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Contribution from the Department of Chemistry, Gorlaeus Laboratories,
State University Leiden, 2300 RA Leiden, The Netherlands

Coordination Chemistry of Optically Active Ligands. Crystal Structures of *trans*-((*S*)-1-Amino-2-propanol)((*R*)-1-amino-2-propanol)bis(isothiocyanato)nickel(II) and *trans*-Bis((*S*)-1-amino-2-propanol)bis(isothiocyanato)nickel(II)[1]

GER NIEUWPOORT and GERRIT C. VERSCHOOR*

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The crystal and molecular structures of *trans*-((*S*)-1-amino-2-propanol)((*R*)-1-amino-2-propanol)bis(isothiocyanato)nickel(II) and *trans*-bis((*S*)-1-amino-2-propanol)bis(isothiocyanato)nickel(II) have been determined by single-crystal X-ray analysis using three-dimensional diffractometer data. *trans*-((*S*)-1-Amino-2-propanol)((*R*)-1-amino-2-propanol)bis(isothiocyanato)nickel(II), $Ni(NCS)_2(C_3NOH_9)_2$, crystallizes in the triclinic space group $P\bar{1}$. The lattice constants at 22 °C are $a = 5.3988\ (7)$ Å, $b = 7.4107\ (7)$ Å, $c = 9.1592\ (16)$ Å, $\alpha = 99.67\ (1)°$, $\beta = 95.28\ (1)°$, $\gamma = 91.89\ (1)°$, $Z = 1$, and $V = 359.3$ Å^3. The structure was solved with the use of Patterson and Fourier techniques and refined by full-matrix least-squares procedures. The resulting conventional *R* factor based on 5072 significant reflections is 0.047. *trans*-Bis((*S*)-1-amino-2-propanol)bis(isothiocyanato)nickel(II), $Ni(NCS)_2(C_3NOH_9)_2$, crystallizes in the triclinic space group $P1$. The lattice constants at 22 °C are $a = 5.386\ (2)$ Å, $b = 7.353\ (3)$ Å, $c = 9.259\ (5)$ Å, $\alpha = 100.19\ (4)°$, $\beta = 94.82\ (4)°$, $\gamma = 91.66\ (3)°$, $Z = 1$, and $V = 359.3$ Å^3. Starting with the parameters of the first compound, containing the racemic ligand, the second structure was refined to a conventional *R* value 0.045, with the use of 1942 significant reflections. The difference in stability between $Ni(NCS)_2$((*S*)-ap)((*R*)-ap) and $Ni(NCS)_2$((*S*)-ap)$_2$ is reflected by the small difference in melting points, which are 188 and 174 °C, respectively. This difference is apparently not due to changes in the hydrogen-bonding system but to small deformations of the coordination octahedron and a less favorable conformation of one of the ligands in the latter compound.

Introduction

Up to the present, no detailed structural studies have been reported in which the difference between coordination of racemic and optically active isomers of chelating ligands are investigated.[2a] During the preparation of coordination compounds of racemic and optically active 1-amino-2-propanol (ap), only small differences in behavior were found.[2b,c] The differences were too small to be detected by techniques such as IR and UV spectroscopy. Also, the X-ray powder diffractograms of $Ni(NCS)_2$((*S*)-ap)((*R*)-ap) and $Ni(NCS)_2$((*S*)-ap)$_2$ are almost identical. Only the DTA diagrams of these two complexes yielded a difference in melting point of 14 °C, i.e., $Ni(NCS)_2$((*S*)-ap)((*R*)-ap) 188 °C and $Ni(NCS)_2$((*S*)-ap)$_2$ 174 °C.

According to the earlier work of Corey and Bailar[3] in *trans*-bis(diamine)metal compounds, which can occur in the $\delta\delta$, $\lambda\lambda$, and $\delta\lambda$ forms, the $\delta\delta$ and $\lambda\lambda$ forms are predicted to be more stable than the racemic $\delta\lambda$ forms. In these calculations, however, only the interactions between nonbonded hydrogen atoms were included. The frequent occurrence of the $\delta\lambda$ form in solid crystals is therefore usually explained by specific intermolecular forces such as hydrogen bonding.[2a,4] In addition, the requirements for close packing of rigid molecules[5] and the statistical preference for symmetrical molecules favor the $\delta\lambda$ conformation.

