disordered contributors, with the bowed π-surface of **L1** within the structure of **2**; (Bottom) The extended structure of compound **2** viewed parallel to the primary solvent channels. All hydrogen atoms are omitted for clarity.

The origin of different coordination tendencies between the bis-2-picolyl NDI **L1** and the analogous *N*-(2-picolyl)-1,8-naphthalimide is most likely a combination of several contributing factors. The electronic nature of the carbonyl groups in both cases is expected to be reasonably similar, especially as coordination in the naphthalimide case has been shown to be invariant to the presence of an electron withdrawing substituent in the 4-position.14 As such, we would not expect the carbonyl coordination to be prohibited in the case of NDIs on purely electronic grounds.

Given the reliance on crystallization (due to the presumably low binding constants requiring very high concentrations in order to manifest), an argument may be made on the grounds of molecular symmetry and the tendency for these NDI molecules to adopt symmetric conformations in the crystalline state. It may be expected that disruption of the symmetry of the imide group may be more prone to reduction in crystal packing efficiency for NDIs compared to naphthalimides which already lack the D2h symmetry of the parent NDI core, and that this cost is not offset by the relatively small energy gain in coordinating the imide carbonyl. The lower intrinsic solubility of the ditopic NDIs and their tendency to form polymers with N2Cl2 coordination spheres, with precipitation acting as an equilibrium driving force, also most likely has a strong culpability in the coordination modes observed here. In all cases, repeated experimentation at higher stoichiometries, to favour the M2L species, also failed to affect the desired coordination mode, instead reproducibly generating the 1:1 stoichiometry products.

**Solvent exchange experiments**

Given the similarities in connectivity between compounds **1** and **2**, and the seemingly important influence of solvent-NDI interactions within the structures, solvent exchange experiments were carried out.

Crystals of **1** were immersed in acetonitrile, and **2** was immersed in acetone, for seven days each. In this time, the crystals of compound **1** dissolved and recrystallised as **2**, with phase purity ascertained by X-ray powder diffraction. Meanwhile, there was no change in the morphology of **2** after soaking in acetone; X-ray powder diffraction confirmed no phase change took place, and re-collection of the single crystal X-ray diffraction data showed the lattice acetonitrile molecules remained in their original positions. These results would imply that simple solvent exchange between the two phases is not accessible under these conditions, and that acetone is unable to displace acetonitrile from the solvent channels, either due to its steric bulk or its reduced solvation ability, allowing compound **2** to remain stable under the compound **1** formation conditions. This contrasts to the situation *vice versa*, where **1** is driven towards **2** *via* dissolution, presumably with the implication that **2** represents a local energy minimum under these conditions.

**Synthesis and structure of [H2L1][ZnCl4]·2H2O** **3 and (H2L1)2Cl 4**

Following the successful synthesis of the related compounds **1** and **2**, we pursued less polar solvents in an attempt to encourage coordination of the imide oxygen atoms. Compound **L1** was only sparingly soluble in ethyl acetate. However, we found that the addition of a small quantity of aqueous HCl to the mixture afforded crystalline products when combined with ZnCl2 in 1:1 stoichiometry, which analysed for the tetrachlorozincate species [H2**L1**][ZnCl4]·2H2O **3**. While only one crystalline phase of X-ray quality was isolated from this mixture, it was clear from elemental analysis of the bulk material that a mixture of products was generally formed in this reaction. Subsequently, on attempting to repeat the synthesis of compound **3** with copper(II) chloride, we were able to isolate a small crop of crystals of the second phase, the hydrochloride salt (H2**L1**)2Cl **4**. Assuming a formula of (H2**L1**)2Clfor the minor phase in the synthesis of **3**, our data suggest a ratio of 2:1 for tetrachlorozincate:dihydrochloride when carrying out this reaction with ZnCl2. In the case of copper(II) chloride, we were unable to generate any measurable quantity of the corresponding tetrachlorocuprate. However, this phase may be expected to form under conditions similar to those which gave the zincate species, and analysis of the bulk sample suggested a ~5 mol% impurity of an inorganic-heavy phase. Given the similarity in reaction conditions between the two phases, we were unable to generate either phase in analytical purity, and instead present the single crystal structures of each phase purely as indicative structural models.

