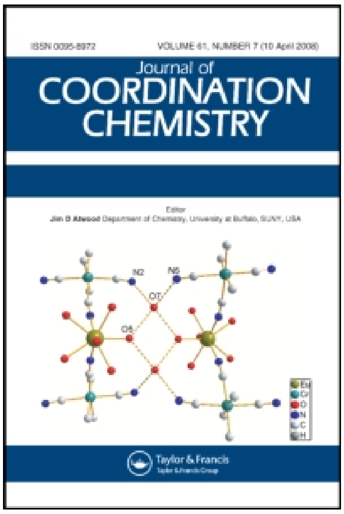

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THE CRYSTAL, MOLECULAR STRUCTURE AND LIGAND BONDING IN TETRAKIS (N,N′-DIMETHYLTHIOUREA) NICKEL (II) BROMIDE DIHYDRATE

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The crystal structure of tetrakis(N,N′-dimethylthiourea)nickel(II) bromide dihydrate has been determined by three-dimensional x-ray diffraction from 1916 counter-data reflections collected at room temperature.

The structure consists of $Ni[SC(NH)_2(CH_3)_2]_4^{2+}$ molecular ions, Br^- ions and waters of hydration. The nickel is located on a center of symmetry and is coordinated to four sulfur atoms in a square planar configuration. The waters of hydration and the bromide ions are involved in hydrogen bonding to the N,N′-dimethylthiourea (dmtu) groups. The orientation of the dmtu groups is such that two bond through the sulfur sp^2 orbital and the others bond through the π-orbitals of the dmtu group. The Ni–S distances are 2.204 ± 0.002 Å and 2.230 ± 0.002 Å, and the Ni–S–C angles are 106.2 ± 0.2Å and 110.3 ± 0.3°. The dmtu groups are planar except for methyl hydrogens.

The crystals are monoclinic, $P2_1/a$ with $a = 13.424 \pm 0.002$ Å, $b = 12.321 \pm 0.005$ Å, $c = 8.460 \pm 0.008$ Å $\beta = 107.07 \pm 0.05°$, $\rho_0 = 1.67$ g cm^{-3}, $\rho_c = 1.66$ g cm^{-3} and Z = 2. The structure was refined by full-matrix least-squares to a conventional R of 0.0466.

INTRODUCTION

Thiourea {$[SC(NH_2)_2]$ = tu} and its derivatives bind to metal ions in a variety of modes. For example, with the d^{10} ions, Cu(I) and Ag(I), the sulfur atom bridges metals, utilizing two lone pairs,[1,2] or sulfur may act as a simple sp^2 single lone pair donor,[3,4] or it may behave as a pπ electron pair donor, [1,2] or as a bridging atom using both sp^2 and pπ electron pairs simultaneously.[5] With transition metal ions such as Ni(II) and Co(II), thiourea behaves primarily as a sulfur single sp^2 electron pair donor.[6,7,8] However, one of the thiourea groups in $Cotu_4(NO_3)_2$[7] behaves as a S–C pπ electron pair donor. $Nitu_6^{2+}$ (green) is a normal octahedral Ni^{+2} species as seen from its solution spectra, magnetic moment,[9] and crystal structure[6] and $Nitu_4Cl_2$[8] is an olive green normal distorted octahedral structure. The present compound, (heretofore unreported) on the other hand, is a dark blue crystalline material. Its color and optical solution spectrum invited a crystal structure study which we report herein.

EXPERIMENTAL

Dark blue single crystals were grown by slow evaporation from a solution of equal volumes of 0.0025 M $NiBr_2$ and 0.01 M N,N′-dimethylthiourea (dmtu). Preliminary Weissenberg and precession film data showed the crystals to have the following systematic extinctions: for h0l, h = 2n + 1; for 0k0, k = 2n + 1; indicating the space group $P2_1/a$.[10] With two molecules per unit cell the calculated density was 1.66 g cm^{-3}, while the observed density measured in 1,2-dibromethylene and 1,2-dichloroethane mixture was 1.67 g cm^{-3}. A crystal with dimensions 0.30 x 0.30 x 1.00 mm[11] was mounted along the needle axis, c^*, and aligned on a full-circle Picker card-operated automated diffractometer by local variations of well known methods.[12a,b] The cell constants were obtained from a least-squares refinement of the χ, φ and 2θ angles of six general and six axial reflections.[13a] The values obtained were $a = 13.424 \pm 0.002$ A, $b = 12.321 \pm 0.005$ A, $c = 8.460 \pm 0.008$ A, and $\beta = 107.07 \pm 0.05°$ A. Using a Zr filter with MoKα radiation, 3076 independent hkl intensities were measured to 2θ = 60°. Backgrounds were measured at ± 0.75° 2θ from the peak maximum for 20 seconds and the peaks were scanned for forty-five seconds (1.5°, 2θ) by the usual θ–2θ scan technique. Data were collected to 60° in the octants hkl and $\bar{h}$kl. A standard reflection (hkl = 4,4,3)[13b] was measured every ten reflections to monitor the stability of the operation. The total

