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Supramolecular Influences on Metal Ion Coordination: Lead(II) under Eight-coordination

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Crystal structure determinations on the "acid salt" of Pb(II) and dipicolinic acid (pyridine-2,6-dicarboxylic acid, dipicH$_2$), regarded as composed of dimer entities, [Pb$_2$(dipic)$_2$(dipicH$_2$)$_2$(OH$_2$)$_6$], 1, infinitely cross-linked, and on the complex of 2,4-dinitrophenol (2,4-DNPH), a simpler coordination polymer, [Pb(2,4-DNP)$_2$]*n*, 2, show both solid state structures to be influenced by π-stacking of the ligands. Although the Pb(II) coordination environment in 1 can be regarded as "hemidirected" and that in 2 as "holodirected", it is argued that inter-dimer stacking interactions, rather than lone pair effects, are responsible for the distorted 9-coordination of Pb in 1. In 2, Pb adopts close-to-cubic 8-coordination.

Keywords: Lead(II) complexes; π-Stacking; Coordination geometry; Coordination polymers

INTRODUCTION

The solid state coordination chemistry of lead(II) is characterised by a wide range of primary coordination numbers for the metal and coordination geometries which vary from the highly symmetrical to the completely asymmetric [1,2]. The latter characteristic has been described in terms of holo- and hemi-directionality of the coordinate bonds [2], hemidirectionality often seemingly being attributable to the presence of a stereochemically active lone pair on Pb(II), with a critical point for its observation being near a coordination number of eight and with an estimated difference in energy between the two situations of 30–50 kJ mol^{-1} [2]. As for many heavy metals, however, it is frequently difficult to discern an obvious "cut-off point" for a bond distance which allows the coordination sphere of Pb(II) to be unambiguously defined [1,3,4]. Further, the premise that coordinate bonds to Pb(II) are generally weak leads to the hypothesis that solid state structures of Pb(II) compounds may reflect the operation of a variety of weak intermolecular forces in a situation close to balance with coordinate bonding [1,2]. Elsewhere, we have presented evidence that this may be so in the case at least of Pb(II) complexes of aza-aromatic ligands prone to π-stacking interactions [4]. The present, somewhat fortuitous comparison of the structures of the Pb(II) complexes of 2,4-dinitrophenol (2,4-DNPH) and dipicolinic acid (pyridine-2,6-dicarboxylic acid, dipicH$_2$) provides further support for this view.

EXPERIMENTAL

Synthesis

Pb$_2$(dipic)$_2$(dipicH$_2$)$_2$(OH$_2$)$_6$

Crystals of this material suitable for X-ray diffraction measurements were obtained by the "branched tube" method [5] we have previously exploited extensively [1,4]. Thus, a twofold molar ratio of dipicolinic acid (334 mg) was added to an aqueous solution of Pb(CH$_3$CO$_2$)·3H$_2$O (381 mg) filling the heated (60°C) arm, water added to fill the cold (ambient temperature) arm and 15 days allowed for the deposition of colourless, crystalline material in that arm. Analysis: calculated for C$_{28}$H$_{28}$N$_4$O$_{22}$Pb$_2$, C, 28.33; H, 2.38; N, 4.72; found, C, 28.3; H, 2.3; N, 4.7%. (The formulation as a binuclear species is based on the results of the crystal structure determination.)

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TABLE I Crystal and structure refinement data

Compound	**1** $[Pb(dipic)(dipicH_2)(OH_2)_3]_{2n}$	**2** $[Pb(2,4\text{-}DNP)_2]_n$
Empirical formula	$C_{14}H_{14}N_2O_{11}Pb$	$C_{12}H_6N_4O_{10}Pb$
Formula weight	593.5	573.4
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic
Space group	$P-1$	$C2/c$
a/Å	7.063(4)	12.570(4)
b/Å	10.788(6)	17.821(4)
c/Å	11.257(6)	6.742(3)
α/°	92.647(9)	90
β/°	101.358(10)	99.42(3)
γ/°	95.397(9)	90
Cell volume/Å^3	835.4(8)	1489.9(9)
Z	1 (as dimer)	4
Absorption coefficient, μ/mm^{-1}	10.167	11.395
Final R indices, reflections with $I > 2\sigma(I)$	R_1 0.0361, wR_2 0.0895 (3158 reflections)	R_1 0.0423, wR_2 0.1181 (3284 reflections)
R indices (all data)	R_1 0.0383, wR_2 0.0909	R_1 0.0501, wR_2 0.1221

