

On the basis of the observed bond lengths, it would seem possible to represent formally the ligand as the anion derived from the thiolate form of the ligand, although the thione form is observed in free Hbttz. This change may be related to a strong metal–ligand interaction (Jeannin, Jeannin & Lavigne, 1979). Electron donation from the S atom to the metal may induce a decrease in the π -electron density along the C–S_{exo} bond and this would result in a charge displacement from the N lone pair to the C–N bond, in agreement with the observed C–N shortening.

The bond angles in the bttz ligands indicate a distorted geometry because of the steric hindrance arising from the coordination. The S,N coordination alters the thiazole ring geometry by decreasing the C–N–C and S_{exo}–C–S_{endo} angles (by *ca* 4 and 7° respectively) and opening up the S_{endo}–C–N angle (by 5°).

The thiazole ring is also more non-planar than in uncoordinated Hbttz, the largest deviations from the least-squares planes through the benzene rings being for the thiazole S atoms. It is interesting to note that all atoms of the thiazole ring are out of the benzene plane and on the same side, in agreement with the previously reported structure of Mn(CO)₃(bttz)₂ (Jeannin, Jeannin & Lavigne, 1977). The angles between the benzene and thiazole rings of the ligands are 3.1 (8) and 2.2 (8)°.

The most pronounced distortion is the bending of the exocyclic S(1) and S(3) atoms out of the thiazole-ring planes by 0.191 (2) and 0.131 (2) Å, respectively. This does not appear in free Hbttz and is probably a consequence of the particular, bridged linkage of the ligand.

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Structure of a Solvated Nickel(II) Complex of (S)-2'-(N-Benzylpropyl)amino-acetophenone and (R)-Valine Schiff Base, C₂₅H₂₉N₃NiO₃·½C₄H₈O. Conformational Calculation of Diastereomeric Complexes of (R)-Valine and (S)-Valine

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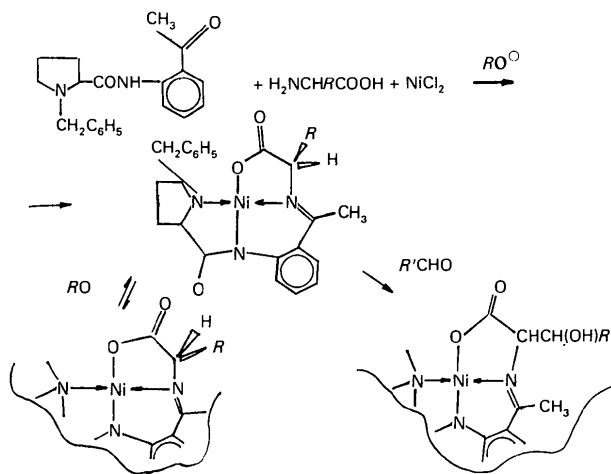
Abstract. {(R)-[N-(1-{2-[N-(S)-Benzylpropylamino]-phenyl}ethylidene)valinato]nickel(II)-tetrahydrofuran (2/1), *M_r* = 514.3, monoclinic, *P*2₁, *a* = 10.779 (1), *b* = 11.800 (5), *c* = 20.014 (2) Å, β = 95.26 (1)°, *V* = 2535 (2) Å³, *Z* = 4, *D_x* = 1.35 Mg m⁻³, Mo *K*α, λ = 0.71069 Å, μ = 0.796 mm⁻¹, *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⁻¹. 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 β -hydroxy- α -amino acids and racemization of certain amino acids (a.a.) in the presence of Cu^{II} and Ni^{II} ions (Belokon', Zeltzer, Ryzhov, Saporovskaya, Bakhmutov & Belikov, 1982; Belokon' *et al.*, 1983, 1984). Ni^{II} and Cu^{II} 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.-M²⁺ 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^{II} 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* α radiation. Cell constants determined by least-squares treatment of 24 automatically centred reflections. θ -2 θ scan, 7513 reflections measured ($1 \leq \theta \leq 33^\circ$, *hkl*, *hk* \bar{l}), 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 Δ/σ 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^{II} (M=Ni, Cu), the Ni²⁺ 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 τ –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 C₈-envelope in (1A) and (2) and close to a C₇-envelope in (1B).

