

Pb(dca)₂ (dca = dicyanamide): a novel 3D compound with unusual coordination modes of dicyanamide

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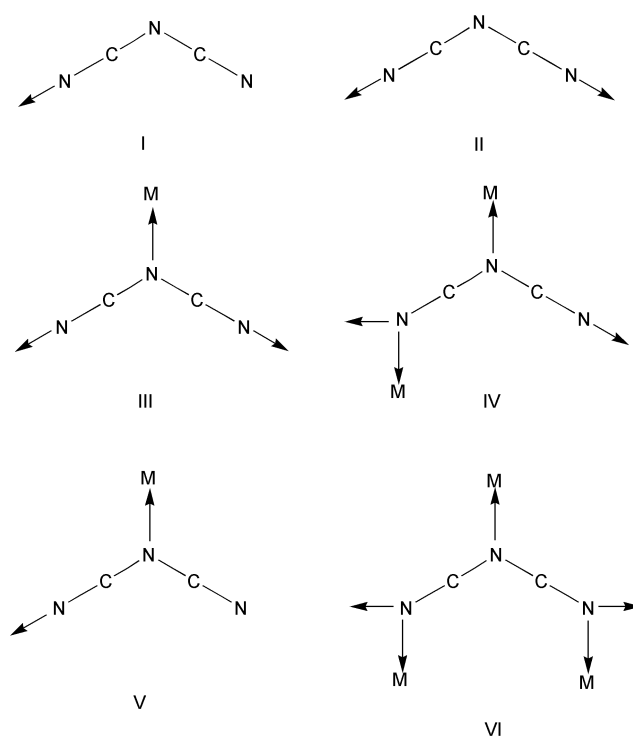
The crystal structure determination of Pb(dca)₂ reveals a new M(dca)₂ structural type with two unusual coordination modes of dicyanamide existing in a novel (4,5,9)-connected 3D-polymeric structure, indicating the versatile coordination behaviour of both dicyanamide and lead atom.

The crystal engineering of coordination polymers containing dicyanamide [(dca, N(CN)₂][−], and especially binary M(dca)₂ compounds, has attracted great attention.^{1,2} The first family of M(dca)₂ with M = Cr, Mn, Fe, Co, Ni possesses a rutile-like structure and interesting magnetic properties.¹ Weak ferromagnetism was found for M = Cr, Mn, Fe below 47, 16, and 19 K, respectively, while the Cu analogue is only paramagnetic down to 2 K. For M = Co and Ni, ferromagnetic ordering occurs between 9 and 21 K, respectively. The second M(dca)₂ structural type occurs in the tetrahedral metal dicyanamide complex Zn(dca)₂, which consists of an extended 2-D layered network with a nearly ideal square Zn...Zn metal array.²

Since dicyanamide has three nitrogen donor atoms, it can exhibit several possible coordination modes. Five coordination modes have been suggested (see Scheme 1), of which four modes were substantiated by X-ray crystallography. The most commonly observed coordination mode is two-connecting, **II**, which has been found in many transition metal compounds and some main group metal compounds.³ The terminal mode **I** occurs in some mononuclear complexes, for example Cu(1,10-phen)₂(dca)₂,⁴ [Cu^{II}(1,10-phen)₂(dca)₂][C(CN)₃],⁵ and Mn(NITpPy)₂(dca)₂(H₂O)₂,⁶ while the three-connecting mode **III** is observed in the rutile-like material M(dca)₂, M = Cr, Mn, Fe, Co, Ni,¹ and the unusual four-connecting mode **IV** occurs in (CH₃)₂Tl(dca).⁷ The possible two-connecting mode **V** has yet to be confirmed, although it is postulated for one isomer of Cu^{II}(dca)₂(imidazole).⁸

As early as 1922, the preparation of Pb(dca)₂ was reported but the structural characterization was not given.⁹ Due to the versatile coordination number and coordination geometry of lead(II) ion, novel coordination mode and novel network structure might be expected for Pb(dca)₂. Herein we report the synthesis and structure of nine-coordinate Pb(dca)₂, **1**, with an unprecedented structural type for M(dca)₂ compounds. The most striking feature of **1** is the occurrence of a novel (4,5,9)-connected 3D-polymeric network with two unusual coordination modes of dicyanamide, one of which has not been reported before.