Pb(2,4DNP)$_2$

$Pb(CH_3CO_2)\cdot 3H_2O$ (381 mg) was dissolved in the minimum volume of hot (80°C) water and added, with stirring, to a solution of 2,4-dinitrophenol (340 mg) in hot ethanol (10 ml). Stirring was continued as more ethanol (20 ml) was added, then the mixture was filtered while still hot and the orange filtrate allowed to evaporate slowly at room temperature. Orange crystals suitable for X-ray crystallography were deposited over 25 days. For analysis, they were washed with water–ethanol (1:1) and dried *in vacuo*. Analysis: calculated for $C_{12}H_6N_4O_{10}Pb$, C, 25.13; H, 1.05; N, 9.77; found: C, 25.2; H, 1.1; N, 9.7%.

Crystallography

The crystal structure determinations were performed by Drs K. A. Lysenko and F. M. Dolgushin of the X-ray Structural Centre, General and Technical Chemistry Division, Academy of Science of Russia, INEOS, Vavilov Street, 28, Moscow B-334, 117813, Russia. Basic crystal and structure refinement data are given in Table I and further data pertinent to the present discussion are given in Tables II and III and in the figures. Full descriptions of the structure solutions have been deposited in cif format with the CCDC, deposition numbers 204098 and 204099.

TABLE II Pb-donor atom distances in **1**, $Pb_2(dipic)_2(dipicH_2)_2(OH_2)_6$, and **2**, $Pb(2,4DNP)_2$

Bonds in **1**	r/Å	Bonds in **2**	r/Å
Pb–O(3)	2.488(4)	Pb–O(1)	2.341(4)
Pb–N	2.556(4)	Pb–O(1A)	2.341(4)
Pb–O(2W)	2.567(4)	Pb–O(1B)	2.546(4)
Pb–O(1)	2.612(4)	Pb–O(1C)	2.546(4)
Pb–O(1W)	2.718(5)	Pb–O(2)	2.800(6)
Pb–O(3)	2.757(4)	Pb–O(2A)	2.800(6)
Pb–O(3W)	3.031(5)	Pb–O(4D)	3.035(6)
Pb–O(7)	3.073(5)	Pb–O(4E)	3.035(6)

RESULTS AND DISCUSSION

It is convenient to consider the present structures together and in terms of a development from a description of the primary coordination spheres of Pb(II) through to that of the complete lattice. In fact, both compounds are coordination polymers but in **1** there are some Pb atoms bridged by carboxylate oxygen atoms which are only 4.355(4) Å apart, so that they may be regarded as lying in pairs, justifying an initial description in terms of a dimeric stoichiometric unit, $Pb_2(dipic)_2(dipicH_2)_2(OH_2)_6$ (Fig. 1). Within both this unit and the "Monomer" section of the polymer **2**, $Pb(2,4DNP)_2$, there is a clear break in Pb/donor atom distances between ~3.1 and ~3.5 Å, leading to the (tentative) conclusion that the metal is 8-coordinate in both cases. Pb–O(N) bond lengths (Table II) defining these coordination spheres cover a similar range for both. The coordination geometry (Fig. 1), however, is quite different. While different ligand symmetries, extensive hydrogen-bonding in **1** (see ahead), and the unusual [2,6] presence of 3 coordinated water molecules/Pb in **1** may explain some differences, it would seem from such initial considerations that the Pb environment in **1** could be described as "hemidirected" and that in **2** as "holodirected". In **2**, the coordination geometry in fact is not greatly distorted from cubic (Fig. 1) and there is clearly no readily identified gap in the coordination sphere, while the view of **1** as a binuclear species shows a major "gap" lying between the tridentate dipicolinate ligand and water molecule 3. This may nonetheless have an explanation other than that of the effect of a stereochemically active lone pair.