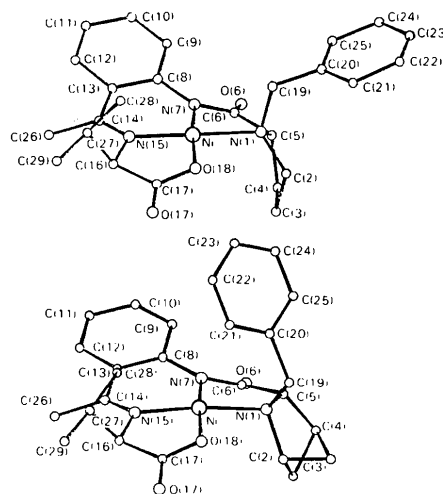


Fig. 1. Geometries of independent molecules (1A) (top) and (1B) (bottom), and numbering of the atoms.

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

$$B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j$$

	Molecule (1A)				Molecule (1B)			
	x	y	z	B _{eq}	x	y	z	B _{eq}
Ni	33721 (7)	0	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)
C(4)	719 (9)	–549 (9)	–68 (4)	7.2 (3)	3858 (16)	1725 (16)	3658 (8)	5.7 (5)
C(5)	1153 (6)	–1105 (7)	611 (4)	4.3 (2)	4592 (7)	2806 (7)	3881 (4)	5.1 (2)
C(6)	2179 (6)	–1945 (6)	562 (4)	4.2 (2)	4347 (6)	2912 (6)	4617 (4)	3.7 (2)
O(6)	1930 (5)	–2876 (5)	323 (3)	6.5 (2)	3130 (6)	3492 (6)	4722 (3)	3.5 (2)
N(7)	3334 (5)	–1552 (5)	806 (3)	3.4 (1)	2797 (5)	4310 (4)	4399 (3)	4.9 (2)
C(8)	4379 (5)	–2258 (6)	862 (3)	3.3 (2)	2519 (4)	3008 (4)	5230 (3)	3.4 (1)
C(9)	4221 (6)	–3437 (7)	988 (3)	4.3 (2)	1561 (6)	3622 (5)	5503 (3)	3.2 (3)
C(10)	5231 (8)	–4176 (7)	1048 (4)	5.2 (2)	1688 (7)	4808 (6)	5535 (4)	4.6 (2)
C(11)	6440 (8)	–3723 (7)	1000 (5)	5.7 (3)	731 (7)	5445 (7)	5781 (5)	5.5 (3)
C(12)	6627 (7)	–2572 (6)	875 (4)	4.6 (2)	–321 (7)	4923 (7)	6018 (4)	5.2 (2)
C(13)	5572 (5)	–1814 (5)	800 (3)	3.3 (2)	–433 (6)	3729 (6)	5994 (4)	4.4 (2)
C(14)	5846 (5)	–630 (6)	715 (3)	3.5 (2)	540 (6)	3067 (6)	5737 (3)	3.5 (2)
N(15)	5050 (4)	161 (5)	838 (3)	3.3 (1)	396 (6)	1825 (6)	5766 (3)	3.5 (2)
C(16)	5454 (6)	1390 (6)	855 (3)	3.8 (2)	1329 (4)	1140 (4)	5700 (2)	2.9 (1)
C(17)	4268 (7)	2109 (6)	900 (4)	4.7 (2)	1159 (6)	–99 (6)	5797 (3)	3.6 (2)
O(17)	4320 (5)	3128 (4)	833 (3)	6.1 (2)	2272 (6)	–688 (6)	5537 (3)	3.5 (2)
O(18)	3288 (4)	1546 (5)	1025 (3)	5.5 (2)	2281 (5)	–1741 (4)	5464 (3)	4.9 (2)
C(19)	1575 (7)	–363 (3)	1809 (4)	5.2 (2)	3186 (4)	–52 (4)	5391 (2)	4.0 (1)
C(20)	347 (7)	–739 (9)	2042 (4)	5.7 (3)	5517 (6)	1480 (8)	5360 (3)	4.4 (2)
C(21)	–445 (8)	140 (14)	2258 (4)	8.9 (4)	5519 (6)	2109 (6)	6032 (4)	4.4 (2)
C(22)	–1569 (10)	–258 (19)	2546 (5)	14.6 (8)	4934 (7)	1637 (10)	6553 (4)	6.2 (3)
C(23)	–1819 (11)	–1393 (20)	2536 (6)	16.1 (9)	4980 (8)	2175 (10)	7174 (4)	7.1 (3)
C(24)	–1029 (14)	–2236 (16)	2334 (7)	13.6 (7)	5582 (8)	3189 (9)	7288 (4)	6.5 (3)
C(25)	115 (11)	–1893 (12)	2057 (5)	9.0 (4)	6186 (8)	3661 (8)	6768 (5)	6.4 (3)
C(26)	7123 (6)	–345 (6)	471 (4)	4.5 (2)	6166 (7)	3120 (7)	6143 (4)	5.1 (2)
C(27)	6388 (6)	1629 (7)	1469 (3)	4.1 (2)	–901 (5)	1387 (7)	5901 (4)	5.0 (2)
C(28)	5748 (8)	1683 (10)	2134 (4)	6.7 (3)	1103 (7)	–386 (6)	6560 (4)	4.4 (2)
C(29)	7138 (9)	2720 (8)	1369 (5)	6.9 (3)	2337 (7)	–177 (9)	6997 (4)	5.8 (3)
C(15)‡	899 (16)	4947 (23)	1749 (8)	17.6 (9)	642 (9)	–1615 (7)	6652 (5)	6.7 (3)
C(25)	1395 (17)	5468 (13)	2321 (7)	13.5 (7)				
C(35)	2570 (16)	4812 (21)	2555 (9)	17.6 (9)				
C(45)	2332 (16)	3728 (16)	2227 (7)	14.2 (7)				
C(55)	1672 (20)	4007 (17)	1461 (15)	26 (1)				

