expected to show changes in uptake properties and molecular geometry analogous to those observed in the diphos complexes. Here the energy of the substrate orbitals is varied by the change in the halide substituent, X. With the more electronegative chlorine atom the overlap between the orbitals is such that back-donation to the oxygen molecule only occurs to the extent that the O–O bond is lengthened to 1.30 Å. With the less electronegative substituent, iodine, more back-donation occurs to give an O–O bond length of 1.51 Å. From the chemical properties of the systems we might expect the M–O distances to be shorter for X = I than for X = Cl. However, within the standard deviations assigned to the M–O distances in these compounds, no significant difference is detected (Table VIII).

In a recent discussion[32] of the bonding of molecular oxygen to transition metals, the coordinated molecule was likened to the excited states of oxygen gas.[33] Indeed, there is considerable resemblance between the excited oxygen species observed spectrally and the coordinated molecule with the filled antibonding molecular orbitals. However, we feel that the range of O–O bond distances found in this series is too great to allow a facile allocation of a different excited state to the oxygen molecule in each of the four complexes.

The electronic factors affecting reversible oxygen uptake in these systems now appear to be well understood. Increased electron density at the metal, either by substitution of better donating ligands (P > I > Cl) or by change of metal (Ir > Rh > Co), will assure increasing uptake properties. It is impossible to predict precisely whether or not a substrate will have molecular orbitals of energy and symmetry suitable for overlap with the oxygen molecular orbitals to form a π bond between the oxygen and the substrate. However, the present range of complexes could be extended. Thus, if a molecular oxygen complex of cobalt were desired, then the system to try would be one in which the energies of the substrate orbitals, which are of course higher than those of the comparable rhodium orbitals, are decreased by using a stronger base as a ligand (*e.g.*, bis(dimethyl-) or bis(diethylphosphino)ethane). It is possible, however, that the higher energies of the cobalt orbitals would favor the formation of a σ bond. Similarly, in the $MX(CO)(P(C_6H_5)_3)_2$ systems, we would expect the X = Br compound to show an O–O bond length intermediate between the Cl and the I complexes, with similar intermediate uptake properties. If Rh were to be substituted for Ir, then the scheme discussed above leads us to predict that the uptake properties of the complex where X = Cl would be much poorer than those where X = I, and owing to the increase in the energies of the substrate orbitals upon the substitution of Rh for Ir, the uptake properties of the rhodium systems would be poorer than the iridium systems. And, indeed, this trend is observed. We were unable to prepare solid samples of the oxygen complex of $RhI(CO)[P(C_6H_5)_3]_2$, though an interaction may occur in solution.[34] We have observed no interaction between O_2 and $RhCl(CO)[P(C_6H_5)_3]_2$.

One lesson may be drawn from these structural studies. Similarity in unit cell dimensions is too often taken to imply similar correspondence in structural parameters. However, in the present instance the two structures with closely similar cell dimensions have widely differing structural parameters (the O–O bond lengths) and different chemical properties (the reversibility of oxygen addition).

Acknowledgment. We are grateful to the National Institutes of Health for their support of this work.

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[32] R. Mason, *Nature*, 217, 543 (1968).

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[34] L. Vaska, private communication.

The Crystal Structure of Bis(isoquinoline-1-carboxaldehyde thiosemicarbazanato)nickel(II) Monohydrate

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Abstract: The crystal structure of bis(isoquinoline-1-carboxaldehyde thiosemicarbazanato)nickel(II) monohydrate was determined. The ligand is a potent tumor inhibitor that was believed to function because of its metal-chelating ability. The formation of the nickel complex involving the tridentate ligand is compatible with the chelation hypothesis. The compound crystallizes in the monoclinic space group C2/c with $a = 17.884$, $b = 17.567$, $c = 15.901$ Å, $\beta = 101.57°$, and eight molecules per cell. The final R for 2464 observed reflections is 0.060. The distorted octahedral molecules are held together by a hydrogen-bond system involving N—H···N, N—H···O, and O—H···S hydrogen bonds. The presence of the rare O—H···S hydrogen bond is an unusual feature of the structure.

