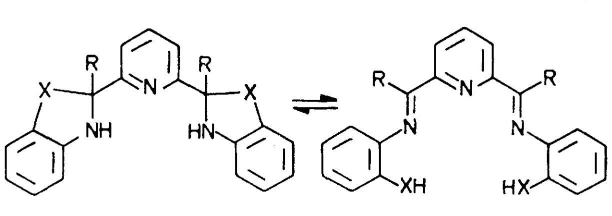
Novel Polynuclear Cadmium Complexes Resulting from Ring-opening Reactions of 2,6-Bis(2-R-2-benzoxazolinyl)pyridine (R = Me or H); *X*-Ray Structures of $[Cd_4(C_{21}H_{17}N_3O_2)_2{\cdot}(MeCO_2)_4]{\cdot}Me_2NCHO{\cdot}H_2O$ and $[Cd_3(C_{19}H_{13}N_3O_2)_2{\cdot}(MeCO_2)_2{\cdot}(Me_2NCHO)_2]$

By David C. Liles, Mary McPartlin, and Peter A. Tasker*
(*Department of Chemistry, The Polytechnic of North London, Holloway, London* N7 8DB)
and Hyacinth C. Lip and Leonard F. Lindoy*
(*Department of Chemistry and Biochemistry, James Cook University of North Queensland, Queensland* 4811, *Australia*)

Summary In solution the 2,6-bis(2-R-2-benzoxazolinyl)-pyridines (R = Me or H) undergo ring opening in the presence of $Cd(MeCO_2)_2$ to give unusual polynuclear complexes with very different structures; the differences may be attributed to steric interactions in the ligand with R = Me preventing this from adopting a near-planar configuration.

It has been demonstrated that a number of ring-opening reactions of benzothiazolines[1,2] and benzoxazolines[3] occur rapidly in the presence of many divalent metal ions to give the corresponding Schiff-base chelates. The isomerisation of compound (Ia) to give the potentially quinquedentate ligand (IIIa) is induced by zinc or cadmium acetate[2] and results in an unusual 'helical' five-co-ordinate geometry in the zinc complex so formed.[4] Extension of this work to include the reactions of the benzoxazolines (IIa) and (IIb)



(Ia) R = Me, X = S
(Ib) R = H, X = S
(IIa) R = Me, X = O
(IIb) R = H, X = O

(IIIa) R = Me, X = S
(IIIb) R = H, X = S
(IVa) R = Me, X = O
(IVb) R = H, X = O

has resulted in the unusual products which we report here.

Solutions of (IIa) or (IIb) and cadmium acetate in 90% acetone–dimethylformamide (dmf), after refluxing for a short time, gave orange crystalline materials (Va) and (Vb) respectively. Analytical and i.r. data indicated the presence of acetate groups and the deprotonated quinquedentate ligands (IVa — 2H$^+$) or (IVb — 2H$^+$) in both complexes, and support the empirical formulation of (Va) as [Cd_2(IVa — 2H$^+$)($MeCO_2$)$_2$]·0·5dmf·0·5H_2O and (Vb) as [Cd_3(IVb — 2H$^+$)$_2$($MeCO_2$)$_2$(dmf)$_2$].

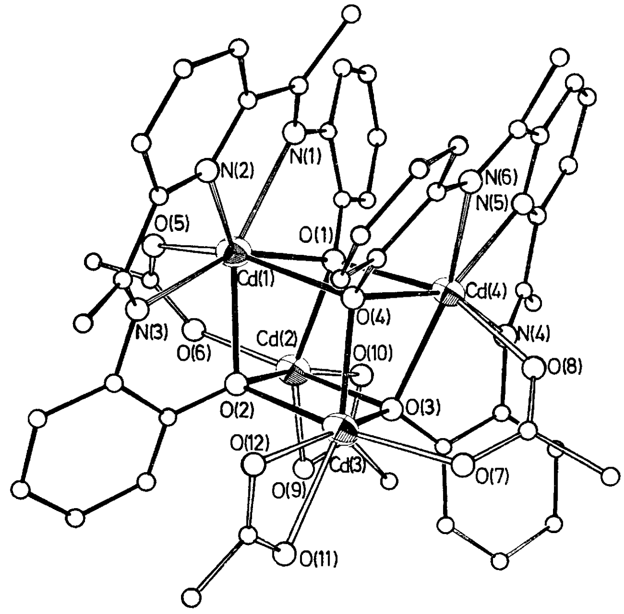


Figure 1. The structure of (Va) [$Cd_4(C_{21}H_{17}N_3O_2)_2(MeCO_2)_4$]. Selected bond lengths (Å) (mean e.s.d. 0·008 Å):

