Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

N,*N*,*N*′,*N*′-Tetrakis(2-pyridylmethyl)-1,2-diaminoethane: a multidentate ligand

Takashi Fujihara,* Miki Saito and Akira Nagasawa

Department of Chemistry, Faculty of Science, Saitama University, Shimo-Okubo 255, Sakura-ku, Saitama 338-8570, Japan

Correspondence e-mail: fuji@chem.saitama-u.ac.jp

Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.003 Å
R factor = 0.054
wR factor = 0.142
Data-to-parameter ratio = 15.1

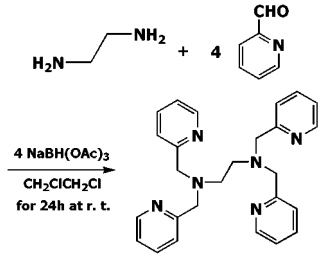
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 14 January 2004
Accepted 16 January 2004
Online 23 January 2004

The reaction of 1,2-diaminoethane and 2-pyridinecarboxyaldehyde in the presence of a reducing agent, sodium triacetoxyborohydride, leads to the title compound, $C_{26}H_{28}N_6$. The molecule has a centre of symmetry.

Comment

The title compound, (I), reveals a wide variety of coordination modes in binding to metal ions, having six N donor atoms, and there are many studies of metal complexes with (I). This compound acts not only as a hexadentate ligand, but also as a pentadentate or a bridging ligand, forming a dinuclear complex in some cases. One of the previous synthetic methods for producing (I) was based on the reaction of 2-picolyl chloride hydrochloride and ethylenediamine, although the yield was not very high. Another synthetic route was an alkylation of ethylenediamine with 2-(chloromethyl)-pyridinium chloride in the presence of hexadecyltrimethylammonium chloride as a phase-transfer catalyst, and this gave the corresponding tetrakis(2-pyridylmethyl)alkanediamines in good yields (Sato *et al.*, 1992; Tamura *et al.*, 2000). This report describes a new synthetic method *via* a reductive amination reaction, and the crystal structure of the product, *viz*. the title compound, (I), is presented.



(I)

As depicted in the Scheme, compound (I) can be obtained from the reductive amination of 2-pyridinecarboxyaldehyde, in 1,2-dichloroethane as a solvent, with sodium triacetoxyborohydride, which is used as a general reducing agent for the reductive amination of aldehydes and ketones (Abdel-Magid *et al.*, 1996). The product was easily purified by chromatography on a short silica-gel column and subsequent recrystallization from *n*-hexane–ethyl acetate. The yield of (I) by the present method (46%) is comparable with that of the reported method using a phase-transfer catalyst (68%). The present method would be convenient for preparing *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)-α,ω-alkanediamine.

The structure of (I), with the atom-numbering scheme, is shown in Fig. 1. This is the first X-ray crystallographic study of the unprotonated form of (I). The ring angles at N in the

pyridine rings are significantly smaller [117.41 (15) and 117.54 (16) at N2 and N3, respectively] than those of the protonated form (*ca* 123°; Gunatilleke & Norman, 2003). Other structural parameters of (I) are comparable with the values reported for related compounds (Mandel & Douglas, 1989).

Experimental

To 1,2-dichloroethane (15 ml) in a flask were added 1,2-diaminoethane (0.3 g, 4.0 mmol) and 2-pyridinecarboxyaldehyde (2.1 g, 19 mmol), and the mixture was stirred for 30 min at room temperature (293 K) under an argon atmosphere. Small amounts of sodium triacetoxyborohydride (3.5 g, 17 mmol) and CH_2ClCH_2Cl (10 ml) were added and the solution was stirred for 24 h at room temperature under an argon atmosphere, yielding a yellow solution. After neutralization with saturated aqueous $NaHCO_3$ (25 ml) to give a weakly alkaline solution, the product was extracted with $CHCl_3$ (20 ml), which had been dried by adding anhydrous Na_2SO_4 (6 g). The crude product was purified by silica-gel column chromatography with toluene–ethanol mixed eluent (20:1 *v*/*v*). A pale-yellow oily residue containing toluene was obtained by evaporation of the solvent under reduced pressure, and this residue was subjected to successive drying *in vacuo*. The resulting crystalline solid was recrystallized from *n*-hexane–ethyl acetate and dried *in vacuo* in a desiccator. Colourless crystals of (I) were obtained in 46% yield [m.p. 383.65–384.15 K; literature value (Anderegg & Wenk, 1967): m.p. 383.15–384.65 K]. Spectroscopic analysis: ^{1}H NMR ($CDCl_3$, TMS_{int}, δ, p.p.m.): 8.48 (4*H*, *d*, ^1J = 5.0 Hz, ^2J = 1.8 Hz), 7.57 (4*H*, *t*, ^1J = 7.7 Hz, ^2J = 1.8 Hz), 7.45 (4*H*, *d*, *J* = 8.1 Hz), 7.11 (4*H*, *t*, ^1J = 7.4 Hz, ^2J = 1.3 Hz), 3.78 (8*H*, *s*), 2.76 (4*H*, *s*); FAB–MS (NBA): *m*/*z* = 425 ($[M + H]^+$, 100%).

