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Lattice Forces in Heavy Metal Picrates: Structural Characterization of Lead and Mercury Species

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Structure determinations for the dimethylsulfoxide (dmso) solvate of lead(II) picrate (picrate = pic = 2,4,6-trinitrophenoxide), formally a centrosymmetric dimer, $[Pb_2(dmso)_4(pic)_4]$, and for unsolvated mercury(I) picrate, a polymer of conventional mercurous dimers, $[Hg_2(pic)_2]_n$, show that, despite considerable differences in the form of the metal unit, there are remarkable similarities in the mode of coordination of the bridging picrate ligands. In both lattices, parallel arrays of picrate rings can be discerned but appear to be associated with short N···O, O···O or O···C contacts rather than C···C. In the Pb compound, there is also evidence of intramolecular contacts to dmso-*S*.

Keywords: Heavy metal picrates; Crystal structures; Weak interactions

INTRODUCTION

Although the syntheses of most metal picrates are essentially trivial, usually involving quantitative reactions of metal oxides, hydroxides or carbonates with picric acid (2,4,6-trinitrophenol = Hpic), crystallographic studies of the products are often difficult, despite the ease of crystallization, because the crystal morphology is commonly that of exceedingly fine needles [1–3]. Lead(II) picrate [4] provides an example of this situation, our numerous efforts to obtain crystals suitable for diffraction measurements from aqueous solution failing until, using a strategy found to be useful in the face of similar difficulties encountered with uranyl picrate [5], the material was converted to its dimethylsulfoxide (dmso) solvate. Attempts to obtain mercury(II) picrate led to confrontation with different problems. The reaction of HgO with the stoichiometric amount of picric acid (twofold molar quantity, assuming it to be a simple acid–base reaction) led to an extremely insoluble, amorphous orange solid. Use of an excess of picric acid led to more soluble material that converted to the amorphous solid on attempts to recrystallize it from neutral water or other solvents. Gradual evaporation of the solution formed with excess acid led to the deposition of a crystalline mercury-containing species along with picric acid, but selection of an orange crystal from this mixture and solution of its structure (as described later) showed it to be the picrate of mercury(I). Despite this unexpected difference in stoichiometry, the structure determinations for these two materials show that, as for related compounds [6–16], their lattices reflect, among other things, the tendency of picrate entities to associate [17].

EXPERIMENTAL

Synthesis and Crystallization

$[Pb_2(pic)_4(dmso)_4]$

Lead(II) picrate was first prepared as its hydrate [4] by adding Hpic slowly to a hot (steam bath), well-stirred slurry of $PbCO_3$ (267 mg) in water (20 mL) until a clear, yellow solution was just obtained. This was filtered, then cooled to precipitate the product as fine, yellow needles (553 mg). For conversion to the dmso solvate, the hydrate (25 mg) was dissolved in methanol (1 mL), and dmso (50 mg) added to the clear, yellow solution. Clusters of needle-like, yellow crystals began to form within 5 min.

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$[Hg_2(pic)_2]_{\infty|\infty}$

Picric acid (2.1 g) was dissolved in hot (steam bath) water (200 mL). Under continuous heating and stirring, HgO (0.50 g) was added gradually, with sufficient time allowed after each addition for all the oxide to dissolve. The final orange–yellow solution was filtered while hot, then allowed stand to cool as crystalline material deposited, some of it having the lath-like, pale yellow form of Hpic crystals, their nature being confirmed by a unit cell determination.

Structure Determinations

Full spheres of 'low'-temperature CCD area-detector diffractometer data were measured (Bruker AXS instrument, ω-scans; monochromatic Mo Kα radiation, $\lambda = 0.7107_3$ Å; T *ca.* 153 K) yielding $N_{t(otal)}$ reflections, these merging to N unique (R_{int} cited) after 'empirical'/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ being used in the full-matrix least-squares refinements, refining anisotropic displacement parameter forms for the nonhydrogen atoms (Pb adduct) or the metal atom only (Hg adduct), $(x, y, z, U_{iso})_H$ being included constrained at estimated values. Conventional residuals R, R_w on $|F|$ (Pb complex), F^2 (Hg complex) are cited at convergence, neutral atom complex scattering factors being used within the context of the Xtal 3.7 program system [18]. Pertinent results are given below and in Table I and the figures, the latter showing 50% probability amplitude displacement envelopes for the nonhydrogen atoms, hydrogen atoms where shown having arbitrary radii of 0.1 Å. Individual variations in procedure are noted as 'variata'. Full (*cif* depositions (excluding structure factor amplitudes) have been made with the Cambridge Crystallographic Data Centre, CCDC 260325 and 260326