A large number of α-(N) heterocyclic thiosemicarbazones with definite carcinostatic activity were reported by French and Blanz.[1] Their hypothesis was that a thiosemicarbazone which could function as a tridentate chelate capable of forming octahedral com-

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[1] F. A. French and E. J. Blanz Jr., *J. Med. Chem.*, 9, 585 (1966).

plexes with metal ions would possess antitumor activity.[2] Isoquinoline-1-carboxaldehyde thiosemicarbazone (ISQTC) was found to have broad carcinostatic activity and also the lowest toxicity.[3] The crystal structure analysis of the nickel complex of ISQTC was undertaken as part of an investigation of a number of thiosemicarbazones and their metal chelates.

Experimental Section

The free ligand, H-ISQTC, was supplied by F. A. French. Crystals of the nickel complex were prepared by diffusing together an alcoholic solution of the ligand and a 0.5 *M* solution of nickel chloride.[4] Thin, dark-red, lath-like crystals several millimeters in length were formed after about 1 week. A long crystal was used for preliminary precession and Weissenberg photographs which indicated the systematic extinctions of *hkl* absent if $h + k = 2n + 1$, *h*0*l* absent for $l = 2n + 1$. The space group is therefore Cc or C2/c. An analysis of the intensity data indicated C2/c as the most probable space group.

A small plate of thickness 0.05 mm was cut to a dimension of 0.16 × 0.15 mm², and this crystal was used for the measurement of the intensities. The unit cell dimensions were determined by the least-squares method from 32 comparatively strong reflections in the region of 2θ from 25 to 35°. Only those reflections for which the molybdenum α_1–α_2 doublet ($\alpha_1 = 0.70926$, $\alpha_2 = 0.71354$ Å) could be resolved were used. The final values together with the estimated standard deviations obtained are $a = 17.884 \pm 0.005$, $b = 17.567 \pm 0.008$, $c = 15.901 \pm 0.005$ Å, $\beta = 101.57 \pm 0.02°$. The density calculated for eight molecules of $\mathrm{Ni(ISQTC)_2 \cdot H_2O}$ per unit cell is 1.451 g/cm³, while the value observed by flotation is 1.42 g/cm³. The thin lathlike nature of the crystals made the density determination less accurate than one would normally expect.

The intensity data were collected using a General Electric XRD-6 automatic diffractometer and employing the stationary-crystal–stationary-counter technique. The radiation used was Mo Kα with reasonable monochromatization achieved by means of a zirconium filter and pulse height analyzer. All the 9300 reflections in the hemisphere with $2\theta \leq 50.0°$ were measured from which 4292 unique reflections were obtained after averaging. The 2464 reflections which were greater than 1.16 times the background count were considered to be observed and were used in the structure analysis. A correction was applied for the variation of the four standard reflections which were measured after every 100 reflections. Since the crystal was very small and the linear absorption coefficient for molybdenum radiation was only 9.9 cm⁻¹, no absorption corrections were applied.

Structure Determination

A three-dimensional Patterson synthesis was computed and the positions of the nickel and two sulfur atoms were deduced. A Fourier synthesis with the phases of these atoms revealed the positions of all the remaining atoms except hydrogen. Their coordinates were refined by a second Fourier synthesis. The *R* index was 0.16.

The refinement was continued by the least-squares method. Four cycles of full-matrix least-squares calculations with individual isotropic temperature factors brought the *R* index to 0.12. A difference map at this stage clearly showed a molecule of water of hydration. When this oxygen atom also was included in the least-squares calculations, the *R* index dropped to 0.089 after four cycles of isotropic refinement, starting from the Fourier coordinates. Block-diagonal least-squares calculations using anisotropic temperature factors gave an *R* index of 0.071 after four cycles. A difference map indicated the possible positions of all the hydrogen atoms. No large spurious peaks were observed in this difference Fourier, indicating the correctness of the structure and refinement. The contributions of the hydrogen atoms were included in subsequent calculations and were not refined. Their thermal motion was assumed to be isotropic and they were given a slightly higher value than the atom to which they were bonded. Four additional cycles of block-diagonal least-squares reduced the *R* index, for the observed reflections only, to 0.060. The indicated shifts in parameters were small (maximum 0.8σ) and thus the refinement was considered complete. The final atomic parameters are given in Tables I–III.[5]

Table I. Final Positional Parameters of Nonhydrogen Atoms and Their Estimated Standard Deviations[a]

