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## Structure of a Solvated Nickel(II) Complex of (S)-2'-(N-benzylpropyl)aminoacetophenone and (R)-valine Schiff base, C<sub>25</sub>H<sub>29</sub>N<sub>3</sub>NiO<sub>3</sub>·1/2C<sub>4</sub>H<sub>8</sub>O. Conformational Calculation of Diastereomeric Complexes of (R)-valine and (S)-valine

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**Structure of a Solvated Nickel(II) Complex of (*S*)-2'-(*N*-Benzylpropyl)amino-acetophenone and (*R*)-Valine Schiff Base,  $C_{25}H_{29}N_3NiO_3 \cdot \frac{1}{2}C_4H_8O$ . Conformational Calculation of Diastereomeric Complexes of (*R*)-Valine and (*S*)-Valine**

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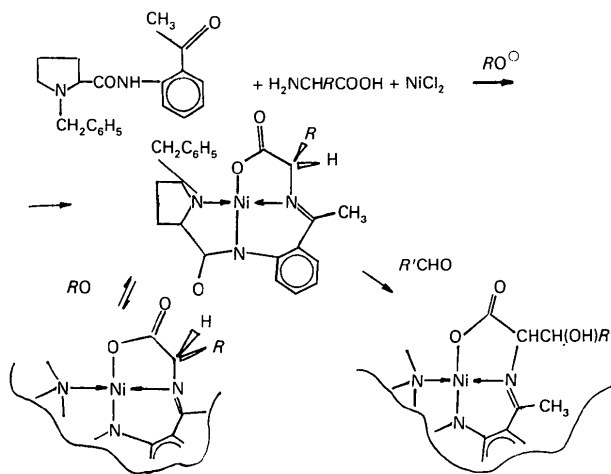
**Abstract.**  $\{(R)\text{-}[N\text{-}(1\text{-}\{2\text{-}[N\text{-}(S)\text{-Benzylpropylamino}]\text{-phenyl}\}\text{ethylidene})\text{valinato}\}\text{nickel(II)-tetrahydrofuran}$  95.26 (1)°,  $V = 2535$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_x =$   
(2/1),  $M_r = 514.3$ , monoclinic,  $P2_1$ ,  $a =$  1.35 Mg m<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu =$   
10.779 (1),  $b = 11.800$  (5),  $c = 20.014$  (2) Å,  $\beta =$  0.796 mm<sup>-1</sup>,  $F(000) = 1088$ , room temperature,  $R$   
 $= 0.055$  for 5284 independent reflections. In the crystal

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there are two independent molecules with markedly different conformations. The calculation of the conformational energy of the (*R*)-valine complex and its (*S*)-valine-containing diastereomer shows that the energy preference of the latter diastereomer is *ca* 2.5 kJ mol<sup>-1</sup>. This preference is in agreement with the equilibrium between diastereomers in solution which is shifted towards the (*S*)-valine complex. The Ni atom has square-planar coordination {Ni—N 1.849 (5), 1.851 (5), 1.961 (5), Ni—O 1.835 (5) Å in molecule *A* [1.866 (5), 1.844 (5), 1.951 (5), 1.850 (5) Å in *B*]}.

**Introduction.** (*S*)-2'-(*N*-Benzylprolyl)aminoacetophenone [(*S*)-BPAAPh] is a reagent used for the asymmetric synthesis of  $\beta$ -hydroxy- $\alpha$ -amino acids and racemization of certain amino acids (a.a.) in the presence of Cu<sup>II</sup> and Ni<sup>II</sup> ions (Belokon', Zeltzer, Ryzhov, Saporovskaya, Bakhmutov & Belikov, 1982; Belokon' *et al.*, 1983, 1984). Ni<sup>II</sup> and Cu<sup>II</sup> complexes of (*S*)-BPAAPh Schiff bases with amino acids are formed as intermediates in both processes according to the following scheme:



Both processes are based on the energy differences between diastereomeric complexes containing (*R*)- and (*S*)-a.a. To develop a new generation of effective chiral reagents whose action is based on a mechanism similar to that of (*S*)-BPAAPh, it is necessary to elucidate the origin of enantioselective effects in the (*S*)-BPAAPh-a.a.-M<sup>2+</sup> complexes. Comparison of the X-ray structures of both diastereomers and conformational calculations on them were expected to facilitate the solution of this problem.