Cd(1) to	Cd(4) to	Cd(2) to	Cd(3) to
O(1) 2·325	O(1) 2·431	O(1) 2·310	O(2) 2·360
O(2) 2·359	O(3) 2·441	O(2) 2·308	O(3) 2·303
O(4) 2·570	O(4) 2·293	O(3) 2·307	O(4) 2·291
O(5) 2·303	O(8) 2·285	O(6) 2·180	O(7) 2·223
N(1) 2·365	N(4) 2·326	O(9) 2·338	O(11) 2·319
N(2) 2·288	N(5) 2·285	O(10) 2·322	O(12) 2·327
N(3) 2·350	N(6) 2·397		

X-Ray single crystal analyses have shown that both compounds have polynuclear structures. The molecule of (Va) is tetranuclear (Figure 1) with a cubane-like 'Cd_4O_4' core similar to the 'M_4Y_4' cores observed recently in complexes of other metals.[5] In contrast the molecule of (Vb) is trinuclear (Figure 2) with crystallographic C_2 symmetry and a large Cd(1)–Cd(2)–Cd(1′) angle of 152°. Each complex has two seven-co-ordinate cadmium atoms with the respective quinquedentate ligands, (IVa — 2H$^+$) or (IVb — 2H$^+$), occupying the equatorial sites of distorted pentagonal bipyramidal geometries. In (Va) the seven-co-ordination is completed by a bridging acetato group, and a bridging oxygen from the second quinquedentate ligand, whereas in (Vb) a bridging acetato group and the oxygen of a dmf molecule occupy the axial sites of each seven-co-ordinate cadmium atom. Seven-co-ordinate cadmium atoms in polynuclear complexes have not previously been observed. The remaining two cadmium atoms in (Va) and the central cadmium atom in (Vb) have distorted octahedral 'O_6' donor sets made up of bridging oxygen atoms from the respective quinquedentate ligands, and acetato groups.

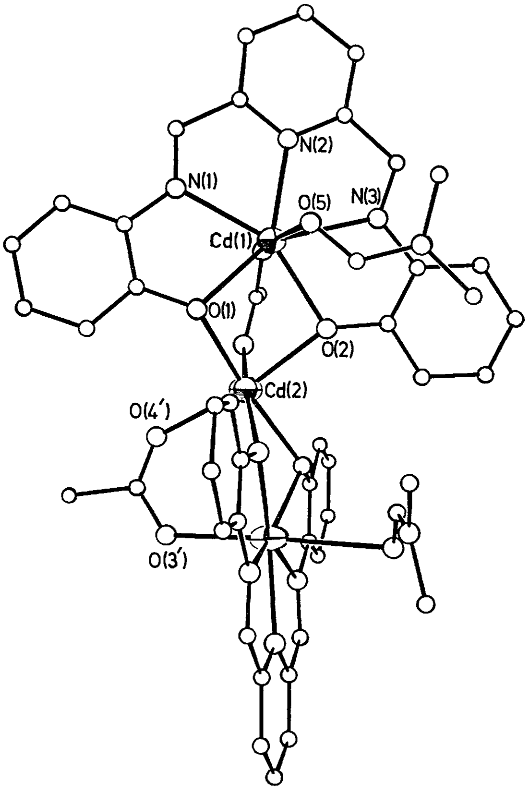


Figure 2. The structure of (Vb) [$Cd_3(C_{19}H_{13}N_3O_2)_2(MeCO_2)_2(dmf)_2$]. Selected bond lengths (Å) (mean e.s.d. 0·02 Å): Cd(1)–O(1) 2·26, Cd(1)–O(2) 2·26, Cd(1)–N(1) 2·35, Cd(1)–N(2) 2·28, Cd(1)–N(3) 2·37, Cd(1)–O(3) 2·31, Cd(1)–O(5) 2·83, Cd(2)–O(1) 2·30, Cd(2)–O(2) 2·27, Cd(2)–O(4) 2·28.

