Hay, B. P., Rustad, J. R., Zipperer, J. P. & Wester, D. W. (1995). *J. Mol. Struct.* **337**, 39–47.

Kamitori, S., Hirotsu, K. & Higuchi, T. (1986). *J. Chem. Soc. Chem. Commun.* pp. 690–691.

Karabatsos, G. J., Vane, F. M., Taller, R. A. & Hsi, N. (1964). *J. Am. Chem. Soc.* **86**, 3351–3357.

Michalides, A., Henschel, D., Blaschette, A. & Jones, P. G. (1995). *Z. Naturforsch. Teil B*, **50**, 1018–1024.

Palenik, G. J., Rendle, D. F. & Carter, W. S. (1974). *Acta Cryst.* **B30**, 2390–2395.

Raithby, P. R., Shields, G. P. & Allen, F. H. (1997). *Acta Cryst.* **B53**, 241–251.

Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Siemens (1994). *XP. Molecular Graphics Program.* Version 5.03. Siemens Analytical X-ray Instruments, Madison, Wisconsin, USA.

Simonov, Yu. A., Fonari, M. S., Dvorkin, A. A., Malinovski, T. I., Lipkowski, J. & Ganin, E. V. (1993). *J. Incl. Phenom. Mol. Recognit. Chem.* **16**, 315–327.

Stoe & Cie (1992a). *DIF4. Diffractometer Control Program.* Stoe & Cie, Darmstadt, Germany.

Stoe & Cie (1992b). *REDU4. Data Reduction Program.* Stoe & Cie, Darmstadt, Germany.

Wijaya, K., Moers, O., Jones, P. G. & Blaschette, A. (1998). *Acta Cryst.* **C54**, 818–820.

Acta Cryst. (1999). C**55**, 1545–1547

N,N'-Bis(2-tosylaminobenzylidene)-1,3-propanediamine†

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Abstract

The conformation of the title molecule, $C_{31}H_{32}N_4O_4S_2$, in the solid state is strongly influenced by intramolecular hydrogen-bond interactions (N—H···N), which probably minimize the steric hindrance of the tosyl groups. The molecule is not planar and with long distances between aminic N atoms [7.724 (3) Å], a major change in conformation will be required for it to act as a tetradentate ligand *via* its four N atoms.

† Alternative name: N,N'-{1,3-propanediylbis[2-(nitrilomethylidyne)-*p*-phenylene]}bis(toluene-4-sulfonamide).

Comment

In recent years, it has been recognized that Schiff base ligands derived from 1,3-diaminopropan-2-ol and salicylaldehyde, pyridine, pyrrole or imidazole (Butcher *et al.*, 1986*a,b*; Borer & Sinn, 1988; Mazurek *et al.*, 1985; Nishida & Kida, 1986) play an important role in the synthesis of model complexes for copper-containing metalloproteins. We are interested in obtaining secondary amides, in particular dianionic N_4 ligands like the title compound, H_2L, derived from the condensation of 1,3-propanediamine and 2-tosylaminobenzaldehyde. These could act as polydentate ligands through their N and O atoms. The molecular structure of the mononuclear complex [N,N'-bis(2-aminobenzylidene)-1,3-propaneamine]nickel(II), which contains a similar ligand without tosyl groups, has been reported previously (Bailey & McKenzie, 1974).
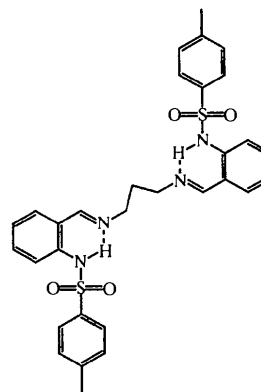
H_2L

To our knowledge, no X-ray crystal structure of either the uncoordinated or the coordinated H_2L ligand has been reported previously. Therefore, we have determined the crystal structure of H_2L so that subsequent changes upon the coordinated form may be investigated.

In this molecule, the N2=C14 and N3=C18 distances of 1.266 (3) and 1.271 (3) Å, respectively, are consistent with C=N double bonding. Both bond angles of 117.8 (2)° around the N2 and N3 atoms confirm their sp^2 character.