In methyl-substituted diamines it has been suggested that the methyl groups would preferably occur in the equatorial positions of the five-membered chelate ring.[3,6] This would yield a $\delta\delta$ conformation for $Ni(NCS)_2$((*S*)-ap)$_2$ and a compound $Ni(NCS)_2$((*S*)-ap)((*R*)-ap) with the $\delta\lambda$ conformation from the racemic ligand. Detailed knowledge of the structures of these compounds was considered of great importance to obtain further insight into possible differences between these and similar isomers. Therefore, the X-ray study was undertaken of both the available isomers of $Ni(NCS)_2(ap)_2$.

Table I. Crystal Data and Experimental Parameters of $Ni(NCS)_2$((*S*)-ap)((*R*)-ap) and $Ni(NCS)_2$((*S*)-ap)$_2$

	$Ni(NCS)_2$-((*S*)-ap)((*R*)-ap)	$Ni(NCS)_2$-((*S*)-ap)$_2$
	(A) Crystal Data	
formula	$Ni(NCS)_2$-$(C_3NOH_9)_2$	$Ni(NCS)_2$-$(C_3NOH_9)_2$
M_r	325.09	325.09
a, Å	5.3988 (7)	5.386 (2)
b, Å	7.4107 (7)	7.353 (3)
c, Å	9.1592 (16)	9.259 (5)
α, deg	99.67 (1)	100.19 (4)
β, deg	95.28 (1)	94.82 (4)
γ, deg	91.89 (1)	91.66 (3)
V, Å^3	359.3	359.3
Z	1	1
d_{obsd}, g/cm^3	1.45	1.46
d_{calcd}, g/cm^3	1.46	1.46
space group	$P\bar{1}$	$P1$
μ(Mo Kα), mm^{-1}	1.622	1.622
cryst dimens, mm	0.40 × 0.10 × 0.04	0.26 × 0.08 × 0.04
calcd transmission factors	0.85–0.94	0.88–0.94
	(B) Experimental Parameters	
radiation	Mo Kα (K$\bar{\alpha}$)	Mo Kα (K$\bar{\alpha}$)
λ, Å	0.710 73	0.710 73
monochromator	graphite	graphite
takeoff angle, deg	2	2
max θ, deg	34	25
data collected	5871	2522
data with $I > 2\sigma(I)$	5072	1942

Experimental Section

Compound Preparation. Crystals of both isomers were prepared by dissolving stoichiometric amounts of $Ni(NCS)_2 \cdot 2EtOH$ (prepared from NH_4NCS and $Ni(NO_3)_2 \cdot 6H_2O$ in absolute ethanol) and either *rac*- or *S*(+)-ap ($[\alpha_D] = 18.6$)[2b,c] in absolute ethanol. After being diluted with sodium-dried diethyl ether, both complexes crystallize upon standing for several days at 4 °C. Only a few well-formed, suitable crystals of $Ni(NCS)_2$((*S*)-ap)$_2$ could be obtained.

Collection and Reduction of the Intensity Data. Rotation photographs and zero-level Weissenberg photographs with Cu Kα radiation showed no symmetry and no systematic absences, which implied that the space group is either $P1$ or $P\bar{1}$. The unit cell parameters were determined with an automatic four-circle diffractometer, Nonius

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[1] Dedicated to the memory of Professor Dr. W. L. Groeneveld, who died on November 6, 1980.