There is no metal–metal bonding in either complex, the shortest Cd–Cd distance being 3·28 Å. The marked difference between the structures of (Va) and (Vb) may be attributed to steric factors arising from the different R groups in the quinquedentate ligands. Whereas in (Vb) (R = H) the 'N_3O_2' donor set is planar to within 0·1 Å, in (Va) (R = Me) there is a marked distortion from planarity with both donor oxygen atoms being 1·2 ± 0·15 Å to one side of the plane of the three donor nitrogen atoms. It is this buckling of the ligand, possibly caused by steric interactions of the methyl groups with the phenyl *ortho*-hydrogen atoms, that enables the oxygen atoms of the quinquedentate ligand in (Va) to achieve the approximately tetrahedral bonding geometry necessary for their triply bridged role in the cubane-like structure. Similar steric interactions of the methyl substituents have previously been invoked to explain the unusual 'helical-twist' observed in the zinc(II) complex of (IIIa — 2H$^+$).[4]

These results emphasise the facility with which d^{10} and d^5 metal ions can act as 'templates' in reactions which involve the definition of unusual co-ordination number and geometry at the template ion. They refute the recent suggestion that the ligands (IVa) and (IVb) co-ordinate through a maximum of four donor atoms at one time.[6]

Intensity data were collected on a Philips PW1100 automatic four-circle diffractometer using graphite-monochromatised Mo-K_α radiation. *Crystal data:* (Va), $Cd_4(C_{21}H_{17}N_3O_2)_2(MeCO_2)_4 \cdot Me_2NCHO \cdot H_2O$, $M = 1463\cdot66$, orthorhombic, space group $P2_12_12_1$, $a = 23\cdot568(7)$, $b = 16\cdot249(3)$, $c = 14\cdot480(2)$ Å, $U = 5545$ Å^3, $D_m = 1\cdot76$, $D_c = 1\cdot75$ g cm^{-3}, $Z = 4$. Block diagonal least-squares refinement of the atomic parameters (Cd atoms anisotropic) using 6268 independent reflections [$I/\sigma(I) > 3$, $3 < \theta < 30°$] has given an R value of 0·051. The structure of the tetranuclear molecule is shown in Figure 1. (Vb), $Cd_3(C_{19}H_{13}N_3O_2)_2(MeCO_2)_2(Me_2NCHO)_2$, $M = 1232\cdot14$, orthorhombic, space group $Iba2$, $a = 21\cdot490(5)$, $b = 11\cdot363(3)$, $c = 19\cdot599(5)$ Å, $U = 4786$ Å^3, $D_m = 1\cdot70$, $D_c = 1\cdot71$ g cm^{-3}, $Z = 4$. Owing to the shortage of data, the phenyl and pyridyl groups in the chelating ligands were treated as rigid bodies (C–C 1·395, C–N 1·340 Å), as were the dmf molecules (Me–N = 1·462, OC–N = 1·351, C–O = 1·230 Å). Full matrix least-squares refinement of the group and atomic parameters (Cd atoms anisotropic) using 859 independent reflections [$I/\sigma(I) > 2$, $3 < \theta < 25°$] has given an R value of 0·048. The structure of the trinuclear molecule is shown in Figure 2.

We thank the S.R.C. for a grant for diffractometer equipment and for a studentship (to D.C.L.), and the Australian Institute for Nuclear Science and Engineering for support.

(*Received*, 11*th May* 1976; *Com.* 528.)

---

[1] L. F. Lindoy and S. E. Livingstone, *Inorg. Chim. Acta*, 1967, **1**, 365, and refs. therein.

[2] L. F. Lindoy and D. H. Busch, *Inorg. Chem.*, 1974, **13**, 2495.

[3] E. Bayer and G. Shenk, *Chem. Ber.*, 1960, **93**, 1184.

[4] L. F. Lindoy, D. H. Busch, and V. Goedken, *J.C.S. Chem. Comm.*, 1972, 683; V. L. Goedken and G. G. Christoph, *Inorg. Chem.*, 1973, **12**, 2316.

[5] B. A. Averill, T. Herskovitz, R. H. Holm, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1973, **95**, 3523, and refs therein.

[6] H. A. Tayim, M. Absi, A. Darwish, and S. K. Thabet, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 395.