The disposition adopted by the 2-tosylaminobenzylidene groups in the solid state is conditioned by two strong N—H···N interactions. The distance between the N atoms are 2.666 (2) and 2.674 (3) Å for N1···N2 and N3···N4, respectively (H1A···N2 = 2.05 and H4A···N3 = 2.11 Å). As expected, these intramolecular hydrogen-bond interactions strongly influence the conformation of the molecule, forming N1—C8—C13—C14—N2—H1A and N4—C24—C19—C18—N3—H4A six-membered rings, with almost perfect plane deviations of 0.0936 and 0.1119 Å, respectively. There is also an intermolecular C—H···O interaction with C12···O2ⁱ = 3.362 (3), H12A···O2ⁱ = 2.57 Å and

$C12—H12\cdots O2^i = 143°$ [symmetry code: (i) $-1 + x$, y, z].

As the bond angles C25—S2—N4 and C5—S1—N1 are quite similar [105.70 (9) and 105.95 (9)°, respectively], both tosyl groups adopt a similar conformation in the molecule. This is probably to minimize their steric hindrance and so they appear in opposite positions.

The two tosylbenzyl rings form an angle of 82.5 (1)° with respect to one another and the aromatic C8–C13 and C19–C24 ring planes form an angle of 81.0 (1)°. The values of the torsion angles C18—N3—C17—C16 [128.8 (3)°] and C14—N2—C15—C16 [−100.4 (3)°] also indicate that the molecule is not planar. This, in conjunction with the opposite spatial disposition of the tosyl groups, results in a long distance between aminic N atoms; $N1\cdots N4 = 7.724 (3)$ Å.

Clearly, this conformation is not suitable for direct coordination to a metal ion in the usual arrangement for a tetradentate ligand, by use of its four N atoms. Therefore, significant rearrangement of the molecule must occur for a possible mononuclear complexation.
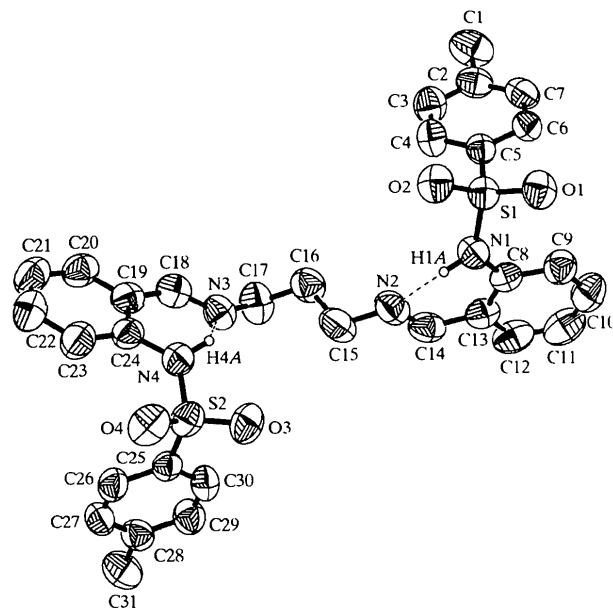

Fig. 1. The molecular structure of H_2L showing 50% probability displacement ellipsoids. H atoms (except those involved in the intramolecular hydrogen bonds) have been omitted for clarity.

Experimental

The title Schiff base was synthesized by condensation of 2-tosylaminobenzaldehyde (Chernova et al., 1971) and 1,3-propanediamine. To a solution of 2-tosylaminobenzaldehyde (5 g, 18.2 mmol) in chloroform (150 ml) was added 1,3-propanediamine (0.76 ml, 9.1 mmol). The mixture was heated (338 K) and stirred for 4 h. The resultant yellow solution was filtered and then concentrated. Yellow crystals formed after

two days of slow evaporation at room temperature [yield 4.3 g (80%), m.p. 418 K]. Elemental analysis for $C_{31}H_{32}N_4O_4S_2$ (%), calculated (found): C 65.6 (65.4), H 4.8 (4.7), N 9.0 (9.2), S 10.3 (9.9). MS (H_3L^+), calculated (found): 588.8 (589.2, 100%).