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Table II. Atomic Positions and Anisotropic Temperature Parameters (Å^2) of Ni(NCS)$_2$((*S*)-ap)((*R*)-ap)[a]

atom	x	y	z	$100U_{11}$	$100U_{22}$	$100U_{33}$	$200U_{12}$	$200U_{23}$	$200U_{31}$
Ni	0.0	0.0	0.0	2.24 (2)	3.12 (2)	4.46 (2)	0.09 (2)	1.31 (3)	0.17 (2)
S	0.5979 (1)	−0.3367 (1)	0.2459 (1)	3.91 (3)	5.71 (4)	9.62 (5)	0.63 (5)	8.18 (7)	0.87 (6)
O	−0.1875 (3)	0.0551 (2)	0.1931 (2)	3.30 (7)	3.84 (8)	5.12 (8)	−1.3 (1)	1.5 (1)	0.9 (1)
N(T)	0.2089 (4)	−0.1870 (3)	0.0932 (2)	3.77 (9)	4.4 (1)	6.2 (1)	0.9 (1)	2.8 (2)	0.2 (2)
N	0.2395 (3)	0.2109 (3)	0.1163 (2)	3.07 (8)	4.05 (9)	5.5 (1)	−1.1 (1)	1.0 (2)	0.8 (1)
C(T)	0.3669 (4)	−0.2514 (3)	0.1570 (2)	3.31 (9)	3.32 (9)	5.1 (1)	0.0 (1)	2.4 (2)	1.5 (2)
C(1)	0.1188 (6)	0.2953 (5)	0.2457 (4)	5.9 (2)	6.8 (2)	7.4 (2)	−5.4 (3)	−3.7 (3)	3.8 (3)
C(2)	−0.0207 (6)	0.1635 (5)	0.3115 (3)	5.7 (2)	7.5 (2)	5.8 (1)	−4.2 (3)	−1.4 (3)	1.9 (2)
C(3)	−0.1585 (6)	0.2385 (5)	0.4398 (3)	6.0 (2)	6.8 (2)	5.2 (1)	0.5 (3)	1.0 (3)	2.1 (2)

[a] U_{ij} is defined as $\exp(-2\pi^2(U_{11}h^2a^{*2} + ... + 2U_{31}lhc^*a^*)$.

Table III. Atomic Positions and Anisotropic Temperature Parameters (Å) of Ni(NCS)$_2$((*S*)-ap)$_2$

atom	x	y	z	$100U_{11}$	$100U_{22}$	$100U_{33}$	$200U_{12}$	$200U_{23}$	$200U_{31}$
Ni	0.0	0.0	0.0	2.08 (4)	4.36 (6)	5.57 (7)	−0.21 (8)	1.62 (9)	0.43 (8)
S(A)	0.592 (1)	−0.331 (1)	0.250 (1)	4.6 (2)	6.3 (4)	9.0 (5)	0.5 (5)	9.3 (7)	−0.8 (6)
S(B)	−0.598 (1)	0.329 (1)	−0.248 (1)	3.4 (2)	7.6 (5)	12.9 (6)	0.3 (5)	8.9 (8)	−1.5 (6)
O(A)	−0.197 (2)	0.063 (1)	0.188 (1)	2.7 (5)	4.3 (7)	4.7 (7)	−1.1 (9)	1 (1)	0 (1)
O(B)	0.180 (2)	−0.060 (1)	−0.193 (1)	2.7 (5)	5.4 (8)	6.4 (9)	0 (1)	5 (1)	1 (1)
N(TA)	0.211 (2)	−0.184 (2)	0.095 (1)	3.0 (6)	4.3 (7)	4.1 (8)	1 (1)	3 (1)	−2 (1)
N(TB)	−0.204 (2)	0.197 (2)	−0.086 (2)	4.5 (8)	7 (1)	10 (1)	−1 (2)	5 (2)	3 (2)
N(A)	0.249 (2)	0.206 (1)	0.114 (1)	2.4 (6)	6 (1)	4 (1)	0 (1)	−2 (1)	1 (1)
N(B)	−0.237 (2)	−0.215 (1)	−0.113 (1)	3.2 (7)	4.7 (9)	8 (1)	−1 (1)	5 (2)	1 (1)
C(TA)	0.364 (2)	−0.253 (2)	0.157 (1)	5.9 (9)	2.8 (8)	1.7 (7)	−2 (1)	2 (1)	2 (1)
C(TB)	−0.366 (2)	0.246 (2)	−0.157 (2)	1.0 (6)	5 (1)	12 (1)	1 (1)	3 (2)	2 (1)
C(1A)	0.202 (2)	0.230 (2)	0.272 (1)	3.2 (5)	4.4 (7)	8.1 (9)	−1 (1)	−1 (1)	0 (1)
C(1B)	−0.111 (2)	−0.307 (1)	−0.242 (1)	3.8 (5)	3.9 (6)	6.1 (7)	0 (1)	−1 (1)	2 (1)
C(2A)	−0.077 (2)	0.223 (1)	0.287 (1)	3.2 (5)	4.3 (7)	4.9 (7)	1 (1)	0 (1)	−1 (1)
C(2B)	0.013 (2)	−0.165 (1)	−0.312 (1)	3.4 (5)	4.8 (7)	4.8 (7)	1 (1)	1 (1)	−1 (1)
C(3A)	−0.136 (4)	0.224 (3)	0.441 (2)	7 (1)	7 (1)	10 (2)	1 (2)	3 (2)	2 (2)
C(3B)	0.152 (3)	−0.247 (3)	−0.439 (1)	5 (1)	8 (1)	3 (1)	−1 (2)	−1 (2)	2 (1)

