Metal Ion Controlled Ring Contraction to Produce an Oxazolidine-containing Schiff Base Macrocycle and the *X*-Ray Structure of the $Pb(NCS)_2$ Complex

Neil A. Bailey,* David E. Fenton,* Ian T. Jackson, Richard Moody, and Cecilia Rodriguez de Barbarin
Department of Chemistry, The University, Sheffield S3 7HF, U.K.

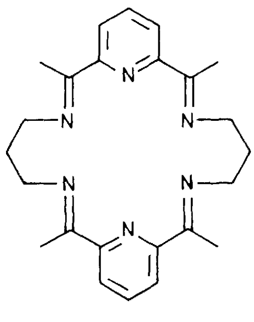
The reaction of 2,6-diacetylpyridine with 1,3-diamino-2-hydroxypropane in methanol in the presence of lead(II) cations leads to the isolation of lead(II) complexes of an oxazolidine-containing Schiff base macrocycle formed by ring-contraction; the ligand is hexadentate and the lead is *N*-bonded to one thiocyanate to form a monocationic complex.

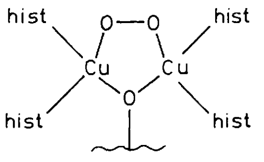
The synthesis of '2 + 2' tetraimino-Schiff base macrocycles, *e.g.* (**1**), from heterocyclic dialdehydes and diketones such as pyridine-2,6-dicarbaldehyde, 2,6-diacetylpyridine, furan-2,5-dicarbaldehyde and thiophene-2,5-dicarbaldehyde, and α,ωdiaminoalkanes is now well established.[1,2] Generally the macrocycles are prepared as metal complexes *via* metal template techniques using alkaline earth metal cations, although those derived from thiophene-2,5-dicarbaldehyde have been prepared as free macrocycles.[2] Homobinuclear transition metal complexes of the macrocycles have been prepared from the alkaline earth metal complexes by employing transmetallation reactions.[3,4]

We have sought to introduce the hydroxy group into the lateral structure of '2 + 2' Schiff base macrocycles as this would provide potential endogenous alkoxy-bridges, on deprotonation, and so lead to model systems for the proposed homobimetallic site in oxyhaemocyanin (**2**).[5]

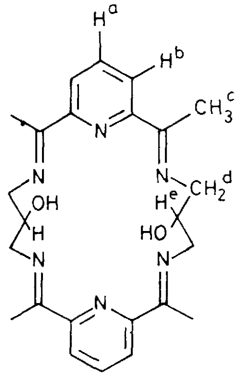
The reaction of 2,6-diacetylpyridine (pda) with 1,3-diamino-2-hydroxypropane (dhp) in methanol in the presence of $Ba(NCS)_2$, or $Ba(ClO_4)_2$, leads readily to the corresponding mononuclear barium complex of the '2 + 2' macrocycle (**3**). In contrast the reaction of pda with dhp in the presence of $Pb(NCS)_2$, or $Pb(ClO_4)_2$, resulted in isolation of the corresponding lead complex of the ring-contracted macrocycle (**4**). Satisfactory analytical and spectral† data were obtained for all the complexes, and the *X*-ray crystal structure of (**4**)·$Pb(NCS)_2$, MeOH was determined.

Crystal data: $Pb(C_{24}H_{30}N_6O_2)(NCS)_2\cdot MeOH$, $C_{26}H_{30}N_8O_2PbS_2\cdot MeOH$, $M = 757.895$ (789.937 with solvent): crystallises from methanol as pale yellow plates; crystal dimensions $0.50 \times 0.45 \times 0.14$ mm. Triclinic, $a = 16.586(17)$, $b = 7.828(6)$, $c = 12.255(8)$ Å, $\alpha = 84.57(6)$, $\beta = 109.48(6)$, $\gamma = 102.80(8)°$, $U = 1463(2)$ Å^3, $Z = 2$, $D_m = 1.72$, $D_c = 1.720$ g cm^{-3}, space group $P\bar{1}$ (C_i^1, no. 2; assumed and confirmed by the analysis), Mo-K_α radiation ($\bar{\lambda} = 0.71069$ Å), μ(Mo-K_α) = 59.94 cm^{-1}, $F(000) = 780$.‡