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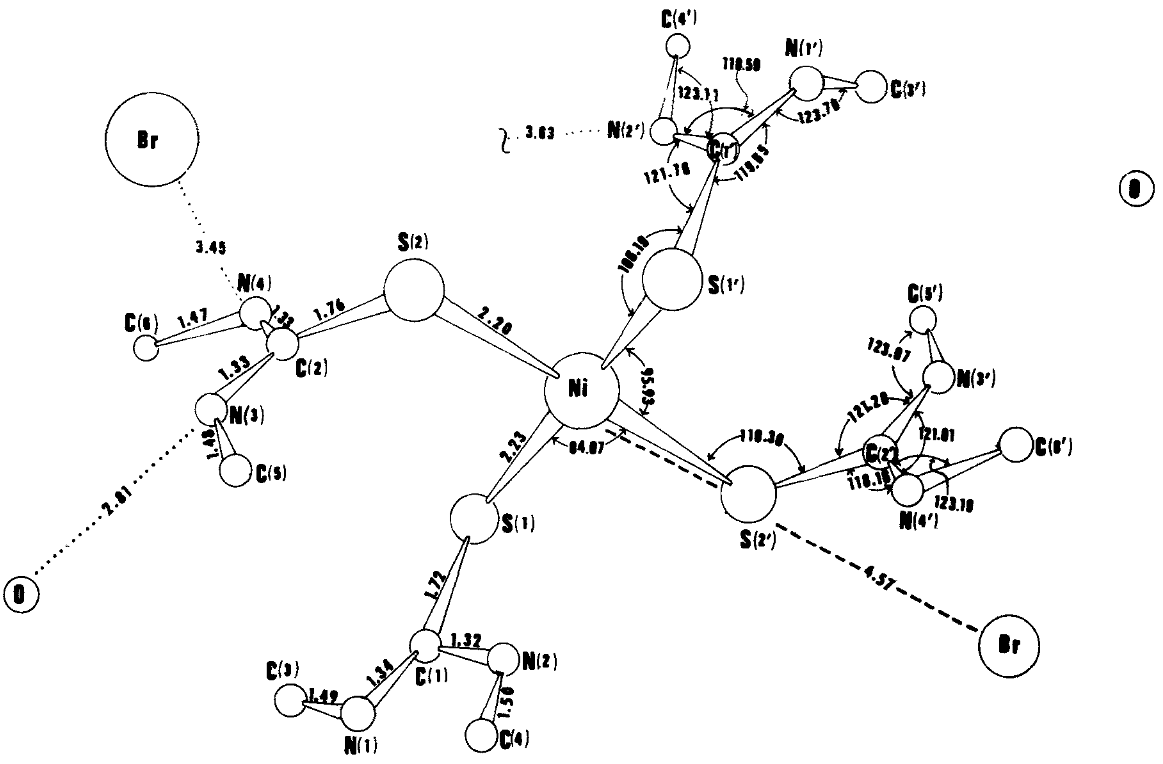


FIGURE 1 A perspective view of the $Ni[SC(NHCH_3)_2]_4^{+2}$ molecular ion showing distances and angles. Possible hydrogen bonds are indicated by dotted lines. For simplicity the N(2') to Br possible hydrogen bond is shown truncated. Primes refer to atoms related by the center of symmetry at the Ni atm. Hence, distances are on one-half of the molecular ion and angles on the other half. The Ni-Br interaction is shown by dashed lines.

variation in the standard reflection from one standard to the next was no more than two percent of the total scan intensity and no more than 1.2σ (definition below). The standard peak showed a slow steady decrease in intensity during the period of data collection, presumably from decomposition, amounting to approximately 21 percent. A 2θ and ω scan were taken of the standard peak and the half-width spread at half-peak height was measured to establish the mosaic spread of the crystal. The spread was no more than 0.20° which indicated that the entire peak was scanned for each reflection.

Forty-eight (48) symmetry related reflections (six groups) were measured to determine the accuracy of the matrix orientation and verify the crystal system. No more than a difference of 1.5 σ appeared in the total scan intensity of any symmetry related reflections. The source to crystal distance was 18 cm while the crystal to counter distance was 23.0 cm. The take-off angle was 3.8° and the counter aperature was 6 mm x 8 mm (high). The incident beam and receiving beam and receiving collimators were both 1.5 mm in diameter.

The net integrated intensity was calculated, assuming a linear variation in background, from the function $I(net) = I(scan) - 1.125(B_1 + B_2)$, where B_1 and B_2 are the background counts. The standard reflection was used to scale the data for each section of ten reflections. The variation of the standard from measurement to the next was well within counting statistics σ, where $\sigma I(net) = [I(scan) + (1.125)^2 (B_1 + B_2)]^{1/2}$. Reflections were considered absent if their I(net) was less than $3.0[1.125^2 (B_1 + B_2)]^{1/2}$. Based on this criterion, 1917 non-zero reflections remained. The I(net) were reduced to relative structure factors by use of the Lorentz-polarization factor. The linear absorption coefficient, μ, is 41.92 cm^{-1}. An absorption