CAD-4. The intensities were measured with the ω–θ scan mode. The observed data were corrected for Lorentz and polarization effects. In a later stage of the refinement, absorption correction was applied with the use of the Monte Carlo method of de Graaff.[7] All crystal data and experimental data are summarized in Table I.

Solution and Refinement of the Structure. The investigation was started with the supposed centrosymmetric structure of Ni(NCS)$_2$((*S*)-ap)((*R*)-ap). A sharpened Patterson synthesis revealed the positions of all atoms with the exception of the hydrogen atoms. Five cycles of least-squares refinement with isotropic temperature parameters resulted in $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.209$. The scattering factors including the anomalous dispersion corrections were taken from ref 8. The hydrogen atoms were located in a difference Fourier map. Seven additional cycles of refinement with anisotropic temperature parameters for the nonhydrogen atoms resulted in $R = 0.047$ and $R_w = [\sum w||F_o|^2 - |F_c|^2|/\sum w|F_o|^2]^{1/2} = 0.060$ for 5072 significant reflections. In this refinement, the following constraints were used: O–H = 0.85, N–H = 0.90, and C–H = 0.95 Å. The positional parameters of the nonhydrogen atoms of this refinement were initially used for an isotropic refinement of Ni(NCS)$_2$((*S*)-ap)$_2$ in space group $P\bar{1}$. Guided by the positions of the maxima in the difference Fourier map, the atoms C(1) (from now on C(1A) and C(1B)) and C(2) were displaced slightly to disturb the inversion symmetry. With use of slack constraints[9] for the bond lengths and bond angles of the ligands, the structure could be refined in space group $P1$. The values of the slack constraints were taken from the refinement of Ni(NCS)$_2$((*S*)-ap)((*R*)-ap) and were adapted to the average values of the A and B molecules during the refinement. Strong correlations appeared to occur between molecule A and molecule B. The positions of the hydrogen atoms, with the exception of the hydroxyl and amine hydrogen of form A, could be located in a difference Fourier map. The analysis was continued with seven cycles of refinement with anisotropic temperature parameters for the nonhydrogen atoms. The refinement resulted in $R = 0.045$ and $R_w = 0.049$. A refinement of the other enantiomorphic isomer yielded significantly higher R values, which indicated that Ni(NCS)$_2$((*S*)-ap)$_2$ had a $\delta\delta$ conformation. The final atomic positions for the two structures are listed in Tables II and III. Tables of observed and calculated structure factors, hydrogen parameters, and slack constraints are available.[10]

Table IV. Intramolecular Bond Lengths (Å) of Ni(NCS)$_2$((*S*)-ap)((*R*)-ap) and Ni(NCS)$_2$((*S*)-ap)$_2$