TABLE III Hydrogen bonding interactions in **1**, $Pb_2(dipic)_2(dipicH_2)_2(OH_2)_6$

D–H···A	d_{D-H}/Å	DH···A/Å	<DHA/°	$d_{D\cdots A}$/Å	A*
O(1W)–H(1WB)	1.11	1.80	166	2.889(8)	O(2) $[-x, -y, -z-1]$
O(1W)–H(1WA)	0.98	1.90	143	2.747(8)	O(4) $[-x, -y, -z]$
O(2W)–H(2WA)	1.09	1.95	145	2.904(8)	O(2) $[-x, -y, -z-1]$
O(2W)–H(2WB)	1.15	2.06	143	3.059(8)	N(2) $[-x, -y, -z]$
O(3W)–H(3WA)	1.00	1.72	166	2.706(8)	O(5) $[x, y, z-1]$
O(3W)–H(3WB)	0.99	1.96	148	2.848(8)	O(2W) $[x+1, y, z]$
O(6)–H(60)	0.89	1.65	174	2.535(8)	O(1) $[x, y, z+1]$
O(8)–H(80)	1.07	1.48	170	2.545(8)	O(3W)

*O, N atom labels are as given in Fig. 1(a).

A feature of both present structures, shared with those of many related complexes [1,7–14], including those of dipicolinic acid [15–18], is evidence for interactions between the large, planar ligands. In both **1** and **2**, parallel arrays of the planes of the aromatic moieties indicate that these interactions are of the "pi-stacking" type, rather than "edge-to-face" or "vertex-to-face" types [7–10]. Within the binuclear unit of **1**, there is "intramolecular" stacking of the tridentate dipicolinate ligand with its nearer-neighbour, unidentate dipicolinic acid ligand, the aromatic ring planes being ~3.3 Å apart, with the shortest atom–atom contact [3.333(4) Å] being between the nitrogen of the acid and a ring carbon bearing a carboxylate of the dipicolinate entity. Projection of the structure perpendicular to the ring plane [Fig. 2(a)] shows the overall form of the "slipped" stacking [7–10,19], which is at least qualitatively understandable in terms of optimising approaches between atoms of opposite charges [20].

In **2**, all the ligands are formally phenoxide monoanions, and a partial view [Fig. 2(b)] of