Compound **1** was obtained as colourless block crystals by the reaction of Pb(NO₃)₂ and Nadca in aqueous solution. The infrared spectrum of **1** shows several infrared peaks at 2149 [vs, ν_{sym}(C≡N)], 2216 [v, ν_{asym}(C≡N)], 2235 [sh,



Scheme 1

ν_{asym}(C≡N)], 2260 [s, ν_{sym} + ν_{asym}(C≡N)], 2287 [sh, ν_{sym} + ν_{asym}(C≡N)], which are consistent with the reported values of CN vibrations for metal-dicyanamide compounds.³

Fig. 1 shows an ORTEP diagram of the asymmetric unit of **1**. There is only one type of lead atom, which is surrounded by nine nitrogen atoms as shown in Fig. 2. All nine nitrogen atoms are from dca ligands with the bond distances varying from 2.639(11) to 3.138(17) Å, and the bond angles from 67.8(4)° to 144.8(5)°. It is very interesting that there are two different types of dca in **1**, as shown in Fig. 2. The first type of dca, N(1)C(1)N(2)C(2)N(3), exhibits the five-connecting mode **VI**, with bond distances Pb(1f)–N(1) = Pb(1g)–N(1) = 2.820(14), Pb(1)–N(3) = Pb(1j)–N(3) = 2.639(11) and Pb(1i)–N(2) = 2.822(17) Å. Interestingly, the two cyanido nitrogen atoms coordinate with two pairs of lead atoms with different bond lengths. This five-connecting mode, **VI**, has not been observed before. In the second type of dca, N(4)C(3)N(5)C(4e)N(6e), the two terminal cyanido nitrogens coordinate with one and two lead atoms, respectively, with Pb(1)–N(4) = 2.655(17) and Pb(1h)–N(6) = Pb(1)–N(6) = 2.662(11) Å. The Pb–N(amide) distance is rather long

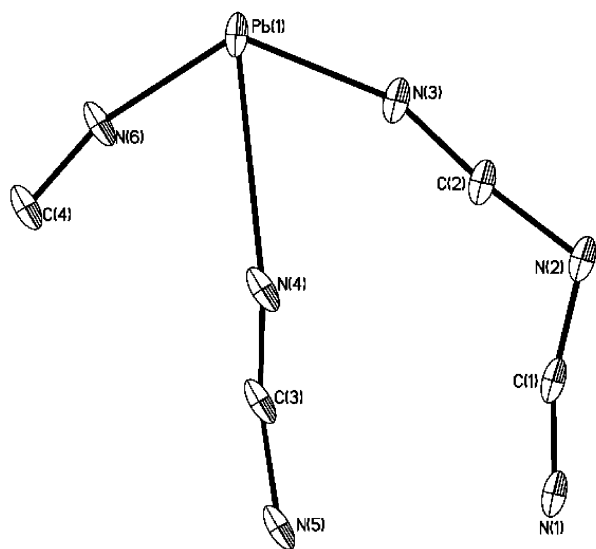


Fig. 1 ORTEP representation of the asymmetric unit of **1**. Thermal ellipsoids are shown at the 50% probability level.

[Pb(1f)–N(5) = 3.138(17) Å], which could be marginally considered as “a weak bond”. Thus, this coordination mode could be considered as a four-connecting mode **IV**, which has previously been observed in (CH₃)₂Tl(dca).⁷ With these two unusual coordination modes, lead and dca form a novel 3D-extended polymeric structure of compound **1**, which demonstrates the power of lead and dca as building blocks in the construction of novel coordination polymers due to their versatile coordination behaviour.

Although many coordination polymers have been reported, they usually exhibit low-connecting networks based on three to four connecting nodes. Examples for high-connecting topological networks have been rarely reported.¹⁰ Seven- and eight-connected topologies have recently been reported for

lanthanide coordination compounds.¹⁰ To our knowledge, a polymeric network containing a nine-connecting centre has not been reported. Compound **1** contains nine-connecting lead centres and also contains four- and five-connecting dca ligands. Thus, it is the first example of a novel (4,5,9)-connected polymeric network.

