

## Ligands for Metal Ion Detection - Crystal Structure of a Fluorophore Precursor

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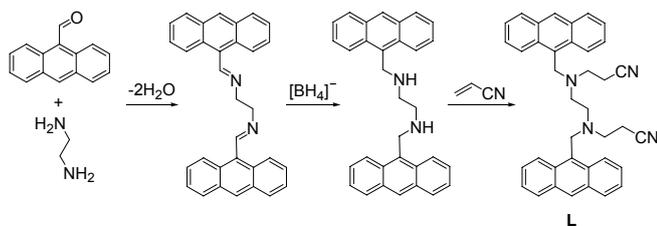
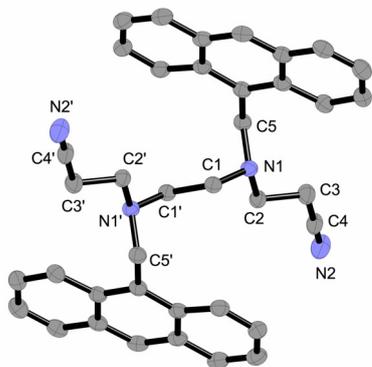
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As part of a programme of chemical synthesis concerned with the preparation of multidentate ligands functionalised so as possibly to be of use in detection of metals by fluorescence measurements,<sup>1</sup> we have prepared the ligand **L** (Scheme 1) by a method involving the initial reductive alkylation of ethane-1,2-diamine by anthracene-9-aldehyde,<sup>2</sup> then reaction of the product with acrylonitrile. We anticipate that this ligand **L** (Scheme 1) should provide a species in which luminescence would be quenched by electron transfer from the amino centres and thus would appear when these centres are involved in metal ion coordination.

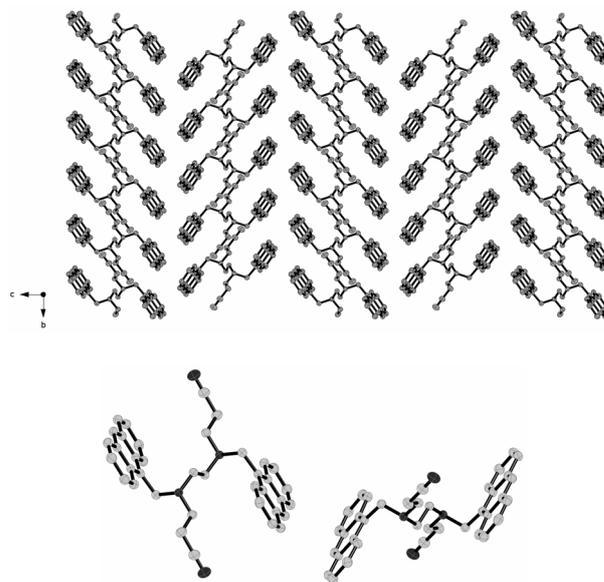
To establish in detail the structure of **L**, we have performed an X-ray structure determination after recrystallising the ligand from dichloromethane. The asymmetric unit of the lattice of the unsolvated compound is comprised of one half of the centrosymmetric molecule, and although the amine-N centres are somewhat flattened, they are pyramidal, so that two diastereo-

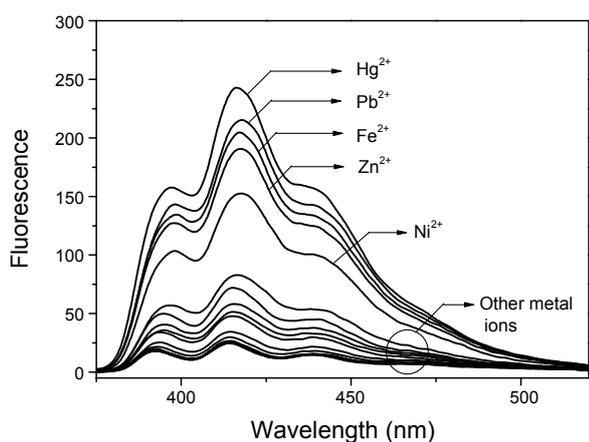
**Scheme 1.** The synthesis of ligand **L****Figure 1.** The *R,S* isomer of **L** found in its crystal lattice, showing partial atom numbering. Symmetry code: ' = 1-x, -y, -z.

mers are possible but it is the *R,S* (meso) form which is seen (Figure 1). A view of the lattice down *a* (Figure 2) shows the formation of layers bordered by the anthryl groups, which appear to link the layers through rather remote edge-to-face aromatic interactions. Weak aromatic-CH $\cdots$ N-nitrile interactions (N2 $\cdots$ H 2.84 and 2.87 Å) may serve to link adjacent molecules so as to form ribbons directed along the *a* axis.