Crystal/refinement Data

$[Pb_2(pic)_4(dmso)_4]$

$C_{32}H_{32}N_{12}O_{32}Pb_2S_4$, $M = 1639.4$. Triclinic, space group P$\bar{1}$ (C_i^1, No. 2), $a = 10.1003(6)$, $b = 11.2872(9)$, $c = 11.6147(9)$ Å, $\alpha = 77.868(2)$, $\beta = 89.884(2)$, $\gamma = 84.785(2)°$, $V = 1289$ Å^3. D_c ($Z = 1$ dimer) $= 2.11_2$ g cm^{-3}. $\mu_{Mo} = 6.8$ mm^{-1}; specimen: $0.09 \times 0.08 \times 0.04$ mm; $'T'_{min/max} = 0.65$. $2\theta_{max} = 75°$; $N_t = 25693$, $N = 13\,031$ ($R_{int} = 0.027$), $N_o = 11\,447$ $R = 0.027$; $R_w = 0.033$ [weights: $(\sigma^2(F) + 0.0003\ F^2)^{-1}$].

$[Hg_2(pic)_2]_{\infty|\infty}$

$C_{12}H_4Hg_2N_6O_{14}$, $M = 857.4$. Orthorhombic, space group *Ibca* (D_{2h}^{27}, No. 73), $a = 6.4260(6)$, $b = 19.625(2)$, $c = 27.921(3)$ Å, $V = 3521$ Å^3. D_c ($Z = 8$) $= 3.23_4$ g cm^{-3}. $\mu_{Mo} = 17.5$ mm^{-1}; specimen: $0.28 \times 0.05 \times 0.02$ mm; $'T'_{min/max} = 0.47$. $2\theta_{max} = 52.5°$; $N_t = 35\,318$, $N = 1806$ ($R_{int} = 0.077$), $N_o = 1373$; $R = 0.061$, $R_w = 0.12$ [weights: $(\sigma^2(F) + 4.3\ F^2)^{-1}$].

Variata

Specimens presented as very fine laths; the refinement model entailed disorder of the picrate group by tilting of the ring over a pair of sites inclined at 32°, with rigid body refinement constraints and site occupancies set at 0.5. Data were remeasured on a second carefully selected specimen, paying attention to overlooked possibilities such as weak super- or primitive lattice reflections, a misassigned noncentrosymmetric lattice or space group, etc., but no further satisfactory improvement of the model could be achieved, the results being similar to those presented.

RESULTS AND DISCUSSION

Analysis of the structure of the compound of stoichiometry Pb(pic)$_2$·2dmso, one such formula unit, devoid of crystallographic symmetry, comprising the asymmetric unit of the structure, serves as a convenient means to introduce the basic issues that concern both of the present complexes. Given that dmso functions as an *O*-donor ligand in simple Pb(II) complexes [19], a complete *O*-environment might be expected for the primary coordination sphere of Pb in Pb(pic)$_2$·2dmso, and indeed a limit of 3 Å for Pb—O establishes both the presence of PbO$_8$ entities

TABLE I The metal coordination environment in $[Pb_2(pic)_4(dmso)_4]$. r(Å) is the lead—oxygen distance; other entries in the matrix are the angles (°) subtended at the metal by the relevant atoms at the head of the row and column. Primed atoms are related by the intradimer inversion center

Atom	*R*	O(2)	O(11)	O(121)	O(21)	O(261)	O(21′)	O(221′)
O(1)	2.479(2)	74.40(7)	125.43(6)	72.23(6)	79.39(6)	71.14(6)	142.53(6)	143.33(6)
O(2)	2.327(2)		79.16(6)	92.46(6)	79.88(6)	129.52(6)	81.16(6)	140.91(7)
O(11)	2.623(2)			61.78(6)	141.14(6)	150.82(6)	75.90(5)	80.60(6)
O(121)	2.804(2)				151.62(6)	110.30(6)	137.65(6)	107.23(6)
O(21)	2.488(2)					58.53(6)	68.55(5)	95.33(5)
O(261)	2.950(2)						105.66(6)	75.22(6)
O(21′)	2.538(2)							61.41(6)
O(221′)	2.866(2)							

Pb—O—S angles are 129.7(1), 125.1(1)°; Pb···Pb′ is 4.1530(3) Å and O(21)···O(21′) is 2.831(2) Å.