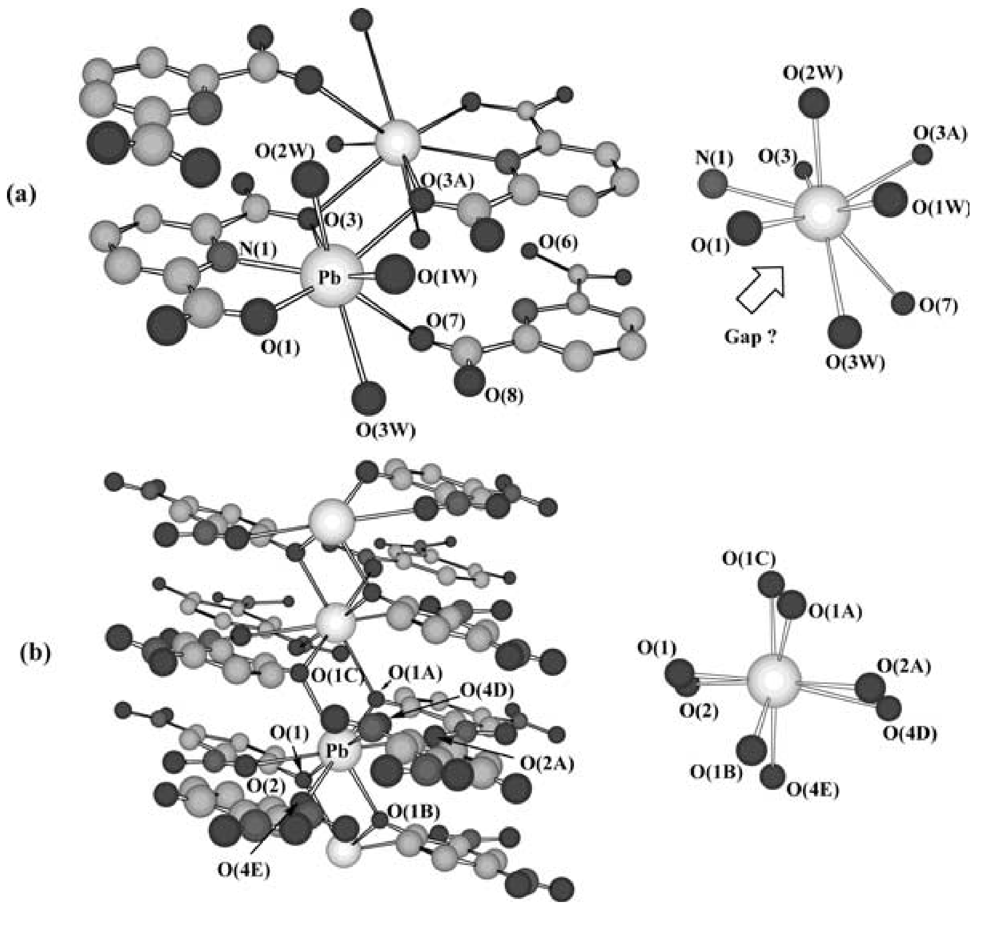

FIGURE 1 (a) The stoichiometric and simplest "dimer" unit present within the lattice of **1**, $Pb_2(dipic)_2(dipicH_2)_2(OH_2)_6$, (Pb···Pb 4.355(4) Å) and the primary coordination sphere of Pb within this unit. Except where noted otherwise, in all figures light atoms (C, N, O) are shown in shades of grey increasing in darkness with atomic number. (b) A view approximately perpendicular to one of the chains of PbO_2Pb rhombs of the coordination polymer present in **2**, $[Pb(2,4\text{-}DNP)_2]_n$, showing the complete (stacked) ligand environment around one Pb atom, and a view of the near-cubic primary coordination sphere of Pb. Each of the ligands attached to one chain serves as a bridge, either through 4-nitro group oxygen coordination or phenoxide/2-nitro group oxygen chelation, to similar chains.

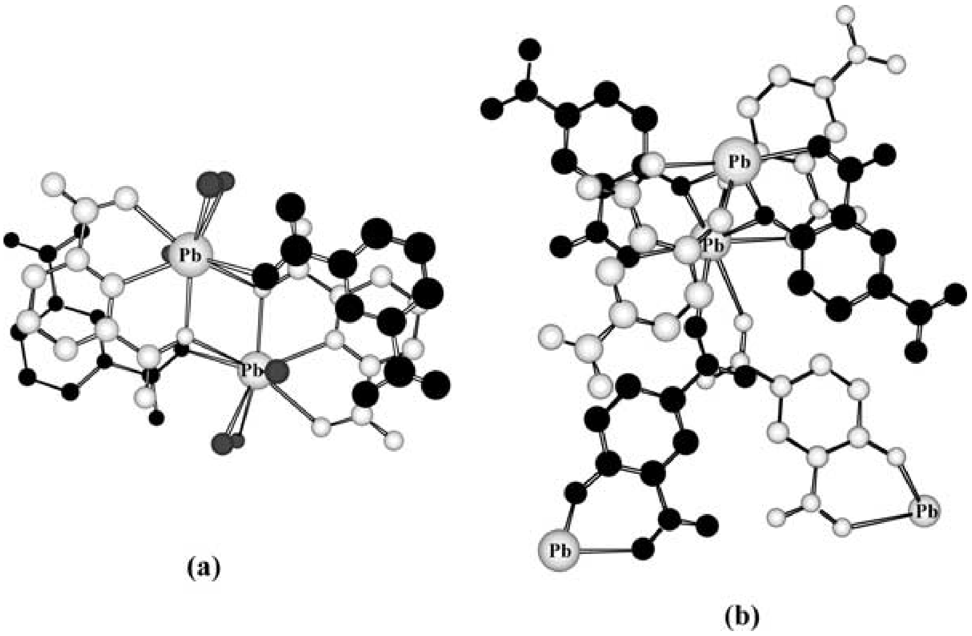

FIGURE 2 (a) A projection perpendicular to the ligand planes showing the form of stacking within the "dimer" unit of **1**. For clarity, all atoms in the dipicolinate anions are shown in white, all atoms in the dipicolinic acid units are shown in black. (b) A projection perpendicular to the ligand planes showing the two aspects of stacking of adjacent ligand units in **2** involved in completing 8-coordination around the central Pb atom of the figure. Pairs of nearest-neighbour, stacked 2,4-dinitrophenoxide ligands are shown with all atoms of one in black, all of the others in white.

the lattice perpendicular to the aromatic ring planes shows two aspects to their stacking. As chelate species through phenoxide and 2-nitro-group oxygen atoms, the ligands flank infinite chains of lead atoms, linked as Pb_2O_2 rhombs as a result of phenoxide bridging. Within each flank, an infinite stack is formed, again with an aromatic ring-plane spacing near 3.3 Å, though the closest atom approach, 3.019(4) Å, is that of a nitro-group oxygen to the carbon attached to phenoxide, the nitro group (as commonly found [11,12]) being slightly tilted from the aromatic ring plane. Eight coordination about each Pb atom is completed by the binding of oxygen atoms from two 4-nitro groups associated with independent chains of $[Pb(2,4\text{-DNP})_2]_n$. These nitro groups also stack, essentially NO upon ON, with an N···O separation of 3.054(4) Å. It is worth noting, once again, how versatile nitrophenoxides may be as ligands [11,12].