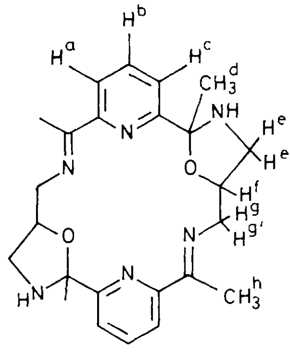

(**1**)



(**2**)



(**3**)



(**4**)

Three-dimensional *X*-ray diffraction data were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet/Syntex R3m diffractometer by the ω-scan method. 4479 Independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz–polarisation effects and for absorption. The structure was solved by standard Patterson and Fourier techniques and refined by block-diagonal least-squares methods. Hydrogen atoms were initially placed in calculated positions [C–H 0.96, N–H 0.96, O–H 0.91 Å, X–C–H(methyl) 111 (X = C,O), C–O–H 110°]; their contributions were included in structure factor calculations ($B = 5.0$ Å^2) but no refinement of positional parameters was permitted. The hydrogen atom on N(2) was found to be disordered, 0.75 : 0.25 (from peak heights). Refinement converged at *R* 0.0359 with allowance for anisotropic thermal motion of all non-hydrogen atoms and for the anomalous scattering of lead and sulphur. Scattering factors were taken from ref. 6; unit weights were used throughout the refinement; computer programs formed part of the Sheffield *X*-ray system.

The structure comprises a monocationic macrocyclic complex of isothiocyanatolead(II) (see Figure 1) with a thiocyanate counter anion and a molecule of methanol of solvation which is hydrogen bonded to an unco-ordinated secondary amine residue [N(5)] of the macrocycle. The lead is bonded to six sites within the macrocycle, two pyridyl and two imino nitrogen atoms and two oxygen atoms, originally substituent hydroxy groups, which became incorporated into two, hinged, oxazolidine rings formed by the addition of the endogenous

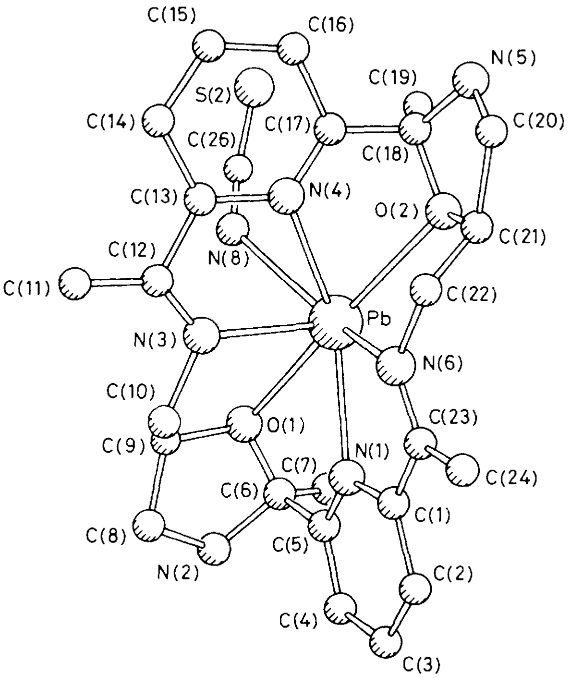


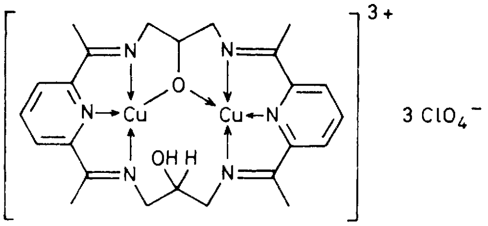
Figure 1. The molecular geometry of the complex cation [(**4**)·PbNCS]$^+$ [Pb–O(1) 2.634(5), Pb–O(2) 2.702(5), Pb–N(1) 2.587(6), Pb–N(3) 2.470(6), Pb–N(4) 2.569(6), Pb–N(6) 2.533(7), Pb–N(8) 2.889(8) Å].

---

† *Spectral data for* (**3**)·$Ba(ClO_4)_2$: ^1H n.m.r. (400 MHz, CD_3OD) δ 2.30 (d, H^c), 3.92 (m, H^d), 4.57 [m (part obscured by solvent), H^e], 7.69 (d, H^b), and 7.87 (t, H^a); mass spectrum *m/z* 434 (*M*, macrocycle = 434); i.r. ν 3450 (OH), 1640 (C=N), and 1090 and 620 cm^{-1} (Cl–O).