The results of an X-ray study of the (*S*)-BPAAPh-(*R*)-Val-Ni<sup>II</sup> complex (1) and conformational calculations on both molecule (1) and its (*S*)-Val-containing diastereomer (2) are given in the present paper. An X-ray study of compound (2) was carried out earlier (Belokon' *et al.*, 1984).

**Experimental.** Complex (1) was prepared by the method previously described (Belokon' *et al.*, 1984). Crystals were obtained by slow evaporation of the solution in a mixture of tetrahydrofuran (THF) and methanol. Yellow approximately isometric crystals, size ~0.5 mm; the X-ray study has shown these to be the THF solvate of complex (1). Hilger & Watts Y/290 diffractometer, graphite-monochromatized Mo *K* $\alpha$  radiation. Cell constants determined by least-squares treatment of 24 automatically centred reflections.  $\theta$ -2 $\theta$  scan, 7513 reflections measured ( $1 \leq \theta \leq 33^\circ$ , *hkl*, *hkl*), 5284 unique with  $I \geq 2\sigma(I)$ . 2 check reflections, monitored periodically for crystal and instrument stabilities, showed only statistical fluctuations. All diffraction intensities corrected for Lorentz-polarization effects, but not for absorption or extinction. Structure solved by standard heavy-atom method and refinement (on *F*) by block-diagonal least squares in isotropic and then in anisotropic approximation for non-hydrogen atoms with unit weights for all reflections. Identification of the O atom in the THF solvate molecule was impossible due to its high thermal vibrations (Table 1), which account also for the low accuracy of the determination of its geometrical parameters (Table 2). Thus, atom C(3) is disordered over two positions with approximately equal populations. Average  $\Delta/\sigma$  in final refinement cycle 0.05; final difference Fourier synthesis excursions within  $\pm 0.5 e \text{ \AA}^{-3}$ . No attempts were made to locate the H atoms.

The absolute configuration was determined by the Hamilton test with the anomalous-scattering correction for Ni atoms only. Final *R* and *wR* values (unobserved reflections not included) are 0.055, 0.058, and 0.057, 0.059 for the inverted structure. Thus, the probability of a true determination of absolute configuration is greater than 99.5%. The goodness of fit is 4.10. All calculations performed using *INEXTL* programs with an Eclipse S/200 computer (Gerr, Yanovski & Struchkov, 1983). Values of *f*, *f'* and *f''* taken from *International Tables for X-ray Crystallography* (1974).

**Discussion.** Atomic coordinates and temperature parameters are given in Table 1; \* projections of the two crystallographically independent molecules of (1) are shown in Fig. 1; bond lengths and angles are listed in Table 2.

Crystals of the THF solvate (1) contain two symmetrically independent molecules [(1*A*) and (1*B*)] differing in the conformations of the chelate rings and the orientations of the benzyl groups. In conformer

\* Lists of structure factors and anisotropic thermal parameters, and details of the least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42201 (47 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(1A) the benzyl group is turned away from the metal atom, while in (1B) its Ph ring shields an apical position of Ni. In (1), and in the previously studied complexes (*S*)-BPAAPH-a.a.-M<sup>II</sup> (M=Ni, Cu), the Ni<sup>2+</sup> ion has a square-planar coordination formed by the O atom of the ionized carboxyl group and the N atoms of the pyrrolidine ring, the ionized amide group and the aldimine group >C=N-, whereas the apical positions remain vacant. The solvating THF molecule is not involved in coordination to Ni. The N atoms of the pyrrolidine ring in (1A) and (1B) have an *R* configuration.

As stated above, the geometries of (1A) and (1B) differ significantly. In molecule (1B), C(3) is disordered, i.e. two conformations of the proline ring are observed. Comparison of the geometries of molecules (1A) and (1B) and the diastereomeric molecule (2) containing (*S*)-Val shows that the *N*-benzylproline fragment is the most flexible: the Ph ring of this group in (1A) is *anti* while in (1B) and (2) it is *syn* to the Ni atom with respect to the N(1)–C(19) bond [torsion angle  $\tau$  –168.3 (5) in (1A), –51.7 (6) in (1B) and –46.0 (5)° in (2)]. The conformation of the proline heterocycle is

also very flexible: close to a C<sub>8</sub>-envelope in (1A) and (2) and close to a C<sub>7</sub>-envelope in (1B).