While the prominence and similar dimensions of aromatic unit stacking in **1** and **2** may be merely coincidental and are certainly not proof that the structures, and in particular the coordination of Pb(II), are controlled by this factor, the results for **1** do contain further evidence that stacking may be a dominant factor. Thus, the lattice of **1** is formed by the assembly of the "dimer" units described above. Hydrogen-bonding (Table III; Fig. 3) clearly plays a role in this assembly and, regarded as a proton complex, the solid is most definitely a coordination polymer, but once again stacking is also involved. This "intermolecular" stacking (Fig. 4) involves the approach of a dipicolinic acid ligand of one dimer to the dipicolinate ligand of another and, concomitantly, the approach of the acid ligand carbonyl oxygen atom considered as the donor to Pb in one dimer to within 3.277(4) Å of a Pb atom in its neighbour. Treating this as a coordinate bond, **1** is thus, like **2**, a coordination polymer through a second set of PbO_2Pb rhombs (in addition to those within the "dimer") but one in which the Pb atoms are *nine*-coordinate (Fig. 4), with no coordination vacancy and therefore, no distortion attributable to the effect of a lone pair, as seemingly apparent in the isolated

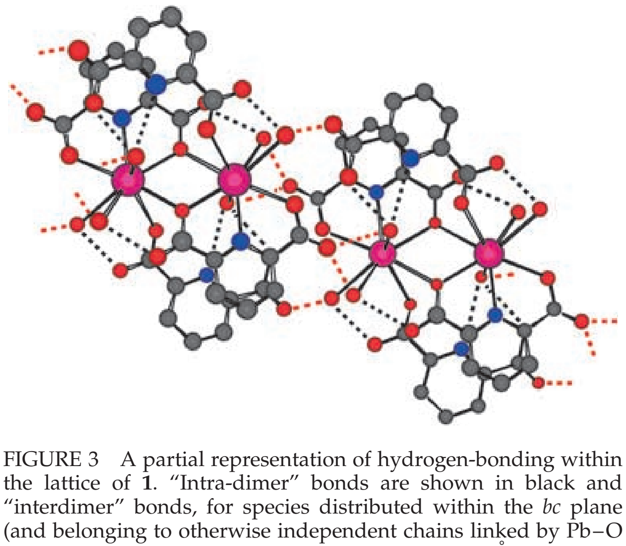

FIGURE 3 A partial representation of hydrogen-bonding within the lattice of **1**. "Intra-dimer" bonds are shown in black and "interdimer" bonds, for species distributed within the *bc* plane (and belonging to otherwise independent chains linked by Pb–O coordination), are shown in red. Only contacts <3 Å are shown. Here, Pb = violet, C = grey, N = blue, O = red.

