

Template Synthesis of a Bimetallic Complex of a 30-Membered Decadentate Macrocyclic Ligand: The Crystal and Molecular Structure of a Lead(II) Complex

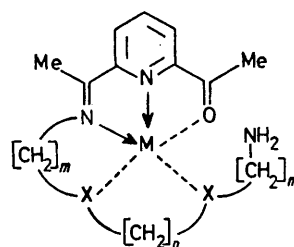
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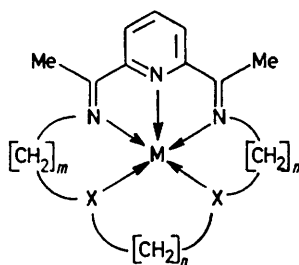
Summary The product of reaction of 2,6-diacetylpyridine with 3,6-dioxaoctane-1,8-diamine in the presence of $\text{Pb}(\text{SCN})_2$ contains two seven-co-ordinate lead(II) ions in a 30-membered, decadentate 'N₆O₄' macrocyclic ligand; in contrast, analogous reactions involving 3,6-diazaoctane-1,8-diamine or 4,7-diazadecane-1,10-diamine yield complexes of the 15- and 17-membered quinquedentate 'N₅' macrocycles.



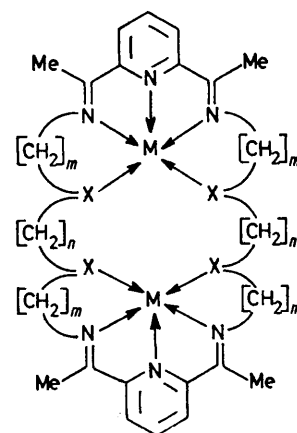
(I)

We have previously described¹ the template synthesis of a range of metal complexes of the quinquedentate macrocyclic ligands of type (II) from 2,6-diacetylpyridine and the appropriate tetrafunctional di-primary amine in the presence of the metal ion [*e.g.* Mg^{II} , Mn^{II} , Fe^{III} , Zn^{II} , Cd^{II} , Hg^{II} , or Ag^{I}]. As demonstrated by *X*-ray structural analysis and other studies these complexes exemplify unusual seven-, six-, and five-co-ordinate geometries based on (in most cases) an approximately pentagonal disposition of macrocycle donor atoms. An example² is the pentagonal bipyramidal complex $[\text{Mn}(2,2,2\text{-N}_3\text{O}_2)(\text{NCS})_2]$, of the 15-membered 'N₃O₂' macrocycle. We now report the structure of a bimetallic complex $[\text{Pb}_2(2,2,2\text{-N}_6\text{O}_4)(\text{SCN})_4]$, containing the 30-membered, decadentate macrocycle (III) (see Scheme) formed in > 80% yield by the condensation of two molecules of 2,6-diacetylpyridine with two molecules of 3,6-dioxaoctane-1,8-diamine in the presence of $\text{Pb}(\text{SCN})_2$ (30 min in dry methanol at 40 °C).

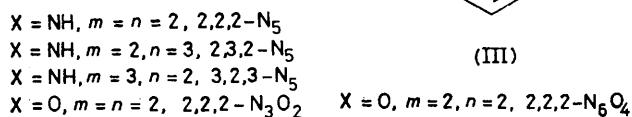
Crystal data: $\text{C}_{34}\text{H}_{42}\text{N}_{10}\text{O}_4\text{Pb}_2\text{S}_4$, $M = 598.5$, orthorhombic, $a = 16.451(13)$, $b = 27.117(15)$, $c = 9.646(7)$ Å, space group *Pnca* (non-standard setting of *Pbcn*, No. 60), $Z = 4$; μ ($\text{Mo-K}\alpha$) = 78.2 cm^{-1} . 1286 independent reflections above background were measured on a G.E. XRD5 diffractometer and refined to R 0.087.†



(II)



(III)



SCHEME

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

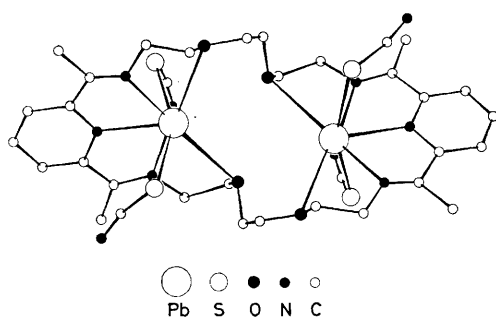


FIGURE. X-Ray structure of $[\text{Pb}_2(2,2,2\text{-N}_6\text{O}_4)(\text{SCN})_4]$.