Analysis of the colourless crystals of complex **3** by X-ray diffraction provided a structural model in the triclinic *P-*1 space group. The asymmetric unit of the complex [H2**L1**][ZnCl4]·2H2O consists of a doubly protonated H2**L1**2+ species, with charge balance provided by a tetrachlorozincate dianion as illustrated in Figure 6. There are also lattice water molecules within the asymmetric unit, best modelled as two molecules distributed across three sites. The **H2L12+** species adopts a clip-type conformation with both pyridyl groups on the same face of the aromatic core, and with the pyridyl nitrogen atoms in an *anti*-conformation to one another, giving the molecule approximate *C*2 symmetry along the normal vector to the NDI mean plane.

The primary intermolecular interactions in the structure of **3** are hydrogen bonds, involving the pyridinium groups, the lattice water molecules, and the tetrachlorozincate anions. Two cyclic motifs, each formed formed from a ZnCl4 anion and two lattice water molecules, are linked and edge-share with a linear and centrosymmetric intermolecular chain (Supporting Information, Figure S30 and Table S1) linking each pyridinium group through four water molecules (taking into account the disorder inherent in these sites). The primary association mode of the NDI groups themselves takes the form of slipped OFF π-π stacked dimers. This interaction is defined by a mean interplanar distance between adjacent π-systems of 3.28 Å and offset 2.22 Å for equivalent NDI cores. The outer surfaces of

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**Figure 6** (A) The structure of complex **3** with partial atom labelling scheme; lattice water molecules are omitted for clarity (B) the structure of compound **4** with partial atom labelling scheme. Selected hydrogen atoms are omitted for clarity. Symmetry codes used to generate equivalent atoms: (i) 1-x, 1-y, 2-z.

these dimers are capped by ZnCl42- dianions offering additional weak intermolecular interactions in the form of anion···π contacts with Cl···mean plane distances of 3.22 Å. In addition, the protonation of the pyridine nitrogen atoms would be expected to increase the polarization of the pyridyl C-H bonds and offer increased potential for C-H hydrogen bond donation; indeed, C-H···O and C-H···Cl contacts are observed with minimum C···X distances 3.218(5) and 3.505(7) Å, and C-H···X angles 151.6 and 139.7°, for X = O and Cl, respectively.

The structural model for compound **4** was generated in the triclinic *P-*1 space group. Unfortunately, the quality of the single crystals generated by this method was invariably poor, and only a low-resolution single crystal diffraction dataset could be obtained. Nonetheless, the structural model generated is supported by X-ray powder diffraction results, suggesting the connectivity model presented herein is indicative of the true structure. The asymmetric unit of **4** contains half of one protonated **H2L1**species and one associated chloride anion in the asymmetric unit. No copper-containing species was observed, nor were any solvent or other guest molecules present within the lattice. The key intermolecular interactions in the structure of **4** are, unsurprisingly, the hydrogen bonding interactions between the pyridinium N-H group and the chloride anion in a simple motif (with N···Cl distance of 2.993(9) Å). The NDI groups also undergo π-π stacking interactions, forming infinite OFF slipped stacks oriented parallel to the *a* axis. The adjacent π systems in these columns exhibit a mean interplanar distance of 3.22 Å, with alternate cores slipped by 3.72 Å (relative to the naphthyl centroid). The reactions to form compounds **1** and **2** were also repeated with cupric chloride dihydrate, but no crystalline material was recovered.

Thermogravimetric analysis of an air-dried sample of the compounds **3/4** mixture revealed a multistep decomposition, there was a gradual weight loss of around 2.5 % between 30 – 200 °C which corresponds to the loss the water molecules from the major **3** phase. Above 300 °C decomposition of the organic framework occurs (Figure S16, ESI). Thermogravimetric analysis of an air-dried sample of crystalline compound **4** illustrated no measurable mass loss below 200 °C which is consistent with the structure of the anhydrate. Above 200 °C decomposition of the organic framework occurs (Figure S17, ESI).

**Structure of *poly*-[AgL1]SbF6****5**

Given the lack of coordinating ability of the imide oxygen atoms of **L1** in the presence of zinc(II), silver(I) was next selected as a softer Lewis acid capable of undergoing reactions with weakly coordinating Lewis bases. The reaction of acetone solutions of **L1** and AgSbF6 (2 eq.) afforded yellow crystals after standing at room temperature overnight. Analysis by X-ray diffraction provided a structural model in the triclinic *P*-1 space group and revealed a formula of *poly*-[Ag**L1**]SbF6 as illustrated in Figure 7.