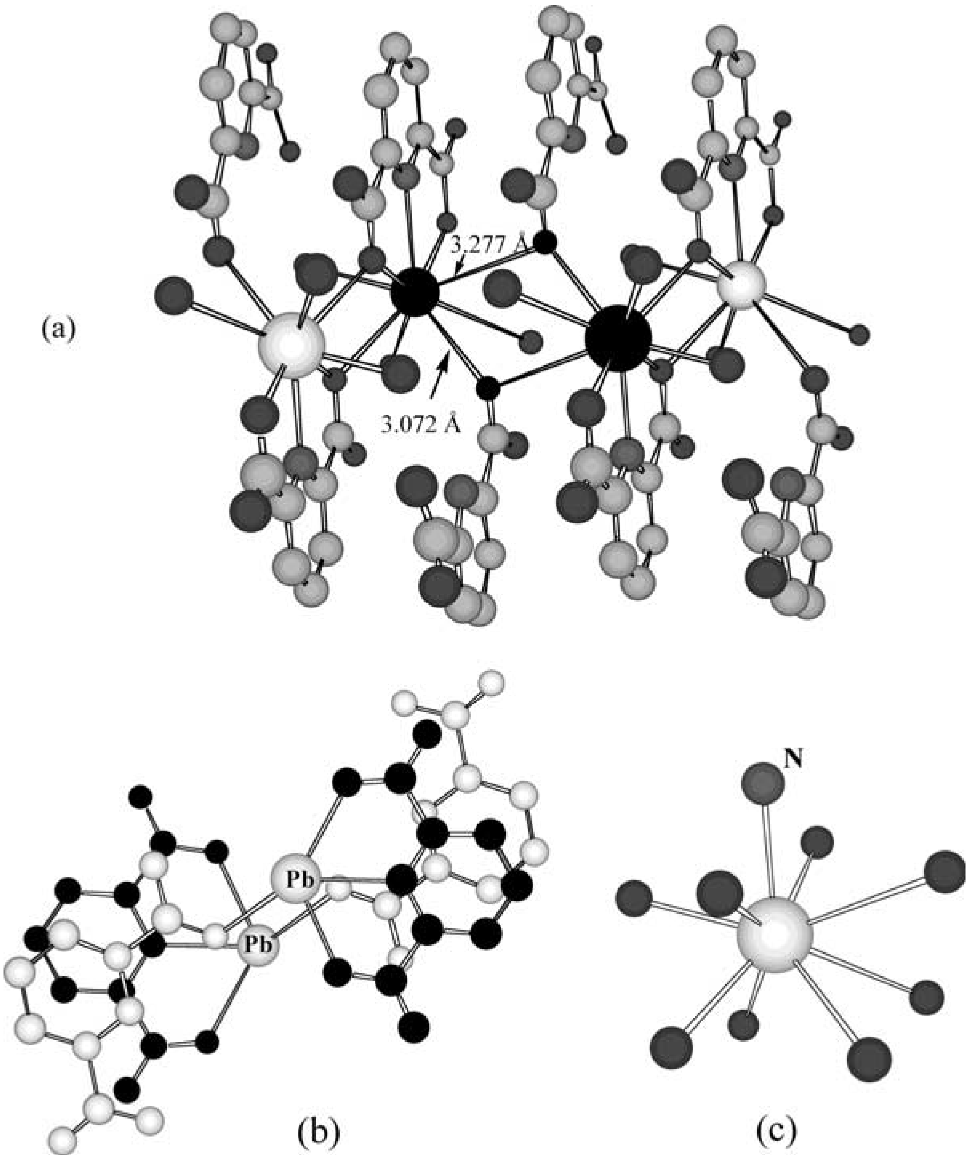

FIGURE 4 "Inter-dimer" stacking in **1** associated with 9-coordination of the Pb atoms. (a) A view of two adjacent "dimers" with the linking PbO_2Pb rhomb highlighted in black. Pb$\cdots$Pb within this rhomb is 5.365(4) Å. (b) A projection perpendicular to the ligand planes showing the "inter-dimer" stacking array, again with all atoms of a given dipicolinate unit shown as black or white. (c) The 9-coordinate Pb atom actually present in **1**.

dimer structure. The obvious question then is whether a coordinate bond has been stretched to result in some ligand stacking or whether it is the stacking interaction which has imposed a positioning of the donor atoms such that only a very weak interaction of the ninth is possible.

In the absence of direct thermodynamic measurements of the individual contributions to the overall lattice stability, this last question is difficult to answer. In the case of the proton complexes of the two present ligands, i.e. in dipicolinic acid (monohydrate) [21] and 2,4-dinitrophenol [22,23], parallel arrays of the aromatic ring planes are observed, suggesting the persistence of stacking even when more numerous opportunities for H-bonding arise than in metal complexes. (Both structures have other interesting features, such as the helical form of part of the H-bonding network in 2,4-DNPH, and overlap in projection of the stacked molecules is different from and more limited than that in the complexes, as seen in related cases [11,12], but this broad conclusion holds.) A more interesting particular comparison arises, however, for the Pb and Na [15] complexes of dipicolinic acid. Both can be regarded as "acid salts" in that both the neutral acid and its conjugate base(s) act as ligands, and both contain metal, acid, anion and water in the ratio 1:1:1:3. Remarkably, the form of two adjacent $Na(dipicH)(dipicH_2)(OH_2)_3$ entities within the lattice is almost identical with that of the $Pb_2(dipic)_2(dipicH_2)_2(OH_2)_6$ "dimer" (Fig. 5). Significantly, the stacking projections in the two systems