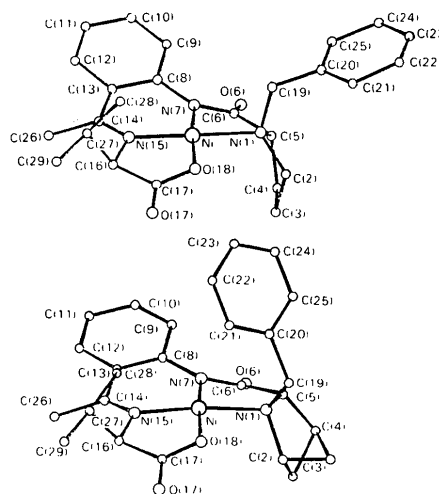


Fig. 1. Geometries of independent molecules (1A) (top) and (1B) (bottom), and numbering of the atoms.

Table 1. Coordinates of non-hydrogen atoms ( $\times 10^4$ , for Ni atoms  $\times 10^5$ ) and their equivalent isotropic temperature factors ( $\text{\AA}^2$ )

$$B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	Molecule (1A)				Molecule (1B)			
	x	y	z	B <sub>eq</sub>	x	y	z	B <sub>eq</sub>
Ni	33721 (7)	9411 (4)	9411 (4)	3.49 (2)	28317 (7)	14823 (8)	53501 (4)	3.07 (2)
N(1)	1595 (4)	–140 (6)	1067 (3)	4.0 (2)	4350 (5)	1728 (4)	4909 (3)	3.7 (2)
C(2)	785 (7)	858 (7)	813 (4)	5.1 (2)	4354 (8)	934 (7)	4310 (4)	5.8 (3)
C(3)†	764 (8)	746 (9)	52 (4)	6.2 (3)	5176 (19)	1581 (21)	3832 (9)	7.6 (6)
					3858 (16)	1725 (16)	3658 (8)	5.7 (5)
C(4)	719 (9)	–549 (9)	–68 (4)	7.2 (3)	4592 (7)	2806 (7)	3881 (4)	5.1 (2)
C(5)	1153 (6)	–1105 (7)	611 (4)	4.3 (2)	4347 (6)	2912 (6)	4617 (4)	3.7 (2)
C(6)	2179 (6)	–1945 (6)	562 (4)	4.2 (2)	3130 (6)	3492 (6)	4722 (3)	3.5 (2)
O(6)	1930 (5)	–2876 (5)	323 (3)	6.5 (2)	2797 (5)	4310 (4)	4399 (3)	4.9 (2)
N(7)	3334 (5)	–1552 (5)	806 (3)	3.4 (1)	2519 (4)	3008 (4)	5230 (3)	3.4 (1)
C(8)	4379 (5)	–2258 (6)	862 (3)	3.3 (2)	1561 (6)	3622 (5)	5503 (3)	3.2 (3)
C(9)	4221 (6)	–3437 (7)	988 (3)	4.3 (2)	1688 (7)	4808 (6)	5535 (4)	4.6 (2)
C(10)	5231 (8)	–4176 (7)	1048 (4)	5.2 (2)	731 (7)	5445 (7)	5781 (5)	5.5 (3)
C(11)	6440 (8)	–3723 (7)	1000 (5)	5.7 (3)	–321 (7)	4923 (7)	6018 (4)	5.2 (2)
C(12)	6627 (7)	–2572 (6)	875 (4)	4.6 (2)	–433 (6)	3729 (6)	5994 (4)	4.4 (2)
C(13)	5572 (5)	–1814 (5)	800 (3)	3.3 (2)	540 (6)	3067 (6)	5737 (3)	3.5 (2)
C(14)	5846 (5)	–630 (6)	715 (3)	3.5 (2)	396 (6)	1825 (6)	5766 (3)	3.5 (2)
N(15)	5050 (4)	161 (5)	838 (3)	3.3 (1)	1329 (4)	1140 (4)	5700 (2)	2.9 (1)
C(16)	5454 (6)	1390 (6)	855 (3)	3.8 (2)	1159 (6)	–99 (6)	5797 (3)	3.6 (2)
C(17)	4268 (7)	2109 (6)	900 (4)	4.7 (2)	2272 (6)	–688 (6)	5537 (3)	3.5 (2)
O(17)	4320 (5)	3128 (4)	833 (3)	6.1 (2)	2281 (5)	–1741 (4)	5464 (3)	4.9 (2)
O(18)	3288 (4)	1546 (5)	1025 (3)	5.5 (2)	3186 (4)	–52 (4)	5391 (2)	4.0 (1)
C(19)	1575 (7)	–363 (3)	1809 (4)	5.2 (2)	5517 (6)	1480 (8)	5360 (3)	4.4 (2)