In summary, a novel (4,5,9)-connected polymeric network with two unusual coordination modes of dicyanamide has been observed in the crystal structure of Pb(dca)₂, **1**, which exhibits a new structural type for M(dca)₂ compounds.

Experimental

Synthesis

Five milliliters of an aqueous solution containing Nadca (0.089 g, 1.0 mmol) was added dropwise to 5 ml of an aqueous solution of Pb(NO₃)₂ (0.17 g, 0.5 mmol) without stirring. The resulting mixture was left at room temperature and single crystals suitable for X-ray single-crystal diffraction analysis appeared after several weeks. Yield: 0.13 g [78% based on Pb(NO₃)₂]. IR(KBr pellets, cm^{−1}): 527 s, 549 s, 649 m, 916 s, 933 m, 1324 vs, 1350 s, 1418 w, 1636 w, 2149 vs, 2216 s, 2235 sh, 2260 s, 2287 sh.

X-Ray crystallography

Data collection for **1** (2.27° ≤ θ ≤ 24.97°) was carried out at 293 K on a Bruker P4 diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) with the ω scan method. The structure was solved by direct methods using SHELXS 97¹¹ and refined by full-matrix least-squares calculation on F² with SHELXL 97.¹² All non-hydrogen atoms were refined anisotropically. Calculations were performed on a PC-586 computer.

CCDC number 189047. See <http://www.rsc.org/suppdata/nj/b2/b206332h/> for crystallographic data in CIF or other electronic format.

Crystal data for 1. C₄N₆Pb, *M* = 339.29, orthorhombic, space group *Pnma*, *a* = 13.501(2), *b* = 3.995(1), *c* = 11.980(2) Å, *U* = 646.2(2) Å³, *Z* = 4, *D*_c = 3.488 g cm^{−3}, μ = 26.039 mm^{−1}, 657 unique reflections measured. The final *R* indices [*I* > 2σ(*I*)] were *R*₁ = 0.038 and *wR*₂ = 0.1240.

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References

- 1 S. R. Batten, P. Jensen, B. Moubaraki, K. S. Murray and R. Robson, *Chem. Commun.*, 1998, 439; S. R. Batten, P. Jensen, C. J. Kepert, M. Kurmoo, B. Moubaraki, K. S. Murray and D.-J. Price, *J. Chem. Soc., Dalton Trans.*, 1999, 2987; M. Kurmoo and C. J. Kepert, *New J. Chem.*, 1998, **22**, 1515; J. L. Manson, C. R. Kmetz, Q. Huang, J. W. Lynn, G. M. Bendele, S. Pagola, P. W. Stephens, L. M. Liable-Sands, A. L. Rheingold, A. J. Epstein and J. S. Miller, *Chem. Mater.*, 1998, **10**, 2552.
- 2 J. L. Manson, D. W. Lee, A. L. Rheingold and J. S. Miller, *Inorg. Chem.*, 1998, **37**, 5966.
- 3 See, for example: J. L. Manson, C. D. Incarvito, A. L. Rheingold and J. S. Miller, *J. Chem. Soc., Dalton Trans.*, 1998, 3705; J. L. Manson, Q.-Z. Huang, J. W. Lynn, H.-J. Koo, M.-H. Whangbo, R. Bateman, T. Otsuka, N. Wada, D. N. Argyiou and J. S. Miller, *J. Am. Chem. Soc.*, 2001, **123**, 162; P. Jensen, S. R. Batten, G. D.