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**Figure 7** The structure of compound **5**, showing the repeat unit with selected atom labelling scheme (top) and the interaction of a hexafluoroantimonate anion with two encapsulating **L1** groups (bottom). All hydrogen atoms are omitted for clarity, and long Ag-O/Ag-F interactions are represented as green dashed lines

The asymmetric unit contains half of one molecule of **L1**, one Ag site occupying a special position, and half of one centrosymmetric hexafluoroantimonate anion. The silver ion adopts a linear 2-coordinate geometry when considering only the strong Ag-N bonds originating from the pyridyl nitrogen atoms (Ag-N distance 2.223(3) Å), however additional longer interactions are observed originating from one of the two imide oxygen atoms (Ag···O distance 2.783(3) Å) and one of the fluorine atoms from the anion (Ag···F distance 2.728(3) Å).Although weak coordination occurs through an imide carbonyl group, no statistically significant differences in covalent bond lengths were observed within the imide or NDI backbone itself.

The extended structure of **5** is a one-dimensional coordination polymer formed from repeating the two-connected **L1** and Ag units as illustrated in Figure 8. The most notable intermolecular interactions in the structure of **5** are the anion···π interactions involving the hexafluorosilicate anion. Each NDI core associates with SbF6- anions on both faces; the minimum separation between the fluorine atom and the NDI mean plane (2.82 Å, for F1) is equivalent for both faces of the aromatic core, and is indicative of a significant intermolecular interaction. We have recently also observed anion···π interactions of similar magnitude in an Ag(I) coordination polymer of a 4- substituted 1,8-naphthalimide,19 and similar interactions have been observed with a variety of hard anions in NDI systems20 and fluorous anions in other extended π systems,21 indicating the generality of such interactions as crystal engineering synthons. Linking each NDI and each hexafluoroantimonate anion on two faces leads to the association of the 1-dimensional chains in **5** into a densely packed 2-dimensional layered structure oriented in the *ac* plane. Inter-layer interactions primarily consist of myriad C-H···O interactions involving the imide oxygen atoms and no void space or lattice solvent was detected within the structure.

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**Figure 8** The extended structure of compound **5** viewed perpendicular to the two-dimensional assembly of polymeric chains and hexafluoroantimonate anions. Hydrogen atoms are omitted for clarity.

Conclusions

Here we have prepared and characterised two new 2-picolyl substituted diimide compounds and reported on their coordination and structural chemistry with *d*-block metal ions in an attempt to ascertain the generality of carbonyl coordination in *N*-(2-picolyl)imide compounds. As well as elucidating the structure of the oxybisphthalimide species **L2**,four new metal complexes or coordination polymers were prepared and crystallographically characterised. *Poly*-[Zn(**L1**)Cl2]·3(C3H6O) **1** and *poly*‑[ZnCl2(**L1**)]·MeCN **2** are structurally-related materials in which the ability of the lattice solvent to participate in n···π interactions with the naphthalenediimide backbone is coupled to the crystal packing, which leaves one or both faces of the aromatic framework available for interactions with the solvent molecules. Complex [H2**L1**][ZnCl4]·2H2O **3** is a hydrogen-bonded tetrachlorozincate species with doubly protonated **H2L1** as a charge balancing cation, while repeating this reaction with copper(II) chloride gives the dihydrochloride salt of **L1** as the major product. Finally, reaction of **L1** with silver(I) hexafluoroantimonate gave a one-dimensional polymer where the anticipated Ag···O interactions were observed, albeit as weak interactions only. These results highlight the subtle differences in coordination and structural chemistry exhibited by these 2-picolyl substituted imides. While the strong N,O-chelates observed in 1,8-naphthalimide systems appear limited to those cases thus far, the interesting structural features here, including the explainable solvent dependence of the channel structures of **1** and **2**, provide useful touchstones for designing extended functional materials.

Conflicts of interest

There are no conflicts to declare

Acknowledgements

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**Table 1** Crystallographic and Refinement Parameters for All Structures