Spectral data for (**4**)·$Pb(NCS)_2$: ^1H n.m.r. (400 MHz, CD_3OD) δ 1.94 (s, H^d), 2.53 (q) and 3.75 (q, $H^{e/e'}$), 2.56 (d, H^h), 2.78 (m) and 4.49 (m, $H^{g/g'}$), 4.35 (m, H^f), 8.22 (d) and 8.31 (d, $H^{a/c}$), and 8.35 (t, H^b); mass spectrum *m/z* 434 (*M*, macrocycle = 434); i.r. ν 3275 (NH), 2050 and 2025 (NCS), 1640 cm^{-1} (C=N).

‡ 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.



(5)

hydroxy group across the adjacent C=N double bond with consequential proton transfer to the nitrogen. A related cyclisation to produce an imidazole ring has been reported.[7] The geometry of the lead macrocycle unit has approximate C_2 symmetry and is folded about an almost linear O–Pb–O spine. The remainder of the co-ordination sphere of the lead is occupied by an *N*-bonded thiocyanate ligand and, more distantly, by the sulphur of an ionic thiocyanate (Pb $\cdots$ S 3.415 Å) in directions which closely comply with the approximate C_2 molecular symmetry. Both thiocyanates are linear but the mode of bonding of the former is bent (Pb–N–C 128.6°). The metal co-ordination geometry is not closely related to any simple polyhedron.

No evidence was obtained from ^{1}H n.m.r. for the existence of an equilibrium in solution between the open and contracted isomers. This was sought as the condensation of aromatic and α,β-unsaturated carbonyl compounds with β-aminoalcohols generally leads to the Schiff base rather than the oxazolidine.[8] The ring contraction here, from an octadentate, 20-membered ring unit to a hexadentate, 18-membered ring unit, is believed to be facilitated by the use of the smaller Pb^{2+} cation (r = 1.21, *cf.*, r = 1.35 Å for Ba^{2+}) and its requirement for the smaller ring cavity.

Transmetallation reactions with (**3**) using copper(II) perchlorate in ethanol gave a complex analysing as (ligand)-$Cu_2(ClO_4)_3 \cdot 2H_2O$. The i.r. spectrum shows the presence of an O–H stretch (3475 cm^{-1}) and C=N groups (1650 cm^{-1}) and the magnetic moment, determined at ambient temperature using a Gouy balance, was 0.6 μ_B per copper(II) atom. This reduced moment is indicative of an oxo-bridged homobinuclear dicopper(II) unit.[9]

In the absence of an *X*-ray structure (crystals grown from alcoholic solvents were not amenable to the technique) it is plausible to suggest for the compound a structure in which one endogenous hydroxy unit is depronated to give an alkoxy-bridged homobinuclear copper(II) complex (**5**).[10] Such a complex can be seen to have the potential to act as a speculative model for the dicopper(II) site in oxyhaemocyanin.

We thank the S.E.R.C. for the award of a studentship (to R. M.) and for funds towards the purchase of the diffractometer, and the Consejo Nacional de Ciencia y Tecnologia (Mexico) for support.

Received, 11th August 1983; Com. 1095

References

1 S. M. Nelson, *Pure Appl. Chem.*, 1980, **52**, 2461 and references therein.
2 N. A. Bailey, M. M. Eddy, D. E. Fenton, G. Jones, S. Moss, and A. Mukhopadhyay, *J. Chem. Soc., Chem. Commun.*, 1981, 628.
3 S. M. Nelson, F. S. Esho, and M. G. B. Drew, *J. Chem. Soc., Chem. Commun.*, 1981, 388.
4 M. G. B. Drew, J. Nelson, F. S. Esho, V. McKee, and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1982, 1837.
5 M. S. Co, K. O. Hodgson, T. K. Eccles, and R. J. Lontie, *J. Am. Chem. Soc.*, 1981, **103**, 984.
6 International Tables for *X*-Ray Crystallography, Kynoch Press, Birmingham, 1974, vol. 4.
7 M. G. B. Drew, J. Nelson, and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1981, 1678.
8 J. W. Cornforth, ch. 6 in 'Heterocyclic Compounds,' vol. 5, ed. R. C. Elderfield, Wiley, New York, 1957.
9 O. Kahn, *Inorg. Chim. Acta*, 1982, **62**, 3.
10 This has now been confirmed by an *X*-ray structure determination of an acetonitrile-aqua adduct of the dicopper complex, V. McKee and J. Smith, *J. Chem. Soc., Chem. Commun.*, 1983, following communication.