	Ni(NCS)$_2$-((*S*)-ap)((*R*)-ap)	Ni(NCS)$_2$(S-ap)$_2$	
		A molecule	B molecule
Ni–O	2.107 (2)	2.102 (7)	2.092 (7)
Ni–N	2.075 (2)	2.071 (6)	2.072 (6)
Ni–N(T)	2.061 (2)	2.056 (6)	2.075 (8)
C(1)–N	1.461 (4)	1.484 (9)	1.488 (8)
C(2)–O	1.453 (3)	1.456 (7)	1.452 (7)
C(1)–C(2)	1.459 (5)	1.519 (8)	1.494 (9)
C(2)–C(3)	1.489 (4)	1.487 (10)	1.491 (8)
S–C(T)	1.631 (2)	1.619 (7)	1.641 (8)
N(T)–C(T)	1.149 (3)	1.147 (7)	1.150 (8)

Table V. Intramolecular Bond Angles (Deg) of Ni(NCS)$_2$((*S*)-ap)((*R*)-ap) and Ni(NCS)$_2$((*S*)-ap)$_2$

	Ni(NCS)$_2$-((*S*)-ap)-((*R*)-ap)	Ni(NCS)$_2$((*S*)-ap)$_2$	
		A molecule	B molecule
N(T)–Ni–O	90.05 (8)	91.3 (5)	90.5 (5)
N(T)–Ni–O	89.95 (8)	91.1 (5)	87.3 (6)
N(T)–Ni–N	89.72 (8)	87.1 (5)	92.5 (5)
N(T)–Ni–N	90.28 (8)	90.5 (5)	89.9 (5)
O–Ni–O	180	177.2 (5)	
N–Ni–N	180	177.4 (5)	
N(T)–Ni–N(T)	180	176.8 (8)	
O–Ni–N	82.14 (7)	83.6 (4)	81.1 (4)
N–Ni–O	97.86 (7)	97.4 (4)	98.0 (4)
Ni–N–C(1)	107.3 (1)	107.1 (7)	107.6 (6)
N–C(1)–C(2)	113.2 (3)	110.3 (8)	110.1 (8)
C(1)–C(2)–C(3)	116.8 (3)	112.8 (11)	113.5 (10)
C(1)–C(2)–O	107.5 (3)	110.2 (8)	103.9 (9)
C(2)–O–Ni	108.9 (1)	109.6 (7)	110.7 (6)
Ni–N(T)–C(T)	162.0 (2)	164.7 (11)	154.1 (14)
N(T)–C(T)–S	177.9 (2)	174.6 (13)	175.4 (15)

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Table VI. Torsion Angles (Deg) of Ni(NCS)$_2$((*S*)-ap)((*R*)-ap), the Two Conformations of Ni(NCS)$_2$((*S*)-ap)$_2$, and CuCl$_2$((*R*,*S*)-ap)

	Ni(NCS)$_2$-((*S*)-ap)((*R*)-ap)	Ni(NCS)$_2$((*S*)-ap)$_2$		CuCl$_2$-((*R*,*S*)-ap)[a]
		A	B	
O-Me-N-C(1)	10.6 (2)	19.5 (8)	12.4 (8)	9 (1)
N-Me-O-C(2)	16.0 (2)	6.1 (8)	18.6 (8)	22 (1)
Me-N-C(1)-C(2)	−37.2 (4)	−41.6 (11)	−41.6 (11)	−37 (1)
Me-O-C(2)-C(1)	−39.4 (3)	−30.3 (12)	−44.3 (9)	−46 (1)
N-C(1)-C(2)-O	52.2 (4)	48.8 (13)	56.7 (11)	55 (1)
N-C(1)-C(2)-C(3)	177.3 (3)	173.3 (12)	177.8 (10)	171 (1)

[a] See ref 11.

