

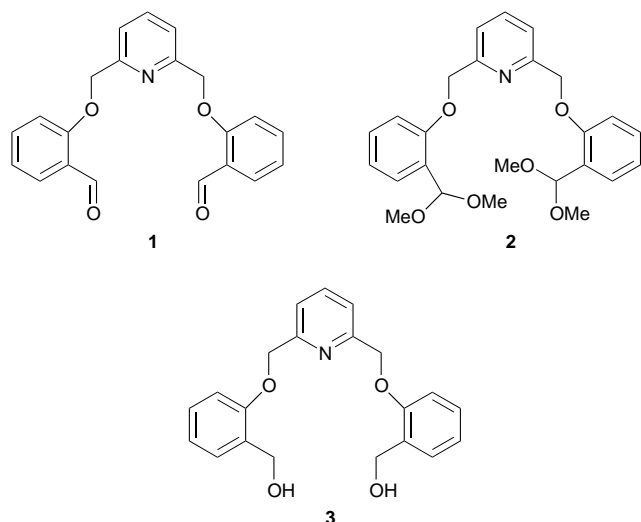
The X-Ray Crystal Structures of Two Derivatives of 2,6-Bis{[2-(dimethoxymethyl)phenoxy]methyl}pyridine

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The X-ray crystal structures of 2,6-bis{[2-(dimethoxymethyl)phenoxy]methyl}pyridine and 2,6-bis{[2-(hydroxymethyl)phenoxy]methyl}pyridine are reported.

We have previously reported that the reaction of 2,2'-[pyridine-2,6-diylbis(methyleneoxy)]dibenzaldehyde (**1**) and bis(2-aminoethyl) ether, in the presence of barium cations as a templating device, can yield a [1+1] macrocyclic Schiff base.¹ Reaction of this macrocycle with cerium nitrate led to the isolation of the complex $[\text{Ce}(\mathbf{1})_2](\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$, hydrolysis of the macrocycle having occurred.² Consequently we have investigated the potential complexation properties of **1** towards the lanthanides³ and have shown that whilst $[\text{Ce}(\mathbf{1})_2](\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ can be formed by the reaction of cerium nitrate with **1** in a mixed methanol–acetonitrile medium a very different white crystalline product is formed when the reaction is carried out in methanol alone. Spectroscopic analysis of this product suggested that acetal formation had occurred to give 2,6-bis{[2-(dimethoxymethyl)phenoxy]methyl}pyridine (**2**), as we had previously noted in the reaction of **1** with lead(II) salts.¹ Recrystallisation of **1** from methanol alone gave no acetal formation, suggesting that **2** is produced as a result of a metal ion activated reaction.



A single crystal X-ray crystal structure determination confirmed the nature of **2** (Fig. 1). The bond angles and distances in the ligand are comparable to those reported for the related compound, pyridine-2,6-dimethanol.⁷

Crystal Data for 2.— $\text{C}_{25}\text{H}_{29}\text{NO}_6$, $M_r = 439.49$, colourless oblong crystals from methanol, crystal dimensions $0.66 \times 0.44 \times 0.25$ mm, monoclinic, $a = 9.609(3)$, $b = 9.327(2)$, $c = 26.101(3)$ Å, $\beta = 96.101(2)^\circ$, $U = 2326.0(9)$ Å³, $Z = 4$, $D_c = 1.255$ g cm⁻³, space group $P2_1/n$, Mo-K α radiation ($\lambda = 0.71069$ Å), $\mu(\text{Mo-K}\alpha) = 0.90$ cm⁻¹, $F(000) = 936$. Three-dimensional, room temperature X-ray data were collected in the range $3.5 < 2\theta < 45^\circ$ on a Siemens P4 diffractometer by the omega scan method. Of the 4186 reflections measured, all of which were corrected for Lorentz and polarisation effects (but not for absorption), 2250 independent

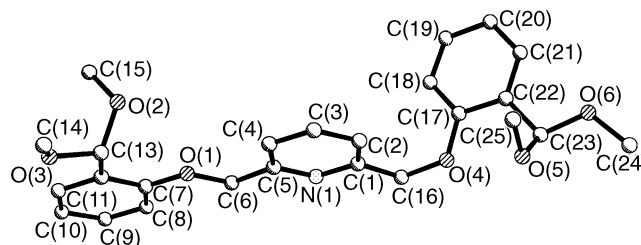


Fig. 1 X-Ray crystal structure of **2**

reflections exceeded the significance level $|F|/\sigma(|F|) > 4.0$. The structure was solved by direct methods and refined by full matrix least squares on F^2 . Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final $R = 0.0571$ ($wR_2 = 0.1700$), for all 3024 data, 289 parameters, mean and maximum δ/σ 0.000, 0.000, with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density -0.312 and 0.390 e Å⁻³. A weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0895P)^2 + 1.1610P]$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXL93⁵ as implemented on the Viglen 486dx computer.

