

**The Pb²⁺ Ion as a Template in the Synthesis of Macrocyclic Ligands;
X-Ray Structure of 3,15,21-Triaza-6,9,12-trioxabicyclo[15.3.1]heneicosal(21),
2,15,17,19-pentaene(thiocyanato)(isothiocyanato)lead(II)**

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Summary Novel, eight co-ordinate complexes, Pb(macrocycle)(NCS)₂, are formed in good yield in hydroxylic solvents by the template condensation of 2,6-diacetylpyridine or pyridine-2,6-dicarbaldehyde with 1,11-diamino-3,6,9-trioxaundecane in the presence of Pb²⁺ ion.

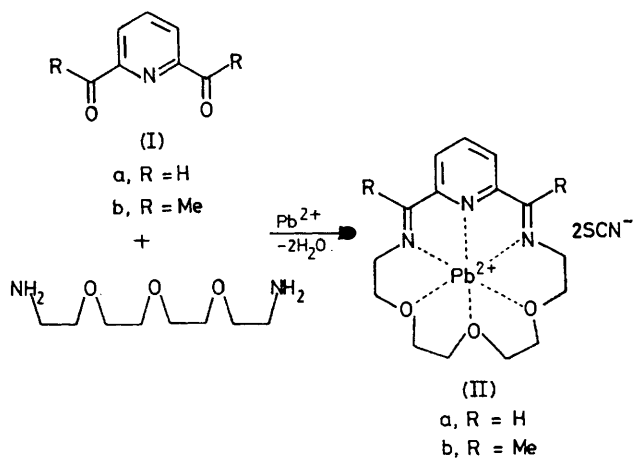
THE synthesis of macrocyclic ligands by Schiff base formation may be facilitated by use of the metal ion template effect.¹ This procedure is well documented for divalent transition metal ions² and has been extended to include S-block cations.³ We now report the application of this technique to the synthesis of macrocyclic complexes of lead(II).

The condensation of either pyridine-2,6-dicarbaldehyde (Ia) or 2,6-diacetylpyridine (Ib) with 1,11-diamino-3,6,9-

trioxaundecane in 1:1 molar ratio in BuⁿOH leads only to resinous gums having properties consistent with oligomeric composition. If, however, the reaction is carried out in the presence of an equimolar amount of Pb(SCN)₂, the complexes 3,15,21-triaza-6,9,12-trioxabicyclo[15.3.1]heneicosal(21),2,15,17,19-pentaene(dithiocyanato)lead(II) (IIa) and the 2,16-dimethyl derivative (IIb) are formed in good yield. Microanalyses of the products are consistent with the proposed formulae and a crystallographic molecular weight determination confirms the molecular formula for (IIa). The absence of free carbonyl stretching frequencies is noted in the i.r. spectra.

The complex (IIa), C₁₇H₂₁N₅O₃PbS₂, *M* 614.7, crystallises from warm, aqueous EtOH as yellow crystals. The crystals are triclinic with *a* = 9.546(2), *b* = 14.744(4),

$c = 7.672(2) \text{ \AA}$, $\alpha = 100.97(4)$, $\beta = 89.19(3)$, $\gamma = 99.68(4)^\circ$,
space group $P\bar{1}$, $Z = 2$. R for 2222 independent reflections,
having $I/\sigma(I) \geq 4$, is currently 0.075.†



The lead ion is found to be located within the cavity of the macrocycle, while the thiocyanate ions lie above and below the macrocycle mean plane to give an effective eight-coordination of the lead. One thiocyanate anion is N-bonded, and the other is S-bonded (see Figure). The lead appears to interact preferentially with the nitrogen atoms of the macrocycle for, while the mean Pb–O distance is 3.07 Å, the mean Pb–N(macrocycle) is 2.60 Å. This bond length is similar to that for the Pb–N(thiocyanate) interaction, 2.63 Å. The Pb–S distance is 2.97 Å and the sulphur atom of the N-bonded thiocyanate group exhibits a long-range interaction with a neighbouring lead ion (Pb–S, 3.42 Å). The lead ion is co-planar with the pyridine ring; the oxygen and remaining nitrogen atoms are at distances +1.03 (O-1), +1.87 (O-2), +0.85 (O-3), +0.15 (N-2) and –0.19 (N-3) Å from the pyridine mean plane.

† 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.

¹ P. B. Donaldson, P. A. Tasker, and N. W. Alcock, *J.C.S. Dalton*, 1976, 2262.

² L. F. Lindoy and D. H. Busch, *Prep. Inorg. Reactions*, 1971, 6, 1.

³ M. G. B. Drew, A. Hamid bin Othman, S. G. McFall, and S. M. Nelson, *J.C.S. Chem. Comm.*, 1975, 818.

⁴ A. H. Norbury and A. I. P. Sinha, *Quart. Rev.*, 1970, 24, 69.

⁵ D. H. Cook and D. E. Fenton, unpublished data.

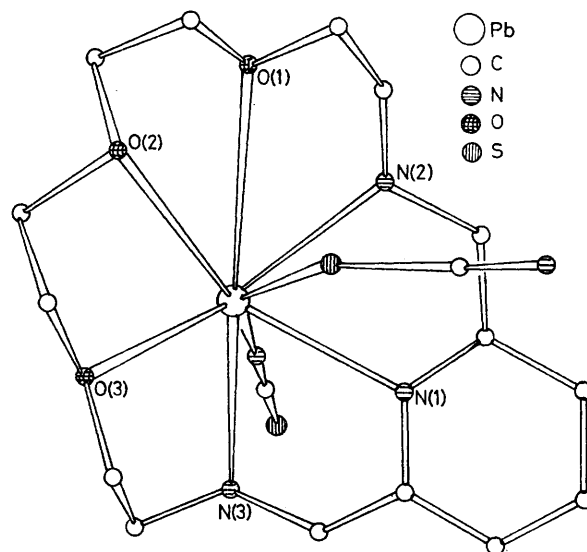


FIGURE. Molecular structure of Pb(macrocycle)(NCS)₂ (IIa).

The Pb–N–CS and Pb–S–CN angles are 167 and 106° respectively and the observed splitting of the C–N stretching frequency (ν_1) in the i.r. spectrum can be attributed to the linkage isomerism exhibited by the thiocyanate ions. Bands are observed at 2085 and 2065 cm⁻¹ for (IIa), consistent with the presence of S- and N-bonded thiocyanates respectively.⁴

A direct comparison can be made between the behaviour of lead(II) and that of the alkaline earth metals calcium, strontium, and barium, as the thiocyanates of these metals also readily form complexes with the macrocycles derived from (Ia) or (Ib), and 1,11-diamino-3,6,9-trioxaundecane under the reaction conditions described herein.⁵

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