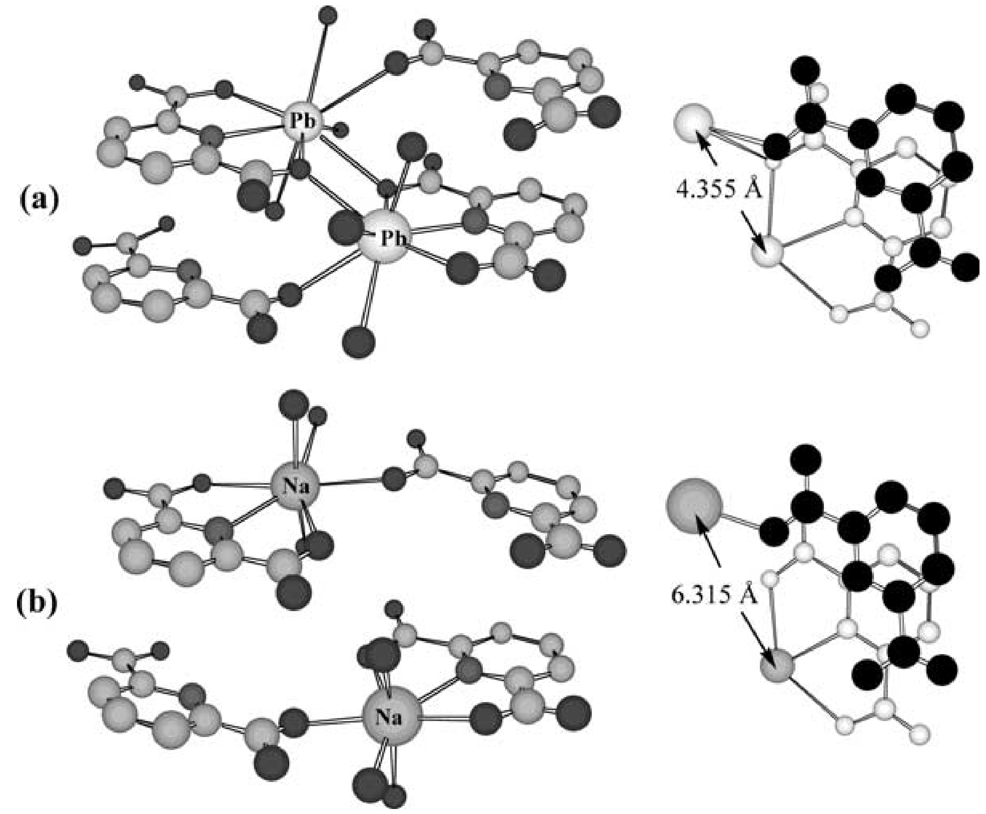

FIGURE 5 A comparison of "dimer" units and "intra-dimer" stacking within the lattices of (a) **1** and (b) [Na(dipicH)(dipicH_2)$(OH_2)_3$] [15].

are closely similar, despite fairly marked differences in the metal···metal separations and in coordination about the metals. This is consistent with the dominance of stacking forces over a difference of one coordinate bond in at least the cases of Na(I) and Pb(II), even the (relatively unusual) 7-coordination of Na perhaps being attributable to enforcement of the tridentate mode of binding of dipicH^- due to the requirements of extended stacking throughout the lattice.

Considering a broad range of nitrophenoxide complexes [11,12], ligand stacking is very common, if not universal, and is especially prominent in polynitro species such as exemplified by lead styphnate (trinitroresorcinolate) [24]. Hence, it seems reasonable to conclude that in **2**, as in **1**, it is interligand attractions—π-stacking—that determine both the coordination number and coordination geometry of the metal. It remains difficult to quantify the energy associated with a single stacking interaction and thus give it a precise ranking within the multitude of supramolecular influences which may be utilised in, for example, the construction of new solid-state arrays [25], though theoretical calculations on picrate ions indicate an attractive van der Waals energy as great as $\sim 40\,\mathrm{kJ\,mol^{-1}}$ [26]. Though this value neglects charge repulsion energies (possibly immaterial when a cation is also present), it happens to agree with a very approximate estimate of stacking energy based on analysis of the structure of basic thorium picrate [27], and it is certainly sufficiently great for stacking to be a major influence on structure, as concluded for the present systems. The value is comparable to the estimated energy difference between hemi- and holo-directed environments and presumably so also to the energy which may be gained in increasing the coordination number of Pb(II) by one when it is already in the range 7–9. Whether stacking interactions of the present ligands and related species can be used in the rational synthesis of new materials remains to be seen.

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