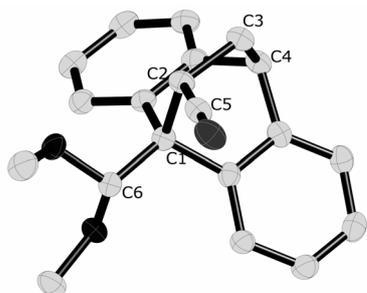
While it might be expected that such a heavily *N*-substituted 1,2-ethanediamine derivative as **L** might be a relatively poor ligand, the fluorescence spectrum of the ligand, even in rather dilute solution, is sensitive to the addition of metal ions such as Hg(II), Pb(II), Fe(II), Zn(II) and Ni(II) (Figure 3). Since the effect is one of fluorescence enhancement, this consistent with the metal ions inhibiting reductive quenching of the excited state by the lone pair electrons on N.

In an initial attempt to conduct the synthesis of **L** under refluxing conditions and to reduce the product, the reaction appeared to fail and the only material isolated in bulk proved to be anthraquinone. However, careful chromatography showed it to be accompanied by a small amount (40 mg isolated after starting from 10 g of anthracene-9-aldehyde) of a colourless cry-

**Figure 2.** (Upper) A view of the lattice of **L** down *a*; (Lower) An edge to face array of anthryl groups.



**Figure 3.** Fluorescence changes of **L** (20  $\mu\text{M}$ ) upon addition of various metal ions such as  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cs}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Rb}^+$ ,  $\text{Sr}^{2+}$  (as perchlorates,  $\times 100$  molar amounts of each) in  $\text{CHCl}_3/\text{CH}_3\text{CN}$  (50:50, v/v) with excitation at 368 nm.



**Figure 4.** One of the two enantiomers of the adduct **A** present in its crystal lattice. Partial crystallographic atom numbering is shown.

stalline material which was again identified by X-ray crystallography as the Diels-Alder adduct of acrylonitrile with the dimethyl acetal of the aldehyde, 9-(1',1'-dimethoxymethyl)-9,10-dihydro-9,10-ethanoanthracene-12-carbonitrile, **A** (Figure 4). Given the low yield of this material, it is not possible to be certain that it was unaccompanied by other isomers but the structure is that of a single regioisomer where the cyano substituent is close to the acetal unit. This « ortho » isomer in fact appears to be the preferred regioisomer in most instances of Diels-Alder reactions of 9-substituted anthracenes.<sup>3</sup> The asymmetric unit in **A** comprises one molecule, which has the same overall geometry as 9-((2'-methoxyethoxy)methoxy)-9,10-dihydro-9,10-ethanoanthracene-12-carbonitrile, in which the acetal group is replaced by an  $-\text{O}-\text{CH}_2-\text{O}-(\text{CH}_2)_2-\text{O}-\text{CH}_3$  chain.<sup>4</sup> The dihedral angle between the two aromatic rings here is  $124.73(9)^\circ$ , very close to that of  $124.9^\circ$  in the other compound. The two  $-\text{O}-\text{CH}_3$  substituents at C6 (crystallographic numbering) are located so as to be as far as possible from the cyano group, and the C6-H bond is nearly parallel to the carbonitrile group. Both enantiomers of **A** are present in the lattice, with homochiral contacts being mediated by  $\text{C3H}\cdots\text{N}$  (nitrile) interactions and heterochiral contacts by  $\text{CH}_3\cdots\pi$  interactions. Since methanol was involved as a co-solvent at least in all steps of the unsuccessful attempt to obtain **L**, it is unclear whether acetal formation pre-

ceded or followed the Diels-Alder adduct formation, although since the successful synthesis involved initial imine formation in methanol, it is perhaps more probable that it followed.