C(20)	347 (7)	–739 (9)	2042 (4)	5.7 (3)	5519 (6)	2109 (6)	6032 (4)	4.4 (2)
C(21)	–445 (8)	140 (14)	2258 (4)	8.9 (4)	4934 (7)	1637 (10)	6553 (4)	6.2 (3)
C(22)	–1569 (10)	–258 (19)	2546 (5)	14.6 (8)	4980 (8)	2175 (10)	7174 (4)	7.1 (3)
C(23)	–1819 (11)	–1393 (20)	2536 (6)	16.1 (9)	5582 (8)	3189 (9)	7288 (4)	6.5 (3)
C(24)	–1029 (14)	–2236 (16)	2334 (7)	13.6 (7)	6186 (8)	3661 (8)	6768 (5)	6.4 (3)
C(25)	115 (11)	–1893 (12)	2057 (5)	9.0 (4)	6166 (7)	3120 (7)	6143 (4)	5.1 (2)
C(26)	7123 (6)	–345 (6)	471 (4)	4.5 (2)	–901 (5)	1387 (7)	5901 (4)	5.0 (2)
C(27)	6388 (6)	1629 (7)	1469 (3)	4.1 (2)	1103 (7)	–386 (6)	6560 (4)	4.4 (2)
C(28)	5748 (8)	1683 (10)	2134 (4)	6.7 (3)	2337 (7)	–177 (9)	6997 (4)	5.8 (3)
C(29)	7138 (9)	2720 (8)	1369 (5)	6.9 (3)	642 (9)	–1615 (7)	6652 (5)	6.7 (3)
C(1S)‡	899 (16)	4947 (23)	1749 (8)	17.6 (9)				
C(2S)	1395 (17)	5468 (13)	2321 (7)	13.5 (7)				
C(3S)	2570 (16)	4812 (21)	2555 (9)	17.6 (9)				
C(4S)	2332 (16)	3728 (16)	2227 (7)	14.2 (7)				
C(5S)	1672 (20)	4007 (17)	1461 (15)	26 (1)				

† C(3) in molecule (1B) is disordered over two positions, with occupation factor 0.5.

‡ C(1S) to C(5S) are the atoms of the tetrahydrofuran solvate molecule.

The three chelate rings in molecules (1A), (1B) and (2) also differ in their conformations, though less than the groups mentioned above. Thus, the proline chelate ring in (1A) and (2) is a half chair, which is somewhat more flattened in molecule (2). The conformation of this ring in molecule (1B) is close to an envelope. The conformation of the six-membered chelate rings in (1A) and (1B) is close to an N(7),C(14)-boat, while in (2) it is close to an N(7)-sofa with flapping of N(7) by 0.338 (6) Å. Finally, the valine chelate ring in (1A) and (1B) has the conformation of a strongly flattened C(17)-envelope, while in (2) it has a conformation close to a C<sub>α</sub>-envelope with the α-atom displaced by 0.370 (6) Å. It should be noted that, in contrast to the proline residue, the valine groups in (1) and (2) are significantly less conformationally labile, with the orientation of their isopropyl residues changing in the molecules studied only within 10°.