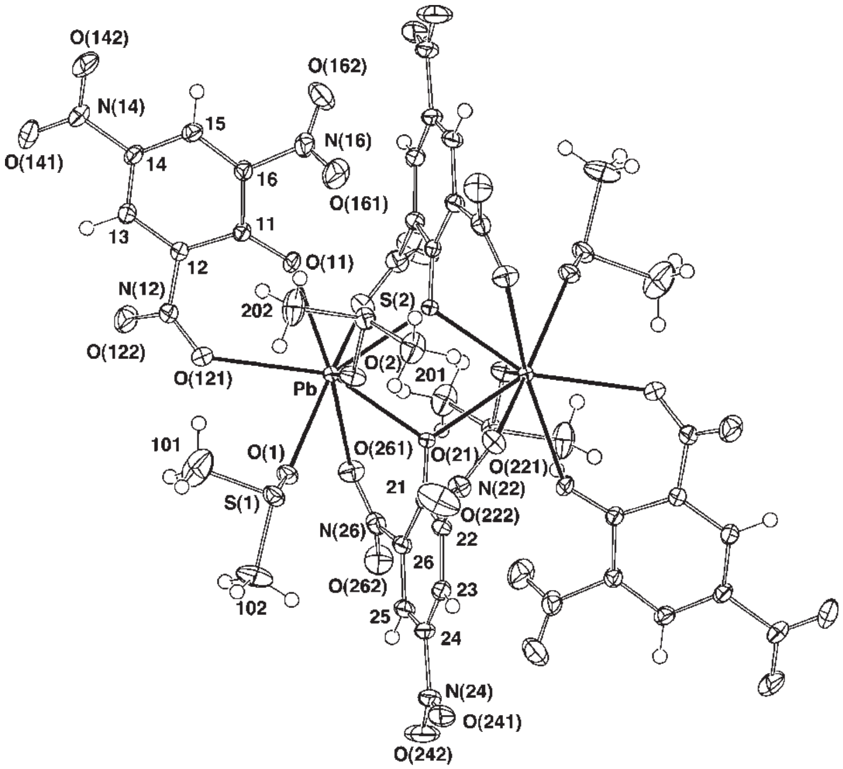


FIGURE 1 Projection of a molecule of $[Pb_2(pic)_4(dmso)_4]$ normal to the $Pb(\mu\text{-}O)_2Pb$ plane.

and the fact that the repeat molecular unit of the structure should be regarded as a centrosymmetric dimer, $[Pb_2(pic)_4(dmso)_4]$ (Fig. 1). The two lead atoms, lying close to the inversion center, are bridged by the phenoxide groups of the pair of ligands **2**, comprising an obligate planar four-membered Pb_2O_2 ring as the molecular core; Pb,Pb′—O distances are 2.488(2), 2.538(2) Å, with Pb,Pb′—O(21)—C(21) angles 121.3(1), 125.9(1)°. This dimer unit bears some resemblance to that identified in $[Pb_2(dipic)_2(dipicH_2)_2(OH_2)_6]$ [20] (dipic = dipicolinate = pyridine-2,6-dicarboxylate), similarly centrosymmetric, although here two tridentate picrate ligands bridge the Pb atoms [4.1530(3) Å apart], with bonding of both metal atoms to the phenoxide donors and of each separately to different flanking nitro-group donors. The planes of the bridging picrates lie twisted relative to the core plane at a dihedral angle of 70.10(7)°, so that each of the quasi-coplanar NO_2 groups is directed towards one or other of the two lead atoms, forming a chelate in association with the central phenoxide, with a pair of such chelates in association with each lead, the interaction of the nitro-oxygen being feebler than that of the phenoxide, despite the bridging nature of the latter. Picrate **1** is associated exclusively with a single lead atom, again as a similarly unsymmetrical chelate, the eight-coordinate environment of the lead being completed by the pair of *cis*-disposed *O*-dmso unidentates, the associated inequivalent Pb—O distances [2.327(2), 2.479(2) Å] being the shortest of the array (Table I). The picrate groups deviate from coplanarity with the C_6 ring, most notably by out-of-plane torsions of the nitro-substituents, particularly those at the 2- and 6-positions, with the lead atoms diversely deviant from the associated C_6 and NO_2 planes, such deviations being most notably pronounced in association with the bridging/bischelate tridentate picrate **2** (Table II).