## Experimental

**Synthesis of 3,6-di(9-anthrylmethyl)-3,6-diazoctane-1,8-dinitrile, L.** Ethane-1,2-diamine (1.4 g) in methanol (10 mL) was added to a solution of anthracene-9-carbaldehyde (9.5 g) in DMF-methanol (120 mL; 1:5, v/v) and the mixture heated at  $90^\circ\text{C}$  for 48 h. The yellow precipitate which formed on cooling was collected, washed with methanol and dried in vacuum. Yield, 7.6 g. The crude product was dissolved in dichloromethane-methanol (200 mL; 2:1, v/v) and  $\text{NaBH}_4$  (6.0 g) added before heating at  $50^\circ\text{C}$  for 12 h. The solvent was removed under reduced pressure and the residue dispersed in water (200 mL) by stirring for 10 min. The insoluble material was washed with water and dried under vacuum. Yield, 7.3 g. This was used for the next reaction without purification. Acrylonitrile (20.0 g) and acetic acid (2.0 g) were added to the crude amine (4.0 g) and the mixture heated at  $60^\circ\text{C}$  for 24 h. The excess acrylonitrile was removed under reduced pressure and the residual oil purified by flash chromatography on alumina using dichloromethane as eluent. The eluate was evaporated down to give yellow powder. Yield, 2.6 g. Crystals suitable for a structure determination were obtained by slow evaporation of a dichloromethane solution of the compound. Anal. calc. for  $\text{C}_{38}\text{H}_{34}\text{N}_4$ : C, 83.48; H, 6.27; N, 10.25. Found: C, 83.37; H, 6.33; N, 10.20%.  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.42 (s, 2H, anthracene-H), 7.26 (m, 4H, anthracene-H), 8.01 (m, 4H, anthracene-H), 7.48 (m, 8H, anthracene-H), 4.39 (s, 4H,  $\text{NCH}_2\text{Ar}$ ), 2.63 (t, 4H,  $J = 6.9$ ,  $\text{NCH}_2\text{CH}_2\text{CN}$ ), 2.53 (s, 4H,  $\text{CNCH}_2-$ ), 1.96 (t, 4H,  $J = 6.9$ ,  $\text{NCH}_2\text{CH}_2\text{N}$ ).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  126.38, 126.30, 77.84, 77.66, 77.59, 77.34, 77.02, 76.94, 51.93, 51.87, 51.42, 51.33, 50.26, 50.21, 30.64, 30.56, 18.58, 16.50. IR (KBr disc,  $\text{cm}^{-1}$ ): 3050 (aromatic C-H), 2957, 2858 (aliphatic C-H), 2246 ( $-\text{C}\equiv\text{N}$ ).

**Crystallography.** Crystallographic data were collected at 100(2) K on a Nonius Kappa-CCD area-detector diffractometer<sup>5</sup> and processed with HKL2000.<sup>6</sup> No absorption correction was done. The structures were solved by direct methods and refined by full-matrix least-squares on  $F^2$  with SHELXTL.<sup>7</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at calculated positions and treated as riding atoms. In the absence of a suitable anomalous scatterer, the Friedel pairs have been merged for **A**.

**Crystal data for L:**  $\text{C}_{38}\text{H}_{34}\text{N}_4$ ,  $M = 546.69$ , monoclinic, space group  $P2_1/n$ ,  $a = 10.6885(8)$ ,  $b = 5.5706(5)$ ,  $c = 23.797(2)$  Å,  $\beta = 93.849(6)^\circ$ ,  $V = 1413.7(2)$  Å<sup>3</sup>,  $Z = 2$ . Refinement of 190 parameters on 2682 independent reflections out of 44394 measured reflections ( $R_{\text{int}} = 0.024$ ) led to  $R_1 = 0.040$ ,  $wR_2 = 0.103$ ,  $S = 1.020$ ,  $\Delta\rho_{\text{min}} = -0.18$ ,  $\Delta\rho_{\text{max}} = 0.15$  e Å<sup>-3</sup>.

**Crystal data for A:**  $\text{C}_{20}\text{H}_{19}\text{NO}_2$ ,  $M = 305.36$ , orthorhombic, space group  $P2_12_12_1$ ,  $a = 7.8698(3)$ ,  $b = 11.0886(7)$ ,  $c = 17.8678(12)$  Å,  $V = 1559.24(16)$  Å<sup>3</sup>,  $Z = 4$ . Refinement of 211 parameters on 1715 independent reflections out of 23740 measured reflections ( $R_{\text{int}} = 0.021$ ) led to  $R_1 = 0.039$ ,  $wR_2 = 0.103$ ,  $S = 1.034$ ,  $\Delta\rho_{\text{min}} = -0.18$ ,  $\Delta\rho_{\text{max}} = 0.17$  e Å<sup>-3</sup>.

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