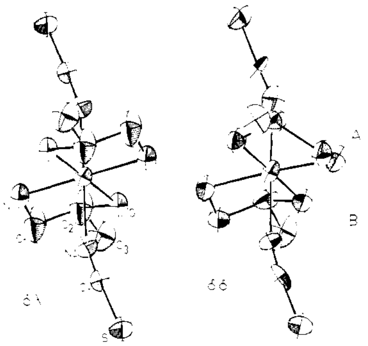

Figure 1. ORTEP projection (probability 50%) of the molecular structures of Ni(NCS)$_2$((*S*)-ap)((*R*)-ap) ($\delta\lambda$) and Ni(NCS)$_2$((*S*)-ap)$_2$ ($\delta\delta$), together with their atomic numbering scheme. In the $\delta\delta$ structure, the two molecules A and B are indicated.

Table VII. Intermolecular Hydrogen Bond Lengths (Å) and Bond Angles (Deg)

		Ni(NCS)$_2$-((*S*)-ap)((*R*)-ap)	Ni(NCS)$_2$((*S*)-ap)$_2$	
			A	B
S···H-O	S position	−1 + *x*, *y*, *z*	−1 + *x*, *y*, *z*	−1 + *x*, *y*, *z*
	S-O	3.216 (2)	3.24 (1)	3.21 (1)
	S-H	2.42 (2)	*a*	2.42 (3)
	H-O	0.83 (2)		0.83 (3)
	S-H-O	164 (1)		159 (1)
O···H-N	O position	1 + *x*, *y*, *z*	1 + *x*, *y*, *z*	1 + *x*, *y*, *z*
	N-O	3.391 (3)	3.25 (1)	3.44 (1)
	O-H	2.55 (2)		2.59 (3)
	H-N	0.88 (2)		0.86 (3)
	O-H-N	159 (2)		170 (2)
S···H-N	S position	1 + *x*, *y*, *z*	−1 + *x*, *y*, *z*	−1 + *x*, *y*, *z*
	S-N	3.766 (2)	3.77 (1)	3.79 (1)
	S-H	3.05 (2)		3.14 (5)
	H-N	0.89 (2)		0.91 (3)
	S-H-N	139 (2)		130 (2)

[a] The hydrogen atoms HO(A), H(1)N(A), and H(2)N(A) could not be located in the difference Fourier map.

Table VIII. Intermolecular Contacts (Å) in Ni(NCS)$_2$(ap)$_2$

	Ni(NCS)$_2$-((*S*)-ap)((*R*)-ap)	Ni(NCS)$_2$((*S*)-ap)$_2$	
		A	B
C(1)-S	3.983 (4)	3.85 (1)	3.90 (1)
C(1)-S	3.696 (3)	3.84 (1)[a]	3.68 (1)
C(3)-S	3.884 (3)	3.87 (1)	3.86 (1)
C(3)-S	3.942 (3)	3.95 (2)	3.94 (2)
N-S	3.770 (2)	3.79 (1)	3.78 (1)

[a] In molecule A a C(2)-S instead of a C(1)-S contact occurs. This is due to the change of the conformation of molecule A.