TABLE II Picrate parameters for $[Pb_2(pic)_4(dmso)_4]$

	Ligand **1**	Ligand **2**
Dihedral angles (°)		
$C_6/CNO_2(2)$	32.95(11)	43.74(12)
$C_6/ONO_2(6)$	58.28(12)	26.45(11)
$C_6/CNO_2(4)$	4.60(12)	9.82(13)
Pb_2O_2/C_6	24.29(8)	70.10(7)
$Pb_2O_2/CNO_2(2)$	42.07(9))	80.04(11)
$Pb_2O_2/CNO_2(6)$	42.23(11)	26.45(11)
Lead atom out-of- plane deviations, δPb (Å)		
C_6	0.034(5)	1.900(4), −1.998(5) (Pb′)
CNO_2 (2)	2.003(5)	1.60 (Pb′)
CNO_2 (6)	–	0.096(6)

C(*n*1)—O(*n*1) are 1.267(3), 1.281(3) Å (*n* = 1, 2); Pb—O(11)—C(11) is 141.4(2)°. Pb,Pb′—O(21)—C(21) 121.3(1), 125.9(1)°; Pb—O(21)—Pb′ 111.45(7)°.

As is very commonly the case in Pb(II) complexes, a particular choice for the radius of the primary coordination sphere leads to a metal environment that appears to contain a vacancy [20–24], perhaps better described as the metal environment being ‘hemidirected’ [22]. As is again commonly found, however, extension of the coordination radius can lead to the detection of presumably more tenuous interactions filling the ostensible vacancy. Thus, in the present case, while the PbO_8 entity resulting from the restriction Pb-(donor atom) < 3 Å is not strongly hemidirected, there is an apparent vacancy, but one that is associated with an 'intermolecular' contact of 3.523(3) Å to a nitro-group-*O* from an adjacent dimer unit (Fig. 2). A question, perhaps one particularly significant for systems where any coordinate bonding may be weak and therefore in balance with a variety of other factors [25–27], then arises as to whether attractive interactions within and between metal coordination environments might explain the 'distorted' geometry of the primary coordination sphere. This is a difficult issue to confront, as it is usually possible to find a large number of