Atom	$x\ (\sigma_x)$	$y\ (\sigma_y)$	$z\ (\sigma_z)$
N1	2,017 (3)	1287 (3)	3,194 (4)
N2	2,169 (3)	1706 (3)	1,668 (3)
N3	2,292 (3)	1904 (3)	883 (3)
N4	2,697 (4)	1500 (3)	−300 (4)
N5	1,266 (3)	181 (3)	1,854 (4)
N6	2,520 (3)	−372 (3)	2,759 (3)
N7	3,169 (3)	−597 (3)	3,299 (4)
N8	4,358 (4)	−262 (4)	3,957 (5)
C1	1,830 (4)	1994 (4)	2,969 (4)
C2	1,998 (4)	1029 (5)	3,989 (5)
C3	1,767 (5)	1483 (5)	4,582 (5)
C4	1,539 (4)	2246 (5)	4,376 (5)
C5	1,309 (5)	2763 (6)	4,957 (6)
C6	1,106 (6)	3495 (6)	4,726 (6)
C7	1,114 (5)	3740 (5)	3,892 (6)
C8	1,348 (5)	3274 (4)	3,315 (5)
C9	1,566 (4)	2515 (4)	3,545 (5)
C10	1,908 (4)	2220 (4)	2,116 (4)
C11	2,520 (4)	1324 (4)	463 (4)
C12	1,260 (4)	−558 (4)	2,023 (4)
C13	620 (5)	513 (4)	1,395 (5)
C14	−20 (5)	87 (5)	1,078 (6)
C15	−28 (4)	−698 (5)	1,197 (5)
C16	−662 (5)	−1164 (6)	831 (6)
C17	−625 (5)	−1920 (6)	933 (7)
C18	43 (5)	−2276 (6)	1,403 (6)
C19	659 (4)	−1836 (5)	1,796 (6)
C20	643 (4)	−1042 (4)	1,691 (4)
C21	1,958 (4)	−834 (3)	2,573 (4)
C22	3,714 (4)	−70 (4)	3,404 (4)
O1	4,404 (3)	805 (4)	980 (4)
Ni	23,652 (5)	6678 (5)	22,026 (5)
S1	25,902 (11)	3781 (10)	7,828 (11)
S2	36,906 (11)	7920 (11)	28,880 (12)

[a] All values are multiplied by 10^{-4} except for Ni, S1, and S2 which are multiplied by 10^5.

The weighting scheme used was $F_o < 2F_T$ if $\sqrt{w} = F_o/2F_T$; $2F_T \geq F_o \leq 5F_T$ if $\sqrt{w} = 1.0$; $F_o > 5F_T$ if $\sqrt{w} = 5F_T/F_o$; $F_o < 0$ (unobserved) if $\sqrt{w} = 0.0$. F_T is the nominal minimum value of F_o, in this case 23.5. The quantity $\Sigma w(|F_o| - |F_c|)^2$ was minimized in the least-squares calculations. The standard deviations were calculated from the inverse matrix element. The standard deviations for bond distances and angles were computed from the standard deviations for the individual atoms involved in the angle or distance. The scat-

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(3) F. A. French and E. J. Blanz Jr., *ibid.*, 25, 1454 (1965).

(4) C. Bridle and T. R. Lomer, *Acta Cryst.*, 19, 483 (1965).

(5) Calculated and observed structure factors for $\mathrm{Ni(ISQTC)_2}$ are deposited as Document No. NAPS-00669 with the ASIS National Auxiliary Publication Service, c/o CCM Information Service, Inc., 22 West 34th St., New York, N. Y. 10001. A copy may be secured by citing the document number and remitting $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.