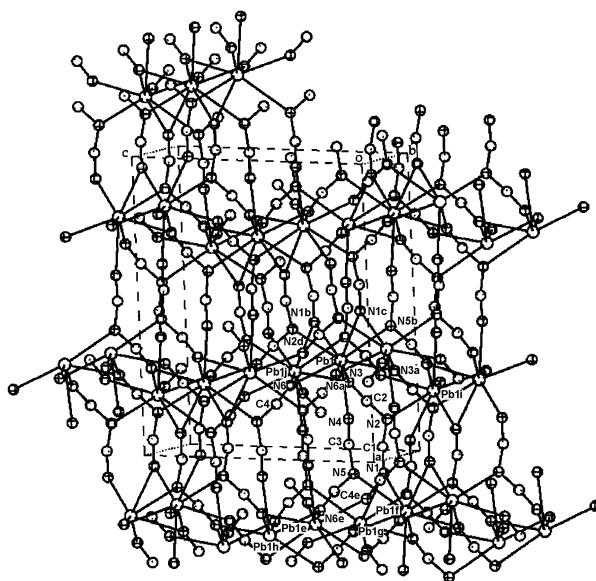


Fig. 2 Crystal packing of compound **1** viewed down the *b* axis. Selected bond lengths (Å) and bond angles (°): Pb(1)–N(3) 2.639(11); Pb(1)–N(3a) 2.639(11); Pb(1)–N(4) 2.655(17); Pb(1)–N(6a) 2.662(11); Pb(1)–N(6) 2.662(11); Pb(1)–N(1b) 2.820(14); Pb(1)–N(1c) 2.820(14); Pb(1)–N(2d) 2.822(17); Pb(1)–N(5b) 3.138(17). N(3)–Pb(1)–N(5b) 67.8(4); N(3a)–Pb(1)–N(5b) 67.8(4); N(3)–Pb(1)–N(6a) 144.8(5); N(3a)–Pb(1)–N(6) 144.8(5). Symmetry codes: a: *x*, 1 + *y*, *z*; b: −0.5 + *x*, *y*, 0.5 − *z*; c: −0.5 + *x*, 1 + *y*, 0.5 − *z*; d: 1.5 − *x*, 2 − *y*, 0.5 + *z*; e: 2 − *x*, 2 − *y*, 1 + *z*; f: 0.5 + *x*, *y*, 0.5 − *z*; g: 0.5 + *x*, −1 + *y*, 0.5 − *z*; h: 2 − *x*, 1 − *y*, 1 − *z*; i: 1.5 − *x*, 2 − *y*, −0.5 + *z*; j: *x*, −1 + *y*, *z*.

- Fallon, D. C. R. Hockless and B. Moubaraki, K. S. Murray, R. Robson, *J. Solid State Chem.*, 1999, **145**, 387; P. Jensen, S. R. Batten, B. Moubaraki and K. S. Murray, *J. Solid State Chem.*, 2001, **159**, 352; J. L. Manson, J. A. Schlueter, U. Geiser, M. B. Stone and D. H. Reich, *Polyhedron*, 2001, **20**, 1423; S. Martin, M. G. Barandika, R. Cortés, J. I. R. de Larramendi, M. K. Urtiaga, L. Lezama, M. I. Arriortua and T. Rojo, *Eur. J. Inorg. Chem.*, 2001, 2107; J. L. Manson, A. M. Arif and J. S. Miller, *J. Mater. Chem.*, 1999, **9**, 979.
- 4 I. Potocnák, M. Dunaj-Jurco, D. Miklos, M. Kablesová and L. Jäger, *Acta Crystallogr., Sect. C*, 1995, **51**, 600.
- 5 I. Potocnák, M. Dunaj-Jurco, D. Miklos and L. Jäger, *Acta Crystallogr., Sect. C*, 1996, **52**, 1653.
- 6 I. Dasna, S. Golhen, L. Ouahab, O. Pena, N. Daro and J.-P. Sutter, *C. R. Acad. Sci. Ser. II, Chimie*, 2001, **4**, 125.
- 7 Y. M. Chow and D. Britton, *Acta Crystallogr., Sect. B*, 1975, **31**, 1934.
- 8 J. Mrozinski, M. Hvastijová and J. Kohout, *Polyhedron*, 1992, **11**, 2867.
- 9 W. Madelung and E. Kern, *Liebigs Ann. Chem.*, 1922, **427**, 1.
- 10 D. L. Long, A. J. Blake, N. R. Champness, C. Wilson and M. Schröder, *Angew. Chem., Int. Ed.*, 2001, **40**, 2444.
- 11 G. M. Sheldrick, SHELXS 97, Program for Crystal Structure Determinations, University of Göttingen, Germany, 1997.
- 12 G. M. Sheldrick, SHELXL 97, Program for Crystal Structure Refinements, University of Göttingen, Germany, 1997.