

First Synthesis of a Macrocyclic Schiff Base from 3,6-Diformylpyridazine: X-Ray Crystal Structure of $[\text{Pb}_2(4 + 4)](\text{ClO}_4)_4$

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Condensation of 3,6-diformylpyridazine with 1,3-diaminopropane in the presence of lead(II) template ions gives the first example of a macrocycle containing pyridazine-diimine head units, and only the second example of a [4 + 4] Schiff base macrocycle; the structure of $[\text{Pb}_2(4 + 4)](\text{ClO}_4)_4$, **1**, is described.

The vast majority of large Schiff base macrocycles are symmetrical (in terms of the metal binding sites they provide) and contain either pyridine or phenol head units, although pyrrole, furan and thiophene head units are also known.¹ Our aim is to develop new areas in macrocyclic chemistry by: (i) introducing unsymmetrical metal binding sites² and (ii) incorporating new heterocyclic dicarbonyls. This paper concerns the latter of these two approaches. To our knowledge, 3,6-diformylpyridazine has never been incorporated into a macrocycle,³ yet simple acyclic pyridazine-containing ligands are known to chelate well to two metal ions.^{4,5} Both homo- and hetero-dimetallic complexes of such acyclic ligands have been prepared, giving complexes with a wide range of interesting properties.^{4,5} Therefore the synthesis of the first macrocycle (Fig. 1) to be derived from 3,6-diformylpyridazine was attempted. The reaction of 3,6-diformylpyridazine^{5,6} and 1,3-diaminopropane in the presence of lead(II) perchlorate, in a dry methanol:acetonitrile solvent mixture at room temp., yielded $[\text{Pb}_2(4 + 4)](\text{ClO}_4)_4$, **1**.[†] A precipitate formed on mixing the reactants but it redissolved over 4 h to leave a yellow solution. On standing overnight, yellow crystals of **1** precipitated from the solution. The IR spectrum of these crystals showed that cyclisation had occurred; an imine C=N stretch was present at 1649 cm^{-1} and no absorptions corresponding to unreacted carbonyl or primary amine were observed. Analysis indicated an empirical formula of $\text{Pb}(2 +$

$2)(\text{ClO}_4)_2$ but this seemed an unlikely molecular formula in view of the known preference of pyridazine to chelate two metal ions. Therefore, in order to resolve this important point, a single crystal X-ray structure determination[‡] was undertaken.

The structure analysis reveals that **1** is in fact a dilead(II) complex of the (4 + 4) macrocycle (Figs. 2 and 3). The complex cation possesses $4m2$ (D_{2d}) crystallographic symmetry. The two lead ions lie on the intersection of two mirror planes. They have crystallographically identical coordination environments; each is bound to four pyridazine and four imine nitrogen atoms. As expected the pyridazine head units chelate the two metal ions. The two mirror planes bisect the angles between the successive pyridazine rings (Fig. 3). Each pyridazine ring is at right angles to those flanking it. The propyl chains link up these head units [C(9) lies on a mirror plane] resulting in the (4 + 4) macrocycle wrapping quite tightly around the two lead ions.

This is only the second example of the formation of a [4 + 4] Schiff base macrocycle. The first example resulted from the condensation of 2,6-diacetylpyridine and 1,3-diaminopropan-2-ol in the presence of manganese(II) perchlorate.⁹ Unlike the manganese [4 + 4] complex, transmetallation reactions of **1** with a wide variety of transition metal ions should be possible and these reactions are under active investigation.⁶

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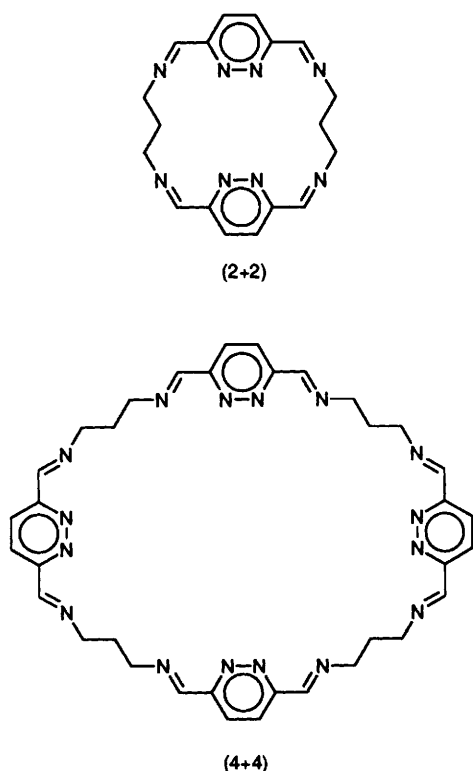


Fig. 1 Macrocyclic ligands (2 + 2) and (4 + 4).