Table II. Final Thermal Parameters with Their Estimated Standard Deviations in Parentheses[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N1	35 (2)	27 (2)	31 (3)	−3 (4)	25 (4)	5 (4)
N2	30 (2)	23 (2)	28 (3)	0 (3)	23 (4)	3 (4)
N3	33 (2)	23 (2)	24 (2)	2 (3)	26 (4)	−2 (3)
N4	43 (3)	24 (2)	26 (2)	9 (4)	27 (4)	8 (4)
N5	23 (2)	28 (2)	41 (3)	10 (4)	6 (4)	−3 (4)
N6	19 (2)	25 (2)	23 (2)	3 (3)	8 (3)	−2 (4)
N7	21 (2)	27 (2)	38 (3)	1 (4)	5 (4)	8 (4)
N8	22 (2)	57 (3)	53 (4)	1 (5)	16 (5)	11 (6)
C1	35 (3)	21 (2)	31 (3)	−5 (4)	33 (5)	−10 (5)
C2	32 (3)	40 (3)	36 (4)	−1 (5)	26 (5)	9 (6)
C3	46 (4)	48 (4)	31 (3)	−5 (6)	36 (6)	0 (6)
C4	36 (3)	45 (4)	35 (4)	−11 (5)	42 (5)	−22 (6)
C5	51 (4)	57 (4)	41 (4)	−7 (7)	44 (7)	−29 (7)
C6	52 (4)	55 (4)	65 (5)	−5 (7)	52 (8)	−59 (8)
C7	52 (4)	41 (4)	62 (5)	−8 (6)	57 (8)	−22 (7)
C8	51 (4)	26 (3)	52 (4)	4 (5)	45 (7)	−18 (6)
C9	33 (3)	28 (3)	36 (3)	−12 (4)	33 (5)	−15 (5)
C10	40 (3)	21 (2)	34 (3)	4 (4)	26 (5)	−4 (5)
C11	24 (3)	29 (3)	30 (3)	−1 (4)	8 (4)	−7 (5)
C12	22 (2)	27 (3)	27 (3)	0 (4)	12 (4)	−2 (4)
C13	36 (3)	34 (3)	52 (4)	10 (5)	6 (6)	14 (6)
C14	28 (3)	56 (4)	49 (4)	7 (6)	−9 (6)	7 (7)
C15	28 (3)	49 (4)	41 (4)	−11 (6)	16 (5)	−3 (7)
C16	34 (4)	72 (5)	48 (4)	−28 (7)	5 (6)	−18 (8)
C17	33 (4)	80 (6)	67 (5)	−45 (7)	16 (7)	−26 (9)
C18	46 (4)	53 (4)	63 (5)	−36 (7)	24 (7)	−14 (8)
C19	32 (3)	39 (3)	51 (4)	−24 (5)	24 (6)	−9 (6)
C20	25 (3)	41 (3)	32 (3)	−8 (5)	20 (5)	−10 (5)
C21	27 (2)	17 (2)	39 (3)	−2 (4)	19 (4)	2 (4)
C22	25 (2)	29 (3)	32 (3)	1 (4)	18 (5)	−9 (5)
O1	35 (2)	56 (3)	88 (4)	7 (4)	25 (5)	−4 (6)
Ni	249 (3)	219 (3)	257 (3)	4 (6)	132 (5)	42 (7)
S1	359 (7)	218 (6)	297 (8)	21 (11)	153 (12)	−13 (11)
S2	301 (7)	318 (7)	344 (8)	−130 (12)	79 (12)	37 (13)

[a] The temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. The values are multiplied by 10^4 except for the nickel and sulfur atoms which are multiplied by 10^5.

tering factor curves given in the "International Tables for X-ray Crystallography"[6] were used in all the calculations.

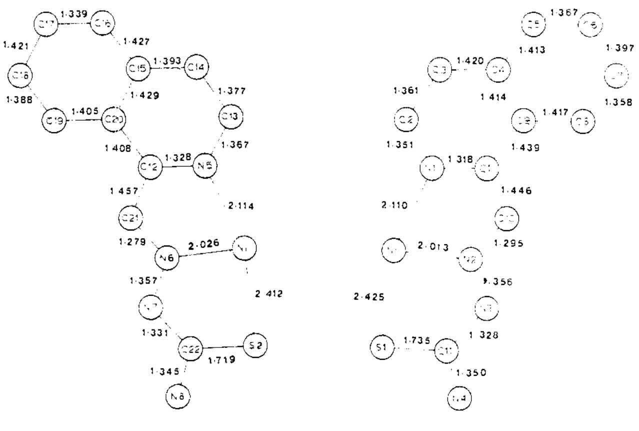

Figure 1. Atomic numbering and bond distances in the chelate rings of bis(isoquinoline-1-carboxaldehyde thiosemicarbazonato)-nickel(II). The estimated standard deviation for the N–N bonds is 0.008 Å, for the C–N bonds 0.009 Å, and for the C–C bonds 0.012 Å.