Crystal data

$C_{31}H_{32}N_4O_4S_2$	Mo $K\alpha$ radiation
$M_r = 588.73$	$\lambda = 0.71073$ Å
Triclinic	Cell parameters from 57
$P\bar{1}$	reflections
$a = 8.866$ Å	$\theta = 3–26°$
$b = 12.9431 (2)$ Å	$\mu = 0.218$ mm^{-1}
$c = 13.9107 (2)$ Å	$T = 298 (2)$ K
$\alpha = 103.112 (1)°$	Plate
$\beta = 102.296 (1)°$	$0.55 \times 0.15 \times 0.05$ mm
$\gamma = 93.030 (1)°$	Yellow
$V = 1510.35 (3)$ Å^3	
$Z = 2$	
$D_x = 1.295$ Mg m^{-3}	
D_m not measured	

Data collection

Siemens CCD diffractometer	5027 reflections with
ω scans	$I > 2\sigma(I)$
Absorption correction:	$R_{int} = 0.017$
empirical (SADABS;	$\theta_{max} = 28.29°$
Sheldrick, 1996)	$h = -11 \rightarrow 11$
$T_{min} = 0.811$, $T_{max} = 1.000$	$k = -17 \rightarrow 17$
13 518 measured reflections	$l = -18 \rightarrow 18$
7404 independent reflections	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.049$	$\Delta\rho_{max} = 0.368$ e Å^{-3}
$wR(F^2) = 0.154$	$\Delta\rho_{min} = -0.249$ e Å^{-3}
$S = 1.017$	Extinction correction: none
7404 reflections	Scattering factors from
372 parameters	International Tables for
H atoms constrained	Crystallography (Vol. C)
$w = 1/[\sigma^2(F_o^2) + (0.0756P)^2$	
$+ 0.2690P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. Selected geometric parameters (Å, °)

N2—C14	1.266 (3)	N3—C18	1.271 (3)
N1—S1—C5	105.95 (9)	C14—N2—C15	117.8 (2)
N4—S2—C25	105.70 (9)	C18—N3—C17	117.8 (2)
C14—N2—C15—C16	−100.4 (3)	C18—N3—C17—C16	128.8 (3)

Data collection: SMART (Siemens, 1995). Cell refinement: SMART. Data reduction: SAINT (Siemens, 1995). Program(s) used to solve structure: SHELXL93 (Sheldrick, 1993). Program(s) used to refine structure: SHELXL93. Molecular graphics: SHELXTL (Sheldrick, 1997). Software used to prepare material for publication: SHELXL93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1538). Services for accessing these data are described at the back of the journal.

References

Bailey, N. A., McKenzie, E. D. & Worthington, J. M. (1974). *J. Chem. Soc. Dalton Trans.* pp. 763–767.

Borer, L. L. & Sinn, E. (1988). *Inorg. Chim. Acta,* **142,** 197–199.

Butcher, R. J., Diven, G., Mockler, G. M. & Sinn, E. (1986a). *Inorg. Chim. Acta,* **111,** L55–56.

Butcher, R. J., Diven, G., Mockler, G. M. & Sinn, E. (1986b). *Inorg. Chim. Acta,* **123,** L17–19.

Chernova, N. I., Ryabokobbyylko, Y. S., Brudz, V. G. & Boltin, B. M. (1971). *Zh. Neorg. Khim.* p. 1680.

Mazurek, W., Kennedy, B. J., Murray, K. S., O'Connor, M. J., Rodgers, J. R., Snow, M. R., Wedd, A. G. & Zwack, P. R. (1985). *Inorg. Chem.* **24,** 3258–3264.

Nishida, Y. & Kida, S. (1986). *J. Chem. Soc. Dalton Trans.* pp. 2633–2640.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Sheldrick, G. M. (1996). *SADABS. Program for Empirical Absorption Correction of Area Detector Data.* University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXTL. An Integrated System for Solving and Refining Crystal Structures.* University of Göttingen, Germany.