Discussion and Comparison of the Structures

Intramolecular distances and bond angles of both structures are listed in Tables IV and V. The molecular structures are depicted in Figure 1. The crystal packing is shown in Figure 2. The Ni(II) ions are coordinated by two oxygen and two nitrogen atoms of two bidentate coordinating aminopropanol molecules and two nitrogen atoms of the thiocyanate groups. The thiocyanate anions are almost linearly coordinated to Ni(II), but with a significant deviation from 180° for the Ni-N(T)-C(T) angle. In Ni(NCS)$_2$((*S*)-ap)((*R*)-ap), the conformation can be described as $\delta\lambda$, whereas in Ni(NCS)$_2$((*S*)-ap)$_2$ it is $\delta\delta$.[3] The details of the two structures are different in many aspects. First, the thermal motions in the $\delta\lambda$ form (Figure 1) show a marked anisotropy for the C(1) and C(2) atoms. These two carbon atoms appear to oscillate perpendicularly to the C–C bond of ap. This might well be indicative for a puckering motion of the chelate ring in solution.[4] The direction of the anisotropic motion of the atoms of the $\delta\delta$ form is probably influenced by the correlations between the two different δ conformations, A and B, in Ni(NCS)$_2$((*S*)-ap)$_2$. Further inspection of Tables II and III and Figure 1 shows that ligand molecule B in Ni(NCS)$_2$((*S*)-ap)$_2$ is not changed very much compared to Ni(NCS)$_2$((*S*)-ap)((*R*)-ap), while ligand molecule A has a largely different conformation in comparison with the racemic structure. The largest differences occur in the positions of the atoms C(1A) and C(2A). The N-C(1)-C(2)-C(3) torsion angles listed in Table VI indicate that the methyl groups are in trans-equatorial positions. An axial position will be unfavorable because of repulsions between the bulky methyl group and the thiocyanate group. This is in good agreement with the conclusions of Corey and Bailar[3] and Golloghy and Hawkins[6] that an equatorial position has a lower energy than an axial one, forcing the methyl group in equatorial positions. As a result, the conformation in Ni(NCS)$_2$((*S*)-ap)$_2$ is $\delta\delta$ rather than $\lambda\lambda$. Compared with Ni(NCS)$_2$((*S*)-ap)((*R*)-ap), the only change is a conformational change of the chelate ring, which is in accordance with the fact that the volumes of the unit cells of both compounds are exactly the same. The small difference in melting point as measured in the DTA diagrams of the complexes must be due to a slight decrease of the lattice energy of Ni(NCS)$_2$((*S*)-ap)$_2$ compared to that of Ni(NCS)$_2$((*S*)-ap)((*R*)-ap). In studies of diamine compounds,[2a,4-6] the frequent occurrence of the $\delta\lambda$ form in the crystalline state has usually been explained by assuming that the $\delta\lambda$ form is favored by specific intermolecular forces such as hydrogen bonding. Inspection of Table VII and Figure 2 shows that probably only the S···O distances correspond to relatively strong hydrogen bridges. The N···O and S···N distances are listed for reasons of comparison. From the data in Table VII it cannot be concluded therefore that only hydrogen bonds in the $\delta\lambda$ form are responsible for the more favorable lattice energy of this structure. The intermolecular contacts, listed in Table VIII, also add no arguments for a stabilization of the $\delta\lambda$ form compared to the $\delta\delta$ form. The intermolecular contacts for both isomers are identical, within 0.1 Å. Therefore, in these structures other factors must be responsible for the more favorable lattice energy of the $\delta\lambda$ form than the specific intermolecular forces indicated in the diamine studies. A first

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(10) Supplementary material.