Discussion of the Structure

The nickel atom is octahedrally coordinated by the two approximately planar tridentate ISQTC ligands. Therefore, the assumption of French and Blanz[2] regarding the chelating ability of the thiosemicarbazone is confirmed. The intramolecular distances and atom numbering in the molecule are illustrated in Figure 1 and the intramolecular angles are given in Table IV. The nickel atom is coordinated to a nitrogen atom of the isoquinoline ring and a nitrogen and sulfur atom of the thiosemicarbazone group. Because of the approximate planarity of the ISQTC ligand, the sulfur atoms are required to be *cis* to each other. The octahedron distorts

Table III. Positional Parameters ($\times 10^3$) and the Isotropic Thermal Parameter of the Hydrogen Atoms

Atom	Bonded to	x	y	z	B, Å^2
H1	O	376	69	86	5.4
H2	O	456	139	93	5.4
H3	N4	283	118	−77	4.0
H4	N4	268	206	−44	4.0
H5	C2	210	39	409	4.4
H6	C3	181	134	516	4.8
H7	C5	135	263	559	5.7
H8	C6	94	387	513	6.4
H9	C7	100	429	362	6.0
H10	C8	129	346	262	5.0
H11	C10	174	276	187	3.8
H12	N8	428	−41	450	5.6
H13	N8	484	2	410	5.6
H14	C13	62	111	140	5.2
H15	C14	−46	41	72	5.5
H16	C16	−117	−95	44	6.0
H17	C17	−109	−225	95	6.9
H18	C18	5	−285	145	6.4
H19	C19	115	−214	220	4.8
H20	C21	196	−134	266	3.7

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(6) "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, 1962, p 202.

Table IV. Bond Angles (Degrees) in the Molecule and Their Estimated Standard Deviations

a. Angles around Nickel			
S1–Ni–N2	81.1 (2)	S2–Ni–N6	81.3 (2)
S1–Ni–N6	100.6 (2)	S2–Ni–N2	100.4 (2)
N1–Ni–N2	78.2 (2)	N5–Ni–N6	77.7 (2)
N1–Ni–N6	100.0 (2)	N5–Ni–N2	100.5 (2)
N1–Ni–S2	91.5 (2)	N5–Ni–S1	89.5 (2)
N1–Ni–S1	158.9 (2)	N5–Ni–S2	159.0 (2)
N1–Ni–N5	90.3 (2)	S1–Ni–S2	96.2 (1)
N2–Ni–N6	177.5 (2)		
B. Angles in the ISQTC Molecules			
Ni–S1–C11	93.2 (2)	Ni–S2–C22	93.7 (2)
S1–C11–N4	117.9 (5)	S2–C22–N8	118.0 (5)
S1–C11–N3	126.7 (5)	S2–C22–N7	127.3 (5)
N3–C11–N4	115.2 (6)	N7–C22–N8	114.6 (6)
C11–N3–N2	112.8 (5)	C22–N7–N6	112.9 (5)
Ni–N2–N3	125.1 (4)	Ni–N6–N7	124.3 (4)
Ni–N2–C10	116.9 (5)	Ni–N6–C21	116.0 (4)
N3–N2–C10	118.0 (6)	N7–N6–C21	119.6 (5)
N2–C10–C1	116.0 (6)	N6–C21–C12	117.8 (6)
C10–C1–N1	116.5 (6)	C21–C12–N5	114.0 (6)
C10–C1–C9	121.9 (6)	C21–C12–C20	122.5 (6)
N1–C1–C9	121.6 (6)	N5–C12–C20	123.6 (6)
Ni–N1–C1	112.4 (5)	Ni–N5–C12	112.8 (4)
Ni–N1–C2	126.3 (5)	Ni–N5–C13	127.5 (5)
C1–N1–C2	121.3 (6)	C12–N5–C13	119.0 (6)
N1–C2–C3	121.2 (7)	N5–C13–C14	121.0 (7)
C2–C3–C4	120.6 (8)	C13–C14–C15	121.2 (8)
C3–C4–C9	117.9 (7)	C15–C15–C20	117.7 (7)
C3–C4–C5	124.4 (8)	C14–C15–C16	122.8 (8)
C9–C4–C5	117.7 (7)	C20–C15–C16	119.5 (7)
C4–C5–C6	121.7 (9)	C15–C16–C17	120.4 (9)
C5–C6–C7	119.5 (9)	C16–C17–C18	121.1 (9)
C6–C7–C8	121.3 (9)	C17–C18–C19	120.0 (9)
C7–C8–C9	120.0 (8)	C18–C19–C20	120.4 (8)
C8–C9–C4	119.7 (7)	C19–C20–C15	118.7 (7)
C8–C9–C1	122.9 (7)	C19–C20–C12	124.0 (7)
C4–C9–C1	117.4 (7)	C15–C20–C12	117.3 (7)