Crystal data

$C_{26}H_{28}N_6$
M_r = 424.54
Triclinic, $P\overline{1}$
a = 6.228 (1) Å
b = 9.482 (2) Å
c = 10.760 (2) Å
α = 77.66 (3)°
β = 87.74 (3)°
γ = 74.47 (3)°
V = 598.0 (2) Å^3
Z = 1
D_x = 1.179 Mg m^{-3}
Mo *K*α radiation
Cell parameters from 954 reflections
θ = 2.7–22.9°
μ = 0.07 mm^{-1}
T = 298 (2) K
Prism, colourless
0.48 × 0.45 × 0.35 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.966, T_{max} = 0.977
4392 measured reflections
2824 independent reflections
1800 reflections with $I > 2\sigma(I)$
R_{int} = 0.018
θ_{max} = 27.9°
h = −8 → 8
k = −12 → 10
l = −14 → 13

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.142
S = 1.02
2824 reflections
187 parameters
Only coordinates of H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0689P)^2 + 0.0224P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.12 e Å^{-3}
$\Delta\rho_{min}$ = −0.12 e Å^{-3}

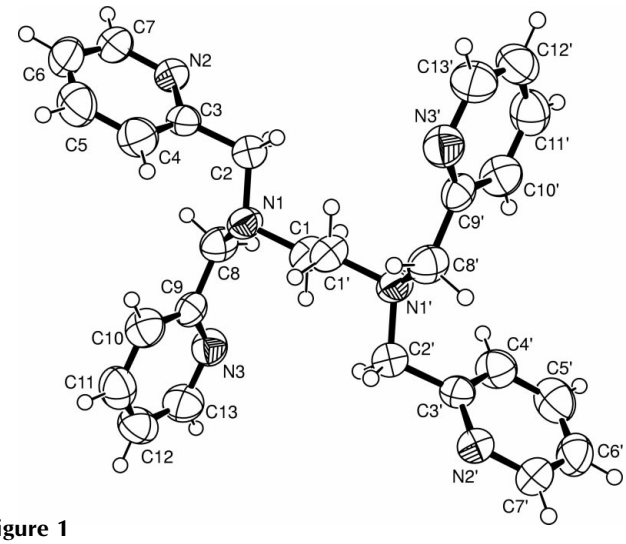


Figure 1
The molecular structure of (I), with 50% probability displacement ellipsoids and the atom-numbering scheme. Atoms labelled with a prime are at symmetry position (−*x*, 1 − *y*, 1 − *z*).

Table 1
Selected geometric parameters (Å, °).

N1—C8	1.459 (2)	C9—C10	1.376 (2)
N1—C1	1.464 (2)	C9—C8	1.499 (2)
N1—C2	1.467 (2)	C1—C1^{i}	1.507 (3)
N2—C3	1.330 (2)	C4—C5	1.384 (3)
N2—C7	1.337 (2)	C7—C6	1.366 (3)
N3—C9	1.331 (2)	C13—C12	1.361 (3)
N3—C13	1.337 (2)	C10—C11	1.368 (3)
C3—C4	1.379 (2)	C5—C6	1.361 (3)
C3—C2	1.504 (2)	C11—C12	1.360 (3)
C3—N2—C7	117.41 (15)	C9—N3—C13	117.54 (16)
N3—C9—C8—N1	−130.8 (1)	N2—C3—C2—N1	−131.5 (2)

Symmetry code: (i) −*x*, 1 − *y*, 1 − *z*.

All H atoms were located in difference Fourier maps and refined with U_{iso}(H) = 1.2U_{eq}(parent atom). The C—H bond lengths are in the range 0.92 (2)–1.03 (2) Å.

Data collection: *SMART-W2K/NT* (Bruker, 2003); cell refinement: *SMART-W2K/NT*; data reduction: *SAINT-W2K/NT* (Bruker, 2003); program(s) used to solve structure: *SHELXTL-NT* (Bruker, 2003); program(s) used to refine structure: *SHELXTL-NT*; molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL-NT*.

References

Abdel-Magid, A. F., Carson, K. G., Harris, B. D., Maryaanoff, C. A. & Shah, R. D. (1996). *J. Org. Chem.* **61**, 3849–3862.
Anderegg, G. & Wenk, F. (1967). *Helv. Chim. Acta*, **50**, 2330–2332.
Bruker (2003). *SAINT-W2K/NT* (Version 5.0), *SMART-W2K/NT* (Version 5.6) and *SHELXTL-NT* (Version 6.14). Bruker AXS, Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Gunatilleke, S. S. & Norman, R. E. (2003). *Acta Cryst.* E**59**, o269–o271.
Mandel, J. B. & Douglas, B. E. (1989). *Inorg. Chim. Acta*, **155**, 55–69.
Sato, M., Mori, Y. & Iida, T. (1992). *Synthesis*, **6**, 539–540.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Tamura, M., Urano, Y., Kikuchi, K., Higuchi, T., Hirobe, M. & Nagano, T. (2000). *J. Organomet. Chem.* **611**, 586–592.