The structure of **2** may be compared with that of the dialcohol, 2,6-bis{[2-(hydroxymethyl)phenoxy]methyl}pyridine (**3**) (Fig. 2), prepared by reduction of **1** using NaBH_4 .⁵ The dialcohol is isolated as the monohydrate $\mathbf{3} \cdot \text{H}_2\text{O}$, and the water molecule helps augment three dimensional molecular aggregation, bridging adjacent molecules of **3** by hydrogen bonding to a pyridine nitrogen atom from one molecule and to an alcoholic oxygen atom from an adjacent molecule.

Crystal Data for 3. H_2O .— $\text{C}_{21}\text{H}_{23}\text{NO}_5$, $M_r = 369.42$, pale yellow prismatic crystals from acetonitrile, crystal dimensions $0.25 \times 0.85 \times 0.08$ mm, triclinic, $a = 11.222(4)$, $b = 11.308(4)$, $c = 7.588(9)$ Å, $\alpha = 81.277(12)^\circ$, $\beta = 105.718(20)^\circ$, $\gamma = 87.139(6)^\circ$, $U = 912.0(11)$ Å³, $Z = 2$, $D_c = 1.350$ g cm⁻³, space group $P1$ (C_1^1 , no. 2), Mo-K α radiation ($\lambda = 0.71069$ Å), $\mu(\text{Mo-K}\alpha) = 0.90$ cm⁻¹, $F(000) = 391.95$. The experimental data were collected at room temperature in the range $6.5 < 2\theta < 50.0^\circ$ on a Stoe Stadi 2 diffractometer by the omega scan method (h from -15 to 15 , k from -15 to 15 , l from 0 to 8). The 1575 independent reflections (of 3187 measured) for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects but not for absorption. The structure was solved by direct methods. Hydrogen atoms were detected and

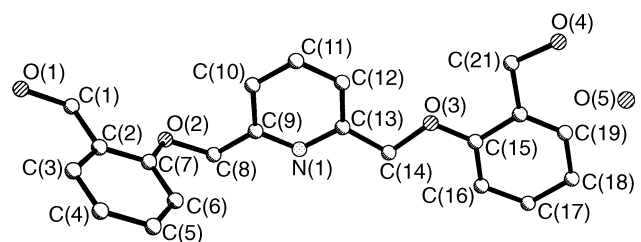


Fig. 2 X-Ray crystal structure of **3**

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placed in calculated positions and refined in riding mode with isotropic thermal vibrational parameters related to those of the supporting atoms. One of the alcoholic H atoms was found to be disordered between sites with necessarily equal population. These hydrogens were constrained with an O—H distance of 1.00 Å and refined in riding mode. Refinement by block cascade least-squares methods converted to a final R of 0.0516 ($R_w = 0.0595$) for 244 parameters, with allowance for thermal anisotropy of all non-hydrogen atoms. A weighting scheme $w^{-1} = [\sigma^2(F) + 0.0035 F^2]$ was used in the final stages of refinement. The maximum value of δ/σ in the final cycle was 0.009 (mean value 0.001). The final difference electron density map showed maximum and minimum of 0.194 and $-0.221 \text{ e \AA}^{-3}$. Complex scattering factors were taken from the program package SHELXTL⁶ as implemented on the Data General DG30 computer.

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Techniques used: X-ray diffraction

References: 7

Figures: 3

Tables 1 and 3: Atomic coordinates and equivalent isotropic displacement parameters for **2** and **3** respectively

Tables 2 and 4: Bond lengths (Å) and bond angles (°) for **2** and **3** respectively

Tables 5–8: Anisotropic displacement parameters, hydrogen coordinates and isotropic parameters

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References cited in this synopsis

- 1 H. Adams, N. A. Bailey, R. Bastida, D. E. Fenton, Y.-S. Ho and P. D. Hempstead, *J. Chem. Res.*, 1992, (S) 190; (M) 1501.
- 2 H. Adams, C. O. Rodriguez de Barbarin, D. E. Fenton, Y.-S. Ho and G. J. Humber, *Inorg. Chim. Acta*, 1995, **232**, 227.
- 3 B. A. Najera, unpublished results, 1996
- 5 G. M. Sheldrick, SHELXL93 Program for crystal structure refinement, University of Gottingen, Germany, 1993.
- 6 G. M. Sheldrick, SHELXTL, An integrated system for solving, refining and displaying crystal structures from diffraction data (Revision 5.1), University of Gottingen, Germany 1985.
- 7 W. Bell, P. I. Coupar, G. Ferguson and C. Glidewell, *Acta Crystallogr., Sect. C*, 1996, **52**, 2520.