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Identification code | **L2** | **1** | **2** | **3** | **4** | **5** |
| Empirical formula | C28H18N4O5 | C35H34Cl2N4O7Zn | C28H19Cl2N5O4Zn | C26H22Cl4N4O6Zn | C26H18Cl2N4O4 | C26H16AgF6N4O4Sb |
| Formula weight | 490.46 | 758.93 | 625.75 | 693.64 | 521.34 | 792.05 |
| Temperature/K | 100(2) | 100(2) | 100(2) | 100(2) | 100(2) | 100(2) |
| Crystal system | orthorhombic | monoclinic | orthorhombic | triclinic | triclinic | monoclinic |
| Space group | *Pccn* | *P*2/*c* | *Pnna* | *P*-1 | *P*-1 | *P*21/*c* |
| a/Å | 19.4892(5) | 11.1935(6) | 10.8226(4) | 9.8295(5) | 4.9197(9) | 8.6209(4) |
| b/Å | 21.6795(5) | 9.2331(5) | 23.0562(8) | 10.6901(5) | 9.297(2) | 17.8581(7) |
| c/Å | 10.5043(3) | 16.7061(8) | 10.5332(3) | 13.3737(7) | 12.906(3) | 8.0036(3) |
| α/° | 90 | 90 | 90 | 98.589(2) | 109.588(15) | 90 |
| β/° | 90 | 94.587(2) | 90 | 94.244(2) | 98.253(15) | 90.903(3) |
| γ/° | 90 | 90 | 90 | 97.801(2) | 91.039(16) | 90 |
| Volume/Å3 | 4438.2(2) | 1721.06(15) | 2628.33(15) | 1370.28(12) | 549.0(2) | 1232.02(9) |
| Z | 8 | 2 | 4 | 2 | 1 | 2 |
| ρcalcg/cm3 | 1.468 | 1.464 | 1.581 | 1.681 | 1.577 | 2.135 |
| μ/mm‑1 | 0.855 | 0.923 | 1.184 | 1.337 | 3.049 | 15.9 |
| F(000) | 2032 | 784 | 1272 | 704 | 268 | 768 |
| Radiation | CuKα (λ = 1.54178) | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) | CuKα (λ = 1.54178) | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 6.098 to 136.678 | 3.65 to 72.844 | 3.532 to 54.192 | 3.094 to 52.858 | 7.364 to 108.732 | 9.906 to 136.506 |
| Index ranges | -23 ≤ h ≤ 23, -24 ≤ k ≤ 26, -12 ≤ l ≤ 12 | -18 ≤ h ≤ 18, -15 ≤ k ≤ 15, -27 ≤ l ≤ 27 | -13 ≤ h ≤ 13, -26 ≤ k ≤ 29, -13 ≤ l ≤ 13 | -12 ≤ h ≤ 12, -13 ≤ k ≤ 11, -16 ≤ l ≤ 16 | -5 ≤ h ≤ 5, -9 ≤ k ≤ 9, -13 ≤ l ≤ 13 | -10 ≤ h ≤ 10, -21 ≤ k ≤ 21, -9 ≤ l ≤ 9 |
| Reflections collected | 44932 | 69088 | 23530 | 23411 | 3697 | 7708 |
| Independent reflections | 4081 [Rint = 0.0371, Rsigma = 0.0198] | 8423 [Rint = 0.0263, Rsigma = 0.0160] | 2901 [Rint = 0.0340, Rsigma = 0.0196] | 5636 [Rint = 0.1076, Rsigma = 0.1091] | 1337 [Rint = 0.2359, Rsigma = 0.2619] | 2253 [Rint = 0.0405, Rsigma = 0.0407] |
| Observed Reflns [I>=2σ (I)] | 3971 | 7226 | 2542 | 3371 | 660 | 1653 |
| Data/restraints/parameters | 4081/0/334 | 8423/29/244 | 2901/0/196 | 5636/5/388 | 1337/1/167 | 2253/0/193 |
| Goodness-of-fit on F2 | 1.024 | 1.059 | 1.198 | 0.988 | 0.964 | 1.036 |
| Final R indexes [I>=2σ (I)] | R1 = 0.0379, wR2 = 0.1018 | R1 = 0.0270, wR2 = 0.0734 | R1 = 0.0351, wR2 = 0.0772 | R1 = 0.0472, wR2 = 0.0800 | R1 = 0.0819, wR2 = 0.1742 | R1 = 0.0362, wR2 = 0.0957 |
| Final R indexes [all data] | R1 = 0.0404, wR2 = 0.1043 | R1 = 0.0363, wR2 = 0.0785 | R1 = 0.0425, wR2 = 0.0794 | R1 = 0.1146, wR2 = 0.0946 | R1 = 0.1767, wR2 = 0.2223 | R1 = 0.0482, wR2 = 0.1055 |
| Largest diff. peak/hole / e Å-3 | 0.26/-0.22 | 0.64/-0.38 | 0.34/-0.41 | 0.53/-0.81 | 0.41/-0.48 | 1.03/-0.93 |
| CCDC No. | 1872943 | 1872944 | 1872945 | 1872946 | 1872947 | 1872948 |