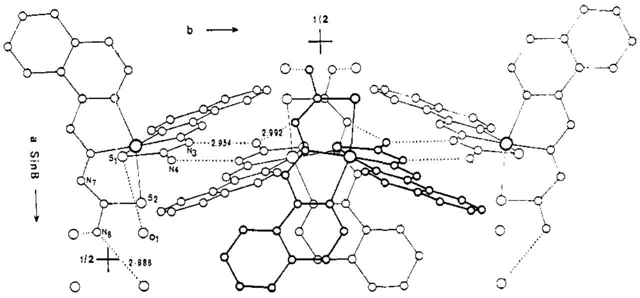

Figure 2. View down the *c* axis, illustrating the molecular packing and hydrogen-bonding scheme.

Table V. Ni–S Distances (Å) in Ni(II) Octahedral Complexes

Compound	Ni–S, Å	Coordinating atoms	Ref
Bis(isoquinoline thiosemicarbazonato)nickel(II) monohydrate	2.424 (2), 2.412 (2)	2S, 4N	Present work
Bis(thiourea)nickel(II) thiocyanate	2.564 (9), 2.531 (6)	4S, 2N	6
Tetra(thiourea)nickel(II) chloride	2.46	4S, 2Cl	7
Thiosulfate tetra(thiourea)nickel(II) monohydrate	2.396, 2.399, 2.442, 2.469	5S, 1O	8
trans-Dichlorotetrakis(ethylenethiourea)nickel(II)	2.490 (6), 2.451 (5)	4S, 2Cl	9
	2.443, 2.482	4S, 2Cl	9
Dichlorotetrakis(trimethylenethiourea)nickel(II)	2.465 (5), 2.491 (5)	4S, 2Cl	10
Bis(2-thioimidazolidine)nickel(II) thiocyanate	2.507 (8), 2.544 (14)	4S, 2N	11
Bis(thioacetamide)nickel(II) thiocyanate	2.446 (10), 2.546 (10)	4S, 2N	12

so that the S···S distance is increased to 3.601 ± 0.004 Å. Some distortion may be introduced because of the four five-membered chelate ring systems present in the molecule. Least-squares planes were calculated for all four chelate rings, and in all cases the rings were definitely nonplanar. The deviations from planarity ranged from −0.057 to +0.084 Å, with an average deviation of 0.038 Å. However, these deviations are sufficiently small so that the rings can be viewed as being approximately planar.

The nickel–sulfur bond lengths of 2.425 and 2.412 Å (both ±0.002 Å) are in the low end of the range 2.4–2.6 Å generally accepted for Ni–S distances in octahedral molecules. However, in all cases given in Table V,[7–13] the nickel atom is bonded to at least four sulfur atoms. Since longer Ni–S bonds would reduce the distortions due to S···S contacts between ligands, presumably the shorter bonds are an electronic effect. The two Ni–S bond lengths are significantly different according to criteria proposed by Cruickshank and Robertson.[14] The longer Ni–S1 distance may be a consequence of the rarely encountered O—H···S hydrogen bond formed between S1 and the water molecule (see Figure 2). The environment of S1 is therefore chemically different from S2. The corresponding C11–S1 bond is also longer than C22–S2, but the difference is not significant.

The C–S bond distances (C11–S1 = 1.735 (7) and C22–S2 = 1.719 (7) Å) appear to be significantly longer than those reported in free thiosemicarbazones (1.678 ± 0.002 Å in 4-formylpyridine thiosemicarbazone,[15] 1.684 ± 0.004 Å in 2-keto-3-ethoxybutyraldehyde bis(thiosemicarbazone),[16] 1.695 ± 0.004 Å in 2-formylthiophene thiosemicarbazone[17]). A similarly significant increase in the C–S distance has been observed in free thiourea and the thiourea–nickel(II) complex.[7] The previous conclusion by Nardelli and coworkers[18]