Molecules (1A) and (1B) show a pyramidal distortion of the Ni-atom square-planar coordination: the Ni atom is displaced from the mean plane of the coordinating atoms by 0.026 (1) Å in (1A) and by 0.073 (1) Å in (1B). At the same time the tetrahedral distortion is not significant: the folding of the square formed by N(1), N(7), N(15) and O(18) is 4.3 (3) and 1.4 (3)°, respectively.

In complex (2) no pyramidal distortion of the Ni coordination is observed in contrast to (1), while the tetrahedral distortion is more distinct: folding angle 11.0 (3)°. Moreover, the coordination of N(1) in both diastereomers is somewhat distorted in comparison with the ideal tetrahedral one. Thus, the angle formed between the vector Ni–N(1) and the axis of the N lone-pair orbital with the orientation calculated for ideal tetrahedral hybridization of N(1) is 6.7, 6.1 and 5.8° for 1(A), 1(B) and (2), respectively. Similar angles calculated for N(7) and N(15), assuming *sp*<sup>2</sup> hybridization, are 8.7, 12.9 and 6.1, and 8.8, 11.8 and 8.5°, respectively. Therefore the above-mentioned angular deviation is minimal in complex (2).

The purpose of the conformational calculation for diastereomers (1) and (2) was to compare their conformational energies (*U*<sub>conf</sub>) (which gives a quantitative evaluation of the molecular steric strain), and to elucidate the *U*<sub>conf</sub> dependence on the benzyl-group orientation. The following terms were included in the calculation: *U*<sub>conf</sub> = *U*<sub>b</sub> + *U*<sub>a</sub> + *U*<sub>nb</sub> + *U*<sub>t</sub>. Here the energies of bond stretching (*U*<sub>b</sub>) and bond-angle deformation (*U*<sub>a</sub>) were calculated according to Hook's law, the energy of non-bonded interactions (*U*<sub>nb</sub>) was calculated using the '6-exp' potential, and, for the torsion energy, a potential *U*<sub>t</sub> = *U*<sub>0</sub>/2(1 + cos *nφ*) was used (*U*<sub>0</sub> is a torsion

Table 2. Bond lengths (Å) and bond angles (°) for molecules (1A) and (1B), and for the solvate