Siemens (1995). *SMART* and *SAINT. Area Detector Control and Integration Software.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Molecular aggregation in selected crystalline 1:1 complexes of hydrophobic D- and L-amino acids. III.† The L-leucine and L-valine series

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Abstract

The amino acids L-leucine (L-Leu) and L-valine (L-Val) have been cocrystallized with D-aminobutanoic acid (D-Abu), D-2-aminopentanoic acid (D-Nva) and D-methionine (D-Met) to form six complexes, L-Leu:D-Abu, $C_6H_{13}NO_2 \cdot C_4H_9NO_2$, L-Leu:D-Nva, $C_6H_{13}NO_2 \cdot C_5H_{11}-NO_2$, L-Leu:D-Met, $C_6H_{13}NO_2 \cdot C_5H_{11}NO_2S$, L-Val:-D-Abu, $C_5H_{11}NO_2 \cdot C_4H_9NO_2$, L-Val:D-Nva, $C_5H_{11}NO_2 \cdot C_5H_{11}NO_2$ and L-Val:D-Met, $C_5H_{11}NO_2 \cdot C_5H_{11}NO_2S$. A

† Part II: Dalhus & Gorbitz (1999b).

fourth L-Leu complex, with D-Val, $C_6H_{13}NO_2 \cdot C_5H_{11}-NO_2$ has also been studied. The crystals of these amino acid complexes are all divided into distinct hydrophilic and hydrophobic layers. The D- and L-amino acids are all related by pseudo-inversion in the L-Leu complexes and by pseudo-glide planes in the L-Val series. Similarities and differences in the crystal packing and molecular conformations of L-Leu/L-Val, as well as of the partner molecules, are discussed.

Comment

In general, the crystal structures of hydrophobic amino acids fall within the following three categories: (*a*) pure enantiomers, (*b*) racemates and (*c*) 1:1 complexes of two different hydrophobic amino acids with opposite chirality at C^α (there are no known crystal structures incorporating two different hydrophobic amino acids with the same chirality at C^α). Previously we have presented the crystal structures of seven complexes involving L-isoleucine (L-Ile; Dalhus & Görbitz, 1999a) as well as five complexes involving D-norleucine (D-Nle; Dalhus & Görbitz, 1999b), all belonging to category (*c*). In the present paper we focus on L-Leu and L-Val complexes.

Since both L-Leu and L-Val have branched side chains, the complexes L-Leu:D-Abu, **1**, L-Leu:D-Nva, **2**, L-Leu:D-Met, **3**, L-Val:D-Abu, **5**, L-Val:D-Nva, **6**, and L-Val:D-Met, **7**, include one branched and one unbranched amino acid, while in L-Leu:D-Val, **4**, both amino acids are branched. All seven crystal structures are divided into distinct hydrophilic and hydrophobic layers (Figs. 1–7). This is a consequence of the dual character of hydrophobic amino acids: the charged α-amino and α-carboxylate groups engage in hydrogen bonding with each other, while the side chains are involved in van der Waals interactions only.

L-amino acid

L-Val : $R_1 = -CH(CH_3)_2$
L-Leu : $R_1 = -CH_2CH(CH_3)_2$

D-amino acid

D-Abu : $R_2 = -CH_2CH_3$
D-Nva : $R_2 = -CH_2CH_2CH_3$
D-Met : $R_2 = -CH_2CH_2SCH_3$
D-Val : $R_2 = -CH(CH_3)_2$
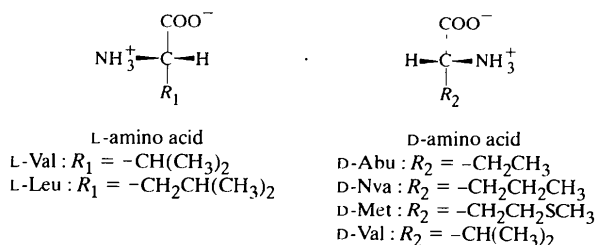
1 = L-Leu:D-Abu
2 = L-Leu:D-Nva
3 = L-Leu:D-Met
4 = L-Leu:D-Val
5 = L-Val:D-Abu
6 = L-Val:D-Nva
7 = L-Val:D-Met

In the four L-Leu complexes **1–4**, the polar parts of the amino acids are related by pseudo inversion in space groups $P2_1$ (**1**, **3** and **4**) and $P1$ (**2**) (Figs. 1–4). The molecular conformation of L-Leu is identical in all four