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Table VI. Hydrogen Bonds

Bond D—H···A[a]	Position of A	D—H, Å	H···A, Å	D···A, Å	D—H···A angle, deg
N4—H3···N7	$x, -y, -\frac{1}{2} + z$	1.00	1.99	2.992 (8)	175
N4—H4···N3	$\frac{1}{2} - x, \frac{1}{2} - y, -z$	1.01	1.96	2.954 (8)	170
N8—H13···O1	$1 - x, y, \frac{1}{2} - z$	0.98	1.95	2.888 (8)	158
N8—H12···O1	$x, -y, \frac{1}{2} + z$	0.94	2.42	3.341 (8)	167
O1—H1···S1	x, y, z	1.14	2.14	3.282 (6)	172

[a] Donor—hydrogen···acceptor. D—H at x, y, z.

that coordination causes an increasing of the single-bond character for C–S bonds seems to remain valid.

The bond lengths of nickel to the nitrogen atoms of the isoquinoline ring (Ni-N1 is 2.110 and Ni-N5 is 2.114 Å, both ±0.006 Å) are equal but significantly different from the nickel to nitrogen distances in the thiosemicarbazone chain (Ni-N6 is 2.026 and Ni-N2 is 2.013 Å, both ±0.005 Å). The question of whether the difference is related to the basicity of the two types of nitrogen atoms or is a result of the approximately planar nature of the ligand cannot be answered at present. However, both Ni-N distances are within the range found in other octahedral nickel complexes.[13] The angles in the chain involved in the N-Ni-N chelate ring are all less than 120°, while two of the angles in the N-Ni-S ring are larger than 120°. Studies in progress on uncomplexed thiosemicarbazones suggest that, as expected, the distances and angles in the ligand change on forming the metal complex.

The isoquinoline rings do not appear to be strictly planar; however, the distances and angles in the isoquinoline group are not precisely determined. Furthermore, the lack of data on the planarity of quinoline or isoquinoline rings makes valid comparisons of this feature impossible.

The packing of the molecules in the unit cell as viewed along *c* is shown in Figure 2. All the interatomic distances less than 4.0 Å were calculated. These distances were either hydrogen-bonded contacts or else the usual van der Waals contacts. The molecules are held together by N—H···N, N—H···O, and O—H···S hydrogen bonds. A summary of the hydrogen-bond dimensions is given in Table VI.

One NH_2 group, N4, forms two strong N—H···N hydrogen bonds, one to N3 with an N4-N3 distance of 2.954 Å and another to N7 with the N4-N7 distance of 2.992 Å. The N4-N3 hydrogen bonds are between two molecules related by a center of symmetry. The configuration is similar to the carboxylic acid dimers. The result is a linking of the molecules along the *b* direction. The second hydrogen-bond N4-N7 system links the molecules in the *c* direction.

The second NH_2 group, N8, forms two short N—H···O contacts to the water molecule. The N8—H···O distance of 2.888 Å is certainly a hydrogen bond. This N—H···O hydrogen bond together with an O—H···S hydrogen bond links the molecules in the *a* direction. The second N8-O contact of 3.341 Å is longer than the usual N—H···O hydrogen bond. However, the H···O distance of 2.42 Å is definitely less than a van der Waals contact of 2.6 Å. The slight shortening of the H···O distance together with the satisfactory N—H···O angle of 167° leads us to suggest that this contact is a very weak N—H···O hydrogen bond.

The hydrogen atoms on the water molecule (O1) were difficult to locate. The long O-H distance of 1.14 Å as well as the short S···H distance of 2.14 Å are a reflection of the inaccurate hydrogen positions. Although the O—H···S hydrogen bond is rare, our value of 3.282 Å for the O1-S1 distance is in excellent agreement with the other reported cases,[19] the range being 3.21–3.37 Å with a mean of 3.28 Å. The presence of a proton between O1 and S1 is indicated by the appropriate maximum in the difference Fourier synthesis and by the hydrogen bonds from N8. Although the angles N8-O1-S are displaced by about 18° from the ideal tetrahedral value, the location of the hydrogen atoms must be in the direction of S1 and S2. The distance from O1 to S2 of 3.518 Å is long and the angles are not suitable for a second O—H···S hydrogen bond.

The result of the hydrogen bonding is a sheet-like structure formed by N—H···N hydrogen bonds extending in the *ab* plane. The sheets are linked by the O—H···S and N—H···O bonds in the *a* direction. It is interesting to speculate upon whether the rare O—H···S hydrogen bond may become an important feature in sulfur-containing molecules of biological importance.

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