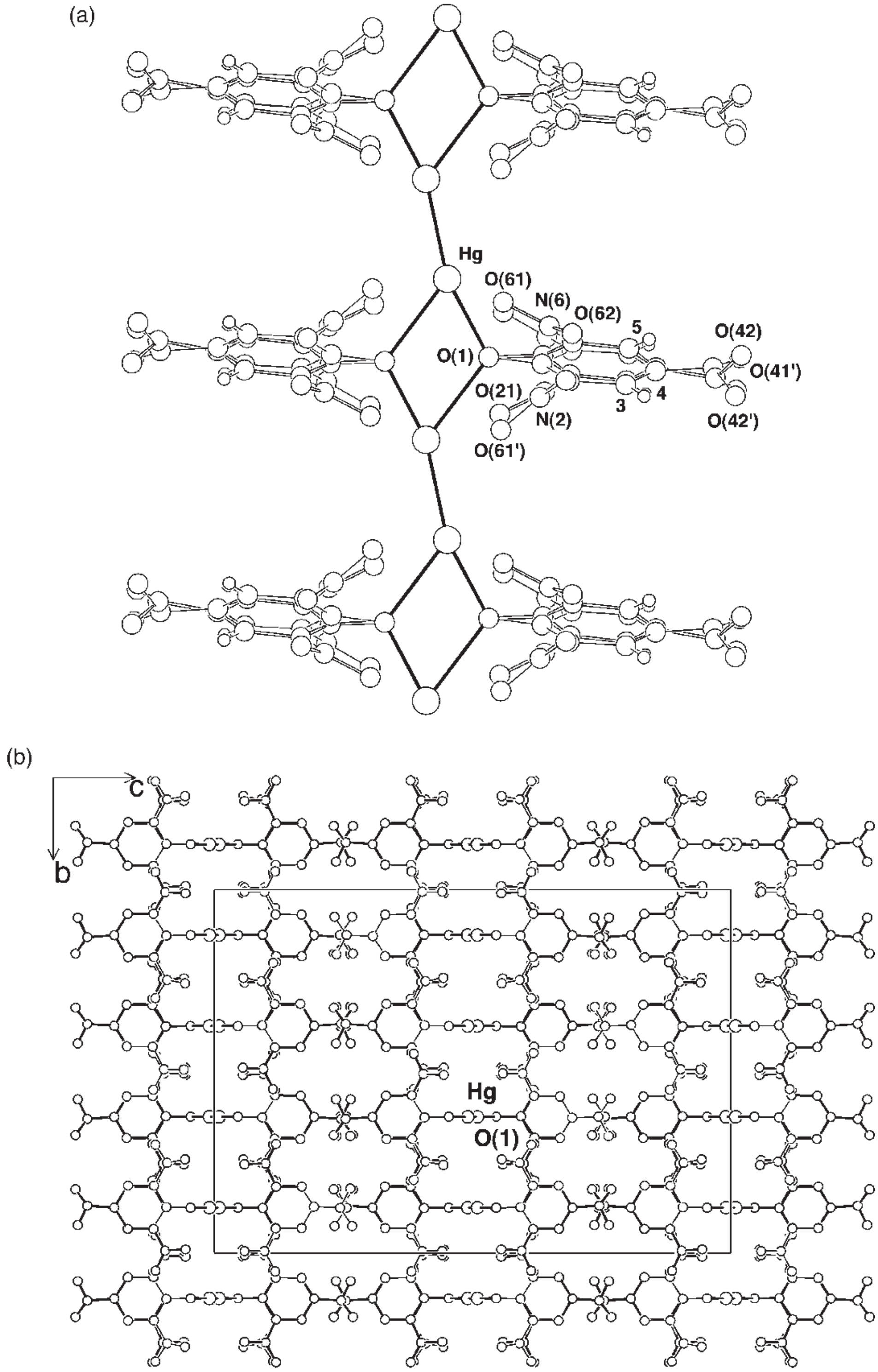
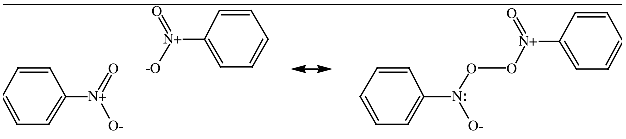


FIGURE 2 (a) Projection of portion of a single polymer strand of $[Hg_2(pic)_2]_{\infty|\infty}$.(b) Unit cell contents of $[Hg_2(pic)_2]_{\infty|\infty}$ projected down *a*.

interatomic 'contacts' between about 3.5 and 4 Å without it being obvious how to resolve any ambiguity as to their origin, and of course many shorter contacts may simply be considered the consequence of associated atoms being connected through a series of very short contacts universally accepted as 'bonds' [28]. It is perhaps worthwhile to contemplate the significance of all contacts as a step beyond simple ascription of all geometric distortions to ill-defined 'steric effects', but it is a process fraught with uncertainty [29].