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

‡ C(15) to C(55) are the atoms of the tetrahydrofuran solvate molecule.

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

Molecule	U_b	U_a	U_{nb}	U_t	U_{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_{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_{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_{conf} was calculated for molecules (1A) and (2) as a function of the benzyl-group rotation defined by the torsion angle τ by optimizing all geometrical parameters at each fixed value of τ , 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 CH_3ONa 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 kJ mol^{-1} . For similar diastereomeric Cu complexes the energy differences are 1.67 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 α -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_{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_{conf} is only 2.5 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_{conf} of this conformer is higher than for (1B) and (2) by 9.6 and 13.5 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_{conf} *vs* the torsion angle of the benzyl

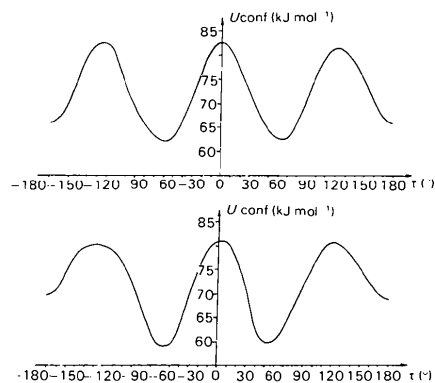


Fig. 2. U_{conf} of (1A) and (2) as a function of the torsion angle τ around N(1)–C(19).

substituent (Fig. 2) shows that three energetically favourable orientations of this group, with torsions of about ± 60 and 180° , 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 τ , does not exceed *ca* 21 kJ mol⁻¹ 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_{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_{conf} separated by a well defined barrier coexisting in a crystal.

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A Trivalent-Uranium Thioether Coordination Compound

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Abstract. Tris(methylcyclopentadienyl)(tetrahydrothiophene)uranium(III), $[\text{U}(\text{C}_5\text{H}_5)_3(\text{C}_4\text{H}_8\text{S})]$, $M_r = 563.57$, orthorhombic, *Pbca*, $a = 15.146$ (5), $b = 27.598$ (8), $c = 9.911$ (4) Å, $V = 4143$ (4) Å³, $Z = 8$, $D_x = 1.81$ g cm⁻³, *Mo K α* , $\lambda(\alpha_1) = 0.70930$ Å, $\mu = 75.3$ cm⁻¹, $F(000) = 2152$, $T = 296$ K, $R = 0.035$ for 1382 observed reflections. The structure consists of uranium-centered monomolecular units in which the uranium atom is coordinated to three cyclopentadiene rings and to the sulfur atom of a tetrahydrothiophene molecule. The average U–C distance is 2.81 ± 0.04 Å and the U–S distance is 2.986 (5) Å.

Introduction. The numbers of structurally characterized complexes with U–S bonds are far fewer than those

with U–O bonds. Several uranyl thiocarbamate and thiocarboxylate complexes as well as a uranyl disulfide complex have been reported (Perry, Zalkin, Ruben & Templeton, 1982, and references therein); the structure of a uranyl thioether has also been reported (Baracco *et al.*, 1975). No structurally characterized U^{III} sulfur complexes have been reported to date.

As part of a study of the synthesis and characterization of trivalent-uranium coordination compounds (Brennan & Zalkin, 1985), we report here the structure of $(\text{C}_5\text{H}_5)_3\text{U}(\text{SC}_4\text{H}_8)$.

Experimental. Red, air-sensitive needles of the tetrahydrothiophene complex were prepared by adding SC_4H_8 to a toluene solution of $(\text{C}_5\text{H}_5)_3\text{U}(\text{OC}_4\text{H}_8)$