	(1A)	(1B)	(1A)	(1B)	(1A)	(1B)		
Ni–N(1)	1.961 (5)	1.951 (5)	N(1)NiN(7)	85.8 (2)	86.9 (2)	C(9)C(10)C(11)	118.3 (7)	121.6 (7)
Ni–N(7)	1.851 (5)	1.844 (5)	N(1)NiN(15)	178.6 (2)	174.0 (2)	C(10)C(11)C(12)	121.7 (8)	119.5 (7)
Ni–N(15)	1.849 (5)	1.866 (5)	N(1)NiO(18)	90.8 (2)	89.3 (2)	C(11)C(12)C(13)	119.7 (7)	119.3 (7)
Ni–O(18)	1.835 (5)	1.850 (5)	N(7)NiN(15)	95.4 (2)	96.0 (2)	C(8)C(13)C(12)	118.6 (6)	119.1 (6)
N(1)–C(2)	1.53 (1)	1.52 (1)	N(7)NiO(18)	175.0 (2)	174.7 (2)	C(8)C(13)C(14)	124.8 (6)	124.6 (6)
N(1)–C(5)	1.509 (9)	1.514 (9)	N(15)NiO(18)	88.0 (2)	87.4 (2)	C(12)C(13)C(14)	116.4 (6)	116.3 (6)
N(1)–C(19)	1.510 (9)	1.509 (8)	NiN(1)C(2)	115.4 (4)	109.2 (4)	C(13)C(14)N(15)	121.7 (6)	121.7 (6)
C(2)–C(3)	1.53 (1)	1.56 (2)	NiN(1)C(5)	104.1 (4)	109.9 (4)	C(13)C(14)C(26)	116.6 (6)	116.2 (6)
		1.65 (2)	NiN(1)C(19)	104.1 (4)	112.8 (4)	N(15)C(14)C(26)	121.7 (6)	122.0 (6)
C(3)–C(4)	1.55 (1)	1.58 (3)	C(2)N(1)C(5)	104.0 (5)	105.4 (5)	NiN(15)C(14)	127.9 (4)	127.3 (4)
		1.55 (2)	C(2)N(1)C(19)	113.8 (6)	106.8 (5)	NiN(15)C(16)	112.2 (4)	112.5 (4)
C(4)–C(5)	1.54 (1)	1.52 (1)	C(5)N(1)C(19)	115.5 (5)	112.5 (5)	C(14)N(15)C(16)	119.7 (5)	119.3 (5)
C(5)–C(6)	1.495 (9)	1.511 (9)	N(1)C(2)C(3)	102.8 (6)	103.0 (9)	N(15)C(16)C(17)	106.8 (5)	107.1 (5)
C(6)–O(6)	1.220 (9)	1.199 (8)			104.5 (8)	N(15)C(16)C(27)	111.0 (5)	110.8 (5)
C(6)–N(7)	1.375 (8)	1.384 (8)	C(2)C(3)C(4)	103.8 (7)	99 (1)	C(17)C(16)C(27)	109.7 (6)	109.7 (5)
N(7)–C(8)	1.398 (8)	1.411 (8)			97 (1)	C(16)C(17)O(17)	119.5 (7)	120.6 (6)
C(8)–C(9)	1.43 (1)	1.407 (9)	C(3)C(4)C(5)	106.3 (7)	103.9 (9)	C(16)C(17)O(18)	115.2 (6)	117.0 (6)
C(8)–C(13)	1.405 (8)	1.398 (9)			102.6 (8)	O(17)C(17)O(18)	125.3 (7)	122.4 (6)
C(9)–C(10)	1.39 (1)	1.40 (1)	N(1)C(5)C(4)	105.4 (6)	107.6 (5)	NiO(18)C(17)	116.4 (5)	114.8 (4)
C(10)–C(11)	1.42 (1)	1.41 (1)	N(1)C(5)C(6)	110.2 (6)	109.6 (5)	N(1)C(19)C(20)	116.5 (6)	111.4 (6)
C(11)–C(12)	1.40 (1)	1.41 (1)	C(4)C(5)C(6)	113.0 (6)	113.7 (6)	C(19)C(20)C(21)	116.3 (8)	120.1 (7)
C(12)–C(13)	1.444 (9)	1.440 (9)	C(5)C(6)O(6)	119.1 (7)	120.7 (6)	C(19)C(20)C(25)	117.4 (8)	121.1 (7)
C(13)–C(14)	1.442 (9)	1.475 (9)	C(5)C(6)N(7)	113.9 (6)	113.2 (5)	C(21)C(20)C(25)	126.2 (9)	118.7 (7)
C(14)–N(15)	1.306 (8)	1.306 (8)	O(6)C(6)N(7)	127.1 (7)	126.1 (6)	C(20)C(21)C(22)	115 (1)	120.5 (8)
C(14)–C(26)	1.540 (9)	1.537 (9)	NiN(7)C(6)	113.1 (4)	113.9 (4)	C(21)C(22)C(23)	118 (1)	121.6 (9)
N(15)–C(16)	1.514 (9)	1.489 (8)	NiN(7)C(8)	124.8 (4)	125.6 (4)	C(22)C(23)C(24)	125 (2)	118.1 (9)
C(16)–C(17)	1.544 (9)	1.518 (9)	C(6)N(7)C(8)	121.7 (5)	119.2 (5)	C(23)C(24)C(25)	118 (1)	120.9 (8)
C(16)–C(27)	1.541 (9)	1.57 (1)	N(7)C(8)C(9)	119.2 (6)	117.2 (6)	C(20)C(25)C(24)	116 (1)	120.1 (7)
C(17)–O(17)	1.212 (9)	1.251 (8)	N(7)C(8)C(13)	120.5 (6)	121.0 (6)	C(16)C(27)C(28)	112.4 (6)	114.1 (6)
C(17)–O(18)	1.292 (9)	1.293 (8)	C(9)C(8)C(13)	120.3 (6)	121.8 (6)	C(16)C(27)C(29)	111.1 (6)	111.0 (6)
C(19)–C(20)	1.51 (1)	1.53 (1)	C(8)C(9)C(10)	121.4 (7)	117.2 (6)	C(28)C(27)C(29)	110.8 (7)	110.6 (7)
C(20)–C(21)	1.43 (2)	1.38 (1)						
C(20)–C(25)	1.39 (2)	1.39 (1)						
C(21)–C(22)	1.47 (2)	1.39 (1)						
C(22)–C(23)	1.37 (3)	1.37 (1)						
C(23)–C(24)	1.39 (3)	1.39 (1)						
C(24)–C(25)	1.45 (2)	1.40 (1)						
C(27)–C(28)	1.56 (1)	1.54 (1)						
C(27)–C(29)	1.54 (1)	1.55 (1)						
			THF solvate molecule					
			C(15)–C(25)	1.36 (2)		C(25)C(15)C(55)117 (2)		
			C(15)–C(55)	1.53 (3)		C(15)C(25)C(35)106 (2)		
			C(25)–C(35)	1.52 (3)		C(25)C(35)C(45)102 (2)		
			C(35)–C(45)	1.45 (3)		C(35)C(45)C(55)107 (2)		
			C(45)–C(55)	1.66 (3)		C(15)C(55)C(45) 90 (2)		