There is a two-fold axis at the centre of the 30-membered macrocycle (Figure) which is non-planar, the two PbN_3O_3 planes (maximum deviation of a contributing atom 0.44 \AA) intersecting at an angle of 65.1° . Each metal ion is seven co-ordinate being bonded to three nitrogens [$2.54(3)$, $2.56(3)$, $2.47(2) \text{ \AA}$] and two oxygens [$2.96(3)$, $2.88(3) \text{ \AA}$] of the ring and, above and below this plane, to two thiocyanate sulphur atoms [$2.91(2)$, $3.00(2) \text{ \AA}$; Pb-S-C angles $102(2)$, $104(2)^\circ$].[†] The Pb...Pb separation is 5.27 \AA . The O-Pb-O angle is very large at $113.7(8)^\circ$ so that the co-ordination geometry of the metal may be considered as hexagonal bipyramidal with one equatorial site unoccupied. Whether this is due to an inability of the half-macrocycle to close around the large lead ion or to some stereochemical activity on the part of a lone pair of electrons on the metal is unclear.

$\text{Pb}(\text{SCN})_2$ is effective also in the template synthesis of macrocycles derived from 2,6-diacetylpyridine and 3,6-diazaoctane-1,8-diamine and 4,7-diazadecane-1,10-diamine,

yielding the complexes $[\text{Pb}(2,2,2\text{-N}_6)(\text{NCS})_2]$ and $[\text{Pb}(3,2,3\text{-N}_6)(\text{NCS})_2]$, respectively. While no structural information is available the presence of the 'single' 15- and 17-membered rings, respectively, in these two complexes was indicated by NaBH_4 reduction of the imino groups and subsequent liberation of the free reduced macrocycles [m/e $277(M^+)$ and $305(M^+)$, respectively]. {A similar procedure confirmed the presence of the 'double' ring in $[\text{Pb}_2(2,2,2\text{-N}_6\text{-O}_4)(\text{SCN})_4]$, m/e $558(M^+)$ }.
Our failure to isolate a 'single' 15-membered $2,2,2\text{-N}_6\text{O}_3$ ring complexed to Pb^{II} cannot simply be due to a mismatch of the sizes of the metal ion and the macrocycle hole since a complex of the corresponding, 15-membered '2,2,2-N₅' ring was successfully prepared. The structural analysis of $[\text{Pb}_2(2,2,2\text{-N}_6\text{O}_4)(\text{SCN})_4]$ shows that the metal ions lie significantly closer to the nitrogen than to the oxygen donors; a similar situation occurs in the Pb^{II} complex of a related 'N₃O₃' macrocycle.³ These observations suggest that the ligand conformation in the first-formed intermediate (I) may control the subsequent kinetic course of the template reaction. If a strong interaction between metal and X occurs then the terminal NH_2 and C=O groups of (I) can be brought into the *cis*-relationship necessary for intramolecular ring closure to yield a 'single' ring (II). Such is presumed to be the case for $\text{X} = \text{NH}$. On the other hand the more weakly co-ordinating ether groups ($\text{X} = \text{O}$) may not compete effectively with solvent for co-ordination sites with the result that the terminal NH and C=O functions are not constrained into close proximity. In these circumstances a preferential intermolecular self-condensation of two molecules of (I) may occur to yield the double ring (III).

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[†] One of the thiocyanate groups showed signs of disorder in that it was not bonded to the metal through sulphur in all unit cells. We introduced a parameter x where $x \text{ NCS}^-$ groups are bonded *via* sulphur and $(1-x)$ *via* nitrogen. x refined to $0.77(2)$. The i.r. spectrum showed two ν_{asym} vibrations of the NCS^- ion at 2010 and 2080 cm^{-1} .

¹ S. M. Nelson, S. G. McFall, M. G. B. Drew, A. H. bin Othman, and N. B. Mason, *J.C.S. Chem. Comm.*, 1977, 167; M. G. B. Drew, A. H. bin Othman, P. D. A. McIlroy, and S. M. Nelson, *J.C.S. Dalton*, 1975, 2507; 1976, 1394, and other papers in this series.

² M. G. B. Drew, A. H. Othman, S. G. McFall, P. D. A. McIlroy, and S. M. Nelson, *J.C.S. Dalton*, 1977, 1173.

³ D. E. Fenton, D. H. Cook, and I. W. Nowell, *J.C.S. Chem. Comm.*, 1977, 274.