In the case of dmso as a ligand, coordination does produce significant geometric distortions of the molecule [30,31] and there is evidence from consideration of a wide range of metal ion/dmso-*O* complex structures [32–34] that variations in the M—O—S bond angle may be associated with the positioning of contacts to sulfur giving it a coordination number of at least 5. In the present case, the S atom of the ligand for which Pb—O is 2.327(2) Å (and for which Pb—O—S is 125.0(1)°) has similar contacts of 3.144(3) Å to phenoxo-*O* and of 3.172(3) Å to picrate nitro-*O*, while the S atom of the ligand for which Pb-O is 2.479(2) Å [Pb—O—S 129.7(1)°] has disparate contacts of 3.055(2) Å to dmso-*O* (i.e. of the other ligand in its half of the centrosymmetric dimer) and 3.806(3) Å to a bridging-picrate nitro-*O*, and of 3.795(3) Å to a bidentate-picrate nitro-*O*. Interestingly, the oxygen atom of this second dmso has a contact of 3.181(3) Å to picrate nitro-*O*, perhaps an example of O···O attractive interactions as was discussed recently in relation to the structures of metal carbonates [35]. The two dmso ligands may also be distinguished in terms of approaches (CH···O interactions?) of the methyl groups to various oxygen atoms. Thus, for the less remote ligand, one methyl group carbon lies within 3.377(3) Å and the other within 3.259(3) Å of picrate nitro-*O* atoms (the second also being within 3.635(3) Å of an aromatic-*C*), while for the more remote ligand, one methyl-*C* falls within 3.377(3) Å of picrate nitro-*O* while the other has no intramolecular contacts but falls within 3.102(2) and 3.383(3) Å of nitro-*O* atoms from adjacent dimers. If this plethora of contacts involves attractive interactions, then the difference between the situations for the two ligands could correspond (ignoring possible directional electronic effects transmitted through Pb) to an energy sufficient to stretch a Pb—O bond by 0.15(1) Å. This is an energy that is difficult to estimate, especially as there is evidence that interligand attractions can considerably inflate the energy required for rearrangement of the Pb(II) coordination sphere [22]. However, if, for example, the energy were to be *ca*. 10% of the mean energy for rearrangement from holo- to hemi-directed Pb(II) [22], it could be *ca*. 5 kJ mol^{-1} and represent a difference between larger contributors.

In general, lattices of picrate-containing crystals are like those of many heteroaromatic and functionalized aromatic compounds in that their phenyl rings lie in parallel planes, a situation indicative of π-stacking interactions, although it is not universally true that such arrays are associated with close contacts of the parallel rings nor, even when there are such contacts, that they involve the ring carbon atoms [36–38]. Certainly in the case of many metal picrates, other nitro-phenoxides and aza-aromatic carboxylates [6–17,20,26,34,37], for example, close contacts most commonly involve the heteroatoms, contacts that in the picrates are usually associated with nitro substituents being twisted out of the plane of the phenyl ring. In [$Pb_2(pic)_4(dmso)_4$], the bridging and chelating picrate entities belong to two independent arrays of parallel planes containing the phenyl rings and close contacts can be observed both within and between these arrays. These are not, however, associated with extensive overlap in projection (perpendicular to the phenyl rings) of adjacent picrates, and the shortest contacts appear to be O···O and to involve 'twisted' nitro groups. Nitro-*O* interactions can be rationalized in terms of a valence bond theory description (for a disposition as seen in many structures) as:



In fact, the bridging-picrate 4-nitro-*O* involved in the 3.523(3) Å approach to Pb is also involved in a short contact [2.922(2) Å] to a chelating-picrate nitro-*O* and it may be that the light-atom:light-atom interaction dominates that of the light-atom:heavy-atom, thus explaining both the elongated Pb—O bond and the distortion of the coordination sphere (as a result of the approach of an extra picrate unit). It might also be useful to regard the lattice as being determined by picrate interactions perturbed by Pb coordination rather than as Pb coordination perturbed by picrate (and possibly other) interactions, a situation for which there is some evidence in the case of the similar Pb(II) complex of dipicolinate [20]. Note that the shortest Pb···Pb contact here [that within the dimer; 4.1530(3) Å] would appear to be too long to be indicative of any significant interaction [39].

Although it is an unsolvated material, the compound currently characterized as mercurous picrate, $Hg_2(pic)_2$, has a crystal structure showing numerous similarities to that of [$Pb_2(pic)_4(dmso)_4$]. The pathway to the formation of this Hg(I) species is obscure, as the crystal selected for a structure determination was not withdrawn until some 5 months after the preparation of the solution formed by the reaction of HgO with aqueous picric acid and, while no change in the appearance of the mixture of materials deposited was obvious in this time, some fibrous, red material did appear to volatilize from the mixture over this period. Thus, it is not certain how rapidly Hg(I) may have been generated. One possibility is that the initial reaction may have involved mercuration of the aromatic ring and that the resulting species underwent slow decomposition to picryl radical (which might couple to give the red material) and Hg(I), but the simplest interpretation of the present observations is that, if this were the pathway to the picrate of Hg(I), then it occurred in the initial period of heating. There is evidence, nonetheless, that solvent extraction of Hg(II) in the presence of picrate is possible [40], although a simple hydrated mercuric picrate was not isolated as part of such work.

