

The Enigma of Lead(II) Coordination – Some Comments

by Jack Harrowfield

Institut de Science et de l'Ingenierie Supramoléculaires, 8, allée Gaspard Monge, F-67083 Strasbourg
(e-mail: harrowfield@isis.u-strasbg.fr)

In a recent report [1] of the crystal structure of polymeric $[\text{NaPb}(\text{en})(\text{ClO}_4)(\text{NO}_2)_2]_n$ (en = ethane-1,2-diamine), *Morsali* has drawn the conclusions that the Pb-atoms are four-coordinate and that a stereochemically active lone pair is present. Although the coordination chemistry of Pb^{II} has been subjected to detailed analyses [2–4], it is frequently the case that the establishment of the coordination number of the metal, and, hence, of its coordination geometry, remain somewhat arbitrary tasks [3–5]. Thus, instances where the situation appears to be clear-cut are of particular interest.

The claim of a strongly hemidirected four-coordination of Pb^{II} in $[\text{NaPb}(\text{en})(\text{ClO}_4)(\text{NO}_2)_2]_n$ implies certain limits, not stated, upon Pb–N and Pb–O distances considered to involve bonding interactions, the general issue of how to describe the origins of atomic contacts within crystalline solids being of considerable current interest [6]. Similarly, a limit must be defined for the Na–O separations taken as bonding, and the eight-coordination assigned to Na in $[\text{NaPb}(\text{en})(\text{ClO}_4)(\text{NO}_2)_2]_n$ is associated with Na–O distances varying from 2.363(6) to 2.949(8) Å. There is little unusual in such a range of distances for Na^{I} [7], but it is even more true of Pb^{II} that Pb (donor atom) separations associated with coordination can vary over a wide range [3–5]. Justification has been advanced for consideration of Pb–O separations at least as great as 3.1 Å, as indicative of (single) bonding [8], and there are many instances of significantly longer contacts, where a similar conclusion appears plausible [5]¹⁾. Thus, it must be noted that in $[\text{NaPb}(\text{en})(\text{ClO}_4)(\text{NO}_2)_2]_n$, the two nitrite ligands described as unidentate on Pb (Pb–O 2.604(5) and 2.629(5) Å, resp.) could be taken as asymmetrically bidentate, since there are contacts from the other anion O-atoms at 2.922(5) and 2.875(5) Å, respectively, to the same metal center²⁾. Further, the N-atoms of the NO_2^- groups, considered to be bound (*via* oxygen) to two other Pb atoms, are found at distances of 3.243(6) and 3.317(6) Å, respectively, from Pb.

If all four of these longer contacts are taken to indicate coordinate bonding, then Pb^{II} is eight-coordinate, a far-from-unusual situation for the metal [2–4]. The coordination geometry, however, remains strongly hemidirected, and, now, further analysis becomes ambiguous. One feature of the lattice of $[\text{NaPb}(\text{en})(\text{ClO}_4)(\text{NO}_2)_2]_n$ is that $\text{Pb}(\text{en})$ units can be considered to lie in columns in such a way that the ethylene bridge of a diamine chelate on one metal lies directly over what could be considered the

¹⁾ For similar difficulties in interpreting $\text{Pb}\cdots\text{Pb}$ separations in terms of metal–metal bonds, see [9].

²⁾ As chelates, the NO_2^- groups form a Δ pair at all Pb centers, consistent with the observation that the material crystallizes as a conglomerate, with all the en chelates being of δ -conformation in the chosen crystal.

coordination ‘hole’ on the adjacent Pb. This results in Pb⋯H contacts of 3.09 and 3.18 Å, respectively, which might be considered indicative of agostic interactions [10]. Alternatively, if a lone pair of electrons is present indeed in an orbital directed to one side of the PbO₆N₂ coordination unit, this may indicate H-bonding (Pb:⋯H), which means, of course, that the lone pair is really no longer ‘lone’. The distinction here of agostic vs. H-bonding is perhaps artificial, since even a coordination number of four exceeds the formal ‘valency’ of Pb^{II}, so that it is not necessary to assume that some valence-shell orbitals would not be used in bond formation. In any case, the structure of [NaPb(en)(ClO₄)(NO₂)₂]_n does not provide unambiguous evidence that the coordination number of Pb is four, nor that the configuration is influenced by ‘lone-pair’ effects. In fact, the metal may be even ten-coordinate (PbO₆N₂H₂) and have a rather distorted coordination geometry, as proposed in the *Figure*, simply because of the rather heterogeneous group of donor atoms to which it is attached.