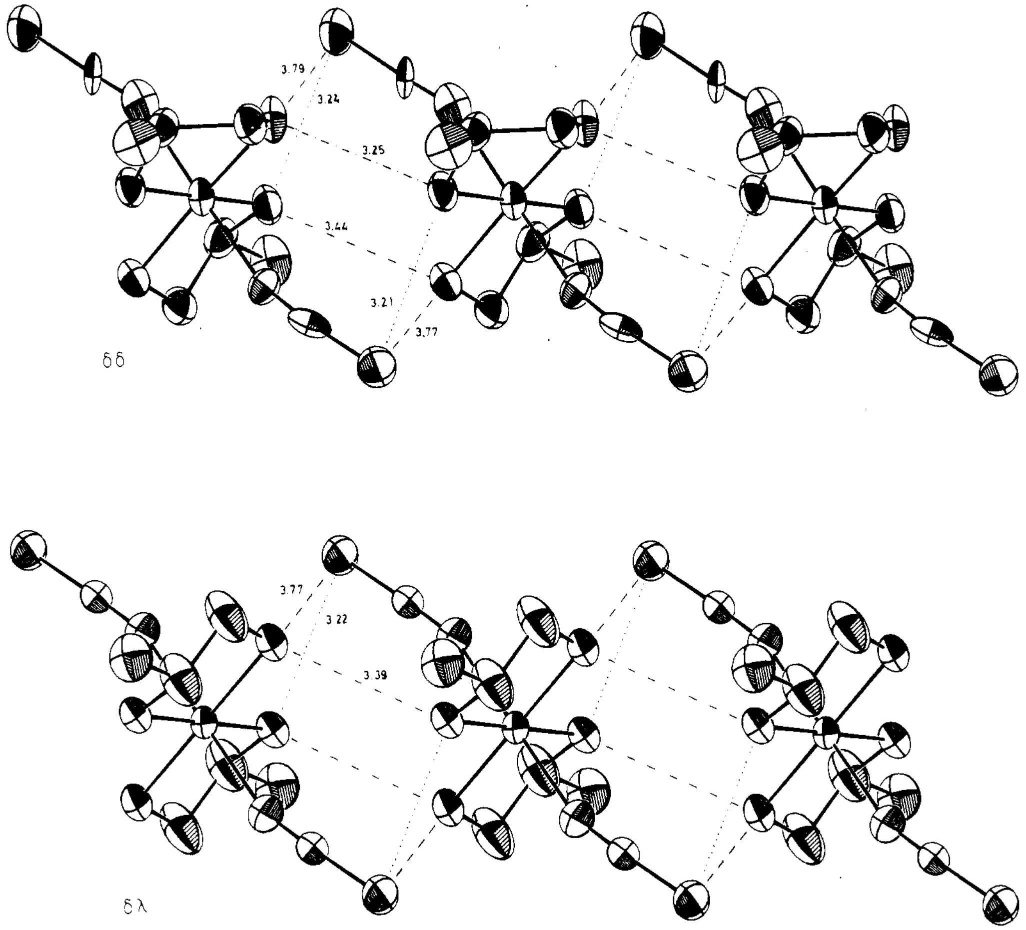

Figure 2. Crystal packing of the δλ and δδ forms of $Ni(NCS)_2(ap)_2$: S···H–O (···); O···H–N (–·–); S···H–N (- - -).

possibility lies in the less distorted coordination octahedron of $Ni(NCS)_2$((*S*)-ap)((*R*)-ap) in comparison with the coordination octahedron of $Ni(NCS)_2$((*S*)-ap)$_2$. The largest deviation of the ideal angles of 90 and 180° amounts to 0.28 (8)° in the first structure. The distortions in the second structure result in a largest deviation of 3.2 (8)°. This difference, however, is not reflected by the ligand field spectra.[2b,c] A second possibility can be found in the fact that the change from δλ to δδ results in a δ form which has an unfavorable strain energy. Comparison of the torsion angles of $Ni(NCS)_2$((*S*)-ap)((*R*)-ap), $Ni(NCS)_2$((*S*)-ap)$_2$, and $CuCl_2$((*R,S*)-ap)[11] (Table VI) indicates that molecule A in $Ni(NCS)_2$((*S*)-ap)$_2$ is significantly different from the other three conformations that have mutually similar torsion angles. This difference in puckering may be the origin for the decrease in stability of the δδ form. A final point that must be mentioned is the flexibility of the Ni–N(T)–C(T) angle which usually is very close to 180° but can occasionally be different from 180°.[12] The relative large deviation, here, and the differences up to 10.6° between the molecules A and B, illustrates that this angle can be adapted to obtain optimal hydrogen bonds and other intermolecular contacts.

Concluding Remarks

The results of this investigation have shown that the coordination behavior of (*S*)-ap and (*R*)-ap is very similar. It appears that the CH_3 substituents in the ligands invariably occupy the equatorial positions in the five-membered chelate rings, which in fact is the driving force for the formation of $Ni(NCS)_2$((*S*)-ap)$_2$ (δδ) and $Ni(NCS)_2$((*S*)-ap)((*R*)-ap) (δλ). The differences in lattice energy between the two isomers appear to be very small, which can be understood from both inter- and intramolecular interactions. Hydrogen-bond differences and packing differences are certainly not responsible for the differences between the δδ and δλ conformations, which is contrary to earlier observations on diamine chelate ligands.

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Registry No. $Ni(NCS)_2$((*S*)-ap)((*R*)-ap), 78656-04-9; Ni($NCS)_2$((*S*)-ap)$_2$, 78656-05-0.

Supplementary Material Available: Listings of structure factors, hydrogen parameters, and slack constraints (13 pages). Ordering information is given on any current masthead page.

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