The lattice of [$Pb_2(pic)_4(dmso)_4$] is well-defined, being devoid of disorder. By contrast, that of $Hg_2(pic)_2$, as modeled, is complicated by extensive disorder but essentially comprises an array of polymeric threads formed as a result of the bridging of Hg_2 units by picrate phenoxide atoms. As modeled in space group *Ibca*, a single Hg(pic) component, devoid of crystallographic symmetry, comprises the asymmetric unit of the structure. The picrates are disposed across the plane at $z = 1/8$ (etc.), with the 4-nitro substituents across $z = 1/4$, 3/4 and with their 2- and 6-nitro substituents overlapping between successive ligands along the *b* dimension. Unease in description of the structure arises in respect of the ligands, each modeled in terms of a pair of mutually tilted components, which may be a consequence of actual disorder, inadequate definition of crystal symmetry or similar factors. Nevertheless, it is possible to observe that the mercury atom lies well out of the plane of its associated picrate (δHg 1.52/1.85(4) Å for the two components), with Hg—O—C 116/125(1)°; the 4-nitro group components are essentially coplanar with their parent ring fragments [interplanar dihedral angle 5.4/6.8(9)°] while the 2- and 6-substituent planes are appreciably twisted [25.1–37.5(10)°], perhaps in consequence of interaction with the mercury atom, Hg···O(n1,n1′) ranging between 2.78(2) and 2.99(2) Å. Similar contacts of an intermolecular nature (<3.1 Å) are also found: Hg···O(21) ($1/2 + x$, $1 - y$, z), (x, y, $1 + z$) 2.95(2), 2.96(2); O(61) ($1 - x$, $1\frac{1}{2} - y$, z) 2.92(2); O(61′) ($1/2 + x$, $1\frac{1}{2} - y$, $1 - z$) 2.99(2) Å are observed. There is also a closer contact, Hg···O(1) ($1/2 - x$, y, z), 2.551(9) Å, leading, as seen in other Hg(I) oxo-ligand complexes [41], to the identification of HgO_2Hg rhombs [Hg—O 2.183(9), 2.551(9) Å; Hg—Hg—O 130.9(2), 164.1(2)°], which may be considered as linked together as a result of Hg—Hg bonds [2.5177(8) Å] (Figure 2a). The two phenoxide rings attached to each rhomb are diametrically opposed and lie near-normal to *a*, with pairs linked either side of the *ab* plane by O—Hg—Hg—O 'rods' inclined to that plane, such that their ring planes are parallel to those of the picrates on adjacent rhombs of the polymer chain. The picrates on one side of a strand interdigitate with those on one side of another but not in such a way that the ring planes are parallel. Instead, they are tilted and overlap only very slightly in projection, in such a way that the closest atomic approaches involve the overlap of their 4-nitro substituents. The sheets that can be considered to be built up in this way lie parallel to one another so that there are further contacts, from one sheet to the next, between the atoms of the 2- and 6-CNO_2 units. The beauty of the resulting lattice can be appreciated from the view down *a* (Figure 2b). The nature of the phenoxide bridge in both the Hg and Pb compounds is fairly similar, with rotation of the picrate unit relative to the Hg—Hg vector meaning that again 2- and 6-nitro-*O* atoms are possibly involved in weak interactions with the metal [Hg—O 2.78(2), 2.99(2) Å]. At least three coordination interactions with Hg are usually observed in Hg(I) compounds [41,42].

CONCLUSIONS

The present structures show once again the remarkable coordinating properties of the picrate ion and illustrate further points of balance between its tendency to self-associate and its ability to satisfy the coordination requirements of a metal ion. The characterization of mercury(I) picrate raises the question as to under what conditions mercury(II) picrate may exist, but its nature does at least explain some of the previously puzzling observations during attempts to prepare the Hg(II) species.

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