Table 3. The  $U_{\text{conf}}$  terms ( $\text{kJ mol}^{-1}$ ) for molecules (1A), (1B) and (2)

Molecule	$U_b$	$U_a$	$U_{nb}$	$U_t$	$U_{\text{conf}}$
(1A)	4.6	51.8	-38.9	48.5	66.0
(1B)	5.4	52.7	-56.8	51.4	52.7
(2)	4.6	46.4	-38.8	38.0	50.2

constant and  $n$  the barrier multiplicity). The calculations were made using the *MOLBD-3* program (Boyd, 1968) with the parameters proposed by Roas, Niketič & Simeon (1982) for metal complexes with amino acids. Since, in contrast to the original paper (Roas, Niketič & Simeon, 1982), the indicated set of parameters was used not for Cu, but for Ni complexes, the average bond lengths in the Ni complexes studied [(1) and (2)] were taken as ideal values for calculating  $U_b$ . The parameters of bonds, bond angles and torsion angles involving C and H of the phenyl and phenylene rings were taken from Boyd, Sanwal, Shary-Tehrany & McNally (1971). The parameters for the planar-trigonal atoms N(7) and N(15) were assumed to be the same as for C( $sp^2$ ).

The optimal geometry was found by minimizing  $U_{\text{conf}}$  on variation of all geometric parameters. The geometry of molecules (1A), (1B) and (2) in the crystal according to the X-ray data was used as an initial approximation. The minimal values of  $U_{\text{conf}}$  found in this way and the contributions of its various terms are listed in Table 3. The differences between experimental and calculated bond lengths and bond angles are small (0.01–0.02 Å and 2–3°). The differences in torsion angles are greater (5–7° and, in some cases, 10–15°). However, in general, the calculated conformations of the chelate rings and of the molecule as a whole are qualitatively close to that experimentally found in the crystal.  $U_{\text{conf}}$  was calculated for molecules (1A) and (2) as a function of the benzyl-group rotation defined by the torsion angle  $\tau$  by optimizing all geometrical parameters at each fixed value of  $\tau$ , which was varied in increments of 20°. Graphs of this function are shown in Fig. 2.

The equilibrium between diastereomers (1) and (2), attained under the effect of  $\text{CH}_3\text{ONa}$  in methanol, is shifted towards (2). The ratio of these diastereomers is 88:12 at 298 K, which corresponds to a difference in their energies of 4.81  $\text{kJ mol}^{-1}$ . For similar diastereomeric Cu complexes the energy differences are 1.67  $\text{kJ mol}^{-1}$  in favour of (*S*)-Val-containing diastereomers (Belokon' *et al.*, 1984). It should be stressed that, according to the conformational calculations, diastereomer (2) is also energetically more favourable than (1) for either conformation of the latter coexisting in the crystal (Table 3). Apparently this is due to differences in non-bonded intramolecular interactions and in conformations of the chelate rings resulting from the inversion of the C(16) chirality. Two of the three chiral centres, *viz* the  $\alpha$ -carbon C(5) and N(1) of

proline, have the same configuration in both diastereomers, whereas the configuration at C(16) is different, *viz* *S* in (2) and *R* in (1).