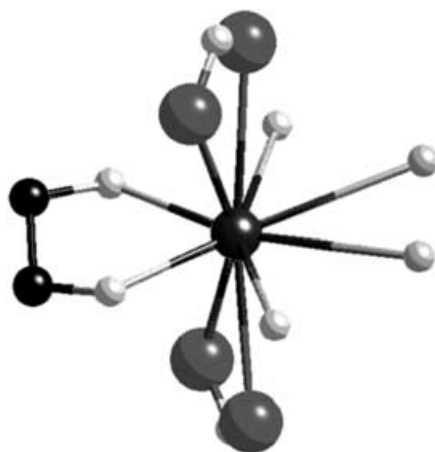


Figure. Structure of ten-coordinate [PbN₂O₄H₂]

Such a description, however, involves considerable indulgence in the chemist’s ‘*own way of deciding which atom is bonded to which in a molecule*’ [6], and it must be noted that the two H-atoms, in particular, have a number of contacts to other atoms (O and N) at distances similar to those from Pb. Given that pairwise Pb⋯donor-atom interaction energies are in general expected to be relatively small [11], that the structure of [NaPb(en)(ClO₄)(NO₂)₂]_n is not molecular, and that the coordination requirements of the two metals present may not be equally easy to satisfy, so that any assessment of the balance of factors operative must be difficult and may require consideration of the whole lattice and not just the local environment of Pb, this complex is, perhaps, an excellent example of one where only an approach such as that of the ‘pixel’ method [6] could be expected to enable discernment of the importance of every influence.

REFERENCES

- [1] A. Morsali, X.-M. Chen, *Helv. Chim. Acta* **2004**, *87*, 3050.
- [2] R. D. Hancock, in 'Perspectives in Coordination Chemistry', Eds. A. Williams, C. Floriani, A. E. Merbach, Verlag Helvetica Chimica Acta, Basel, Wiley-VCH, Weinheim, 1992, p. 129.
- [3] I. Bytheway, L. M. Engelhardt, J. M. Harrowfield, D. L. Kepert, H. Miyamae, J. M. Patrick, B. W. Skelton, A. A. Soudi, A. H. White, *Aust. J. Chem.* **1996**, *49*, 1099, and refs. cit. therein.
- [4] L. Shimoni-Livny, J. P. Glusker, C. W. Bock, *Inorg. Chem.* **1998**, *37*, 1853.
- [5] A. A. Soudi, F. Marandi, A. Ramazani, E. Ahmadi, A. Morsali, *C. R. Chimie* **2005**, *8*, 157, and refs. cit. therein.
- [6] J. D. Dunitz, A. Gavezzotti, *Angew. Chem., Int. Ed.* **2005**, *44*, 1766.
- [7] M. Döbler, 'The Ionophores and Their Structures', J. Wiley & Sons, New York, 1981.
- [8] M. R. S. J. Foreman, T. Gelbrich, M. B. Hursthouse, M. J. Plater, *Inorg. Chem. Commun.* **2000**, *3*, 234.
- [9] S. Hino, M. Olmstead, A. D. Phillips, R. J. Wright, P. P. Power, *Inorg. Chem.* **2004**, *43*, 7346.
- [10] M. Brookhart, M. L. H. Green, L.-L. Wong, *Prog. Inorg. Chem.* **1988**, *36*, 1.
- [11] P. Schwerdtfeger, G. A. Heath, P. Dolg, M. A. Bennett, *J. Am. Chem. Soc.* **1992**, *114*, 7518.

Received April 18, 2005