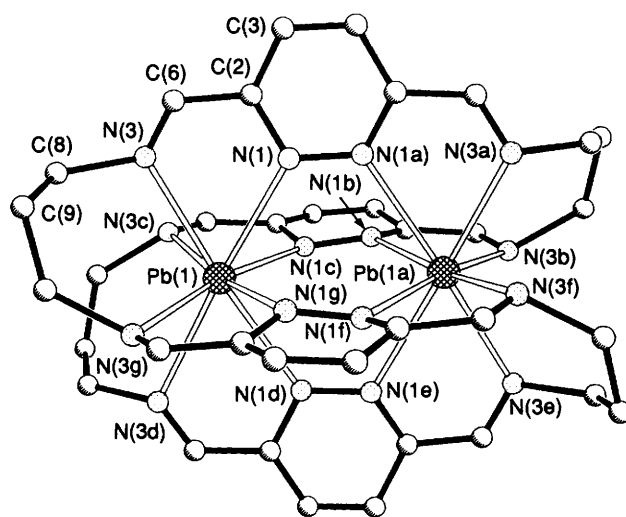


Fig. 2 Perspective view of the $[\text{Pb}_2(4 + 4)]^{4+}$ cation. Selected interatomic distances (Å) and angles (°): Pb(1)–N(1) 2.717(9), Pb(1)–N(3) 2.68(2), Pb(1)–Pb(1a) 4.176(2), N(1)–Pb(1)–N(1c) 77.2(9), N(1)–Pb(1)–N(1d) 116.9(4), N(1)–Pb(1)–N(1g) 71.0(9), N(1)–Pb(1)–N(3) 60.4(4), N(1)–Pb(1)–N(3c) 100.5(5), N(1)–Pb(1)–N(3d) 171.4(7), N(1)–Pb(1)–N(3g) 108.3(6), N(3)–Pb(1)–N(3c) 65.5(8), N(3)–Pb(1)–N(3d) 123.5(7), N(3)–Pb(1)–N(3g) 88.1(8).

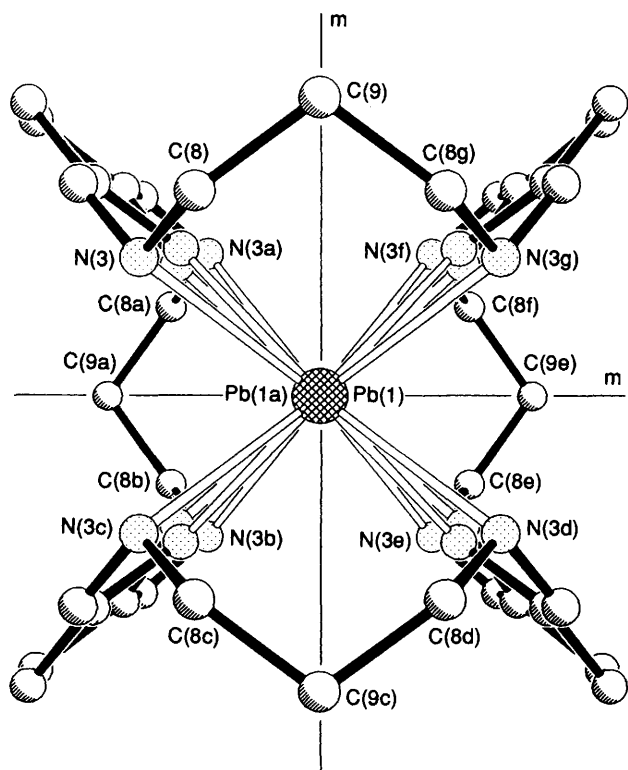


Fig. 3 Perspective view of the $[\text{Pb}_2(4 + 4)]^{4+}$ cation with the two intersecting mirror planes edge on.

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Footnotes

† Yield 47%. Satisfactory C, H, N, Cl, Pb analysis.

‡ *Crystal data*: $\text{C}_{36}\text{H}_{40}\text{N}_{16}\text{O}_{16}\text{Cl}_4\text{Pb}_2$, yellow triangular plate, $0.1 \times 0.6 \times 0.7$ mm, tetragonal, space group $\bar{I}4m2$, $a = 10.598(3)$, $b = 10.598(3)$, $c = 24.621(10)$ Å, $U = 2765(2)$ Å³, $Z = 2$, $\mu = 6.35$ mm⁻¹. Data were collected at 130 K on a Siemens P4 four circle diffractometer using graphite monochromated Mo-K α radiation, 1283 reflections were collected in the range $4 < 2\theta < 50^\circ$ and the 1254 independent reflections were used in the structural analysis after a thin plate absorption correction had been applied. The structure was solved by direct methods (SHELXS-86)⁷ and refined against all F^2 data (SHELXL-93)⁸ to $R_1 = 0.062$ [for 1084 $F > 4\sigma(F)$]; $wR_2 = 0.175$ and goodness of fit = 1.12 for all 1254 F^2 ; 55 parameters; lead and chlorine anisotropic; one perchlorate disordered; racemic twin]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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