The difference in  $U_{\text{conf}}$  could be expected to come mostly from different intramolecular non-bonded interactions between the isopropyl and benzyl groups. Such interaction is possible in molecule (1), where these groups are situated on the same side of the metal-coordination plane, and impossible in molecule (2), where the groups are situated on opposite sides. In fact, when the benzyl group is substituted by H, the enantioselectivity of the asymmetrical synthesis and retroracemization decrease dramatically, thus experimentally confirming the role of these interactions (Belokon' *et al.*, 1982). But the intramolecular non-bonded interactions between the isopropyl and benzyl groups do not result in short contacts even in molecule (1B), where these groups are most closely situated. Indeed, all non-bonded distances between these groups exceed the sums of the van der Waals radii ( $\text{C}\cdots\text{C} > 3.6$  Å). Evidently, to avoid such contacts the chelate rings have to change their conformational and bond angles (see above). The result is an actual decrease in the non-bonded energy term and an increase in the torsion- and bond-angle terms for (1B) as compared with (2) (see Table 3). The final calculated difference in  $U_{\text{conf}}$  is only 2.5  $\text{kJ mol}^{-1}$ , favouring (2).

Another way to avoid intramolecular contacts of the isopropyl and benzyl groups in molecule (1) is to rotate the benzyl group around the N(1)–C(19) bond, putting the Ph ring over the proline fragment and turning it away from the metal ion. This situation is achieved in conformer (1A). The calculated  $U_{\text{conf}}$  of this conformer is higher than for (1B) and (2) by 9.6 and 13.5  $\text{kJ mol}^{-1}$  (see Table 3), respectively. The coexistence of the (1A) and (1B) molecules in a crystal could be explained by their different environments, compensating for the intramolecular interactions. The calculation of  $U_{\text{conf}}$  *vs* the torsion angle of the benzyl

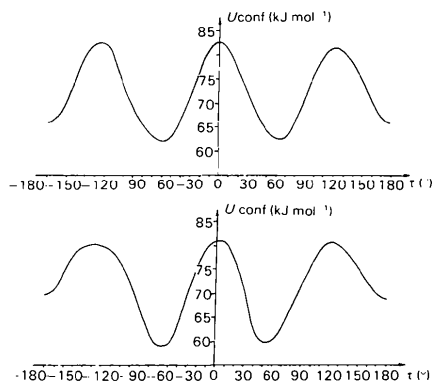


Fig. 2.  $U_{\text{conf}}$  of (1A) and (2) as a function of the torsion angle  $\tau$  around N(1)–C(19).

substituent (Fig. 2) shows that three energetically favourable orientations of this group, with torsions of about  $\pm 60$  and  $180^\circ$ , are possible for both (1) and (2). The benzyl-group location above N(7) is the most energetically favourable and close to the orientation found in molecules (1*B*) and (2) in the crystal. The third possible conformation with  $\tau \approx 180^\circ$  and an *anti* orientation of the benzyl-group with respect to the metal atom is unfavourable: the barrier to rotation around the N(1)–C(19) bond, characterized by the angle  $\tau$ , does not exceed *ca* 21 kJ mol<sup>-1</sup> in molecules (1) and (2). This indicates the possibility of a fairly free rotation of the benzyl-group in the isolated molecules of (1) and (2). However, in solution the relative content of the conformer with  $\tau \approx 180^\circ$  should be greater for (1) than for (2) (Fig. 2), in good agreement with the experimental data (Belokon' *et al.*, 1984).

It is interesting to note that the previous conformational calculations for conformers of various compounds coexisting in crystals (Yelagin, Timofeeva & Zorki, 1980) generally show one rather broad and flat minimum for  $U_{\text{conf}}$  corresponding to different conformers, despite substantial geometric differences between them. The case of molecules (1*A*) and (1*B*) considered here is the first example of conformers which are characterized by different minima of  $U_{\text{conf}}$  separated by a well defined barrier coexisting in a crystal.

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