TABLE Ia

Final atomic positional and thermal parameters and estimated standard deviations.
(esd of last figure in parentheses)
anisotropic temperature factors of the form:

$$\exp-[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl] \times 10^4$$

Atom	x	y	z
Ni	0.0000(–)	0.0000(–)	0.0000(–)
Br	0.3188(1)	–0.1150(7)	0.3197(1)
S(1)	–0.0740(1)	–0.0792(2)	0.1743(2)
S(2)	0.0193(2)	0.1500(2)	–0.1300(2)
C(1)	0.0260(5)	0.1103(6)	0.3492(8)
C(2)	–0.0253(6)	0.2630(6)	–0.0419(9)
C(3)	–0.0915(6)	0.2365(7)	0.4398(10)
C(4)	0.2073(6)	0.0890(8)	0.5311(11)
C(5)	0.1538(6)	0.3051(7)	0.1336(11)
C(6)	–0.1725(6)	0.3794(7)	–0.0320(11)
N(1)	0.0096(5)	0.1808(6)	0.4590(8)
N(2)	0.1197(5)	0.0665(5)	0.3780(8)
N(3)	0.0406(5)	0.3252(5)	0.0704(8)
N(4)	–0.1267(5)	0.2865(5)	–0.0957(8)
O	0.0332(5)	0.4887(5)	0.2983(8)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	32(1)	35(1)	71(2)	–2(1)	16(1)	–8(1)
Br	47(1)	59(1)	180(2)	10(1)	25(1)	18(1)
S(1)	34(1)	48(1)	83(3)	–1(1)	17(2)	12(2)
S(2)	56(1)	39(1)	106(3)	–3(1)	37(2)	–3(2)
C(1)	42(5)	39(5)	72(11)	–7(4)	21(6)	–3(6)
C(2)	46(5)	35(5)	92(13)	–3(4)	15(7)	–7(6)
C(3)	44(5)	78(8)	139(15)	–25(5)	19(8)	22(9)
C(4)	41(5)	94(9)	128(15)	–7(5)	–10(8)	–23(9)
C(5)	37(5)	65(7)	179(17)	4(5)	4(8)	–12(9)
C(6)	31(5)	57(6)	175(16)	–11(5)	15(7)	4(8)
N(1)	46(5)	75(6)	126(12)	–13(4)	25(6)	28(7)
N(2)	39(4)	57(5)	108(11)	3(4)	14(5)	–9(6)
N(3)	32(4)	48(5)	126(11)	–2(3)	14(6)	–8(6)
N(4)	38(4)	50(5)	50(5)	–131(12)	1(4)	–16(6)
O	55(4)	90(6)	176(12)	7(4)	27(6)	–46(7)

[a] (–) indicates fixed parameter.

TABLE Ib

Calculated theoretical hydrogen atom positions.
(only those on Nitrogens)

Atom	x	y	z
H(1)	0.5673	0.3010	0.5603
H(2)	0.6338	0.4866	0.2978
H(3)	0.0139	0.3893	0.1181
H(4)	–0.1753	0.2399	–0.1789

TABLE II
Interatomic distances (A) and angles (degrees)

Bonding distances		Nonbonded Intramolecular distances	
Ni–S(1)	2.230(2)	Ni · · · Br	4.566(09)
Ni–S(2)	2.204(2)	N(3) · · · O	2.810(08)
S(1)–C(1)	1.724(7)	N(1) · · · N(2)	2.288(9)
S(2)–C(2)	1.765(8)	N(3) · · · N(4)	2.317(8)
C(1)–N(1)	1.337(9)	N(2) · · · Br	3.628(6)
C(1)–N(2)	1.323(9)	N(4) · · · $\mathrm{Br}^{\mathrm{III}}$	3.446(6)
C(2)–N(3)	1.334(9)	O · · · $\mathrm{Br}^{\mathrm{III}}$	3.323(6)
C(2)–N(4)	1.334(9)		
N(1)–C(3)	1.486(9)		
N(2)–C(4)	1.498(10)		
N(3)–C(5)	1.475(9)		
N(4)–C(6)	1.466(10)		

Interatomic angles

S(1)–Ni–S(2)	93.9(1)	S(2)–C(2)–N(3)	121.2(5)
Ni–S(1)–C(1)	106.2(7)	S(2)–C(2)–N(4)	118.2(6)
Ni–S(2)–C(2)	110.3(3)	C(1)–N(1)–C(3)	123.8(7)
S(1)–C(1)–N(1)	119.7(5)	C(1)–N(2)–C(4)	123.1(6)
S(1)–C(1)–N(2)	121.8(5)	C(2)–N(3)–C(5)	124.0(6)
N(1)–C(1)–N(2)	118.5(5)	C(2)–N(4)–C(6)	123.2(6)
N(3)–C(2)–N(4)	121.0(6)		

Calculated theoretical hydrogen bond angles

N(2)–H(1) · · · Br	129.9
N(4)–H(4) · · · $\mathrm{Br}^{\mathrm{III}}$	162.0

$^{\mathrm{I}}$x, y, z; $^{\mathrm{II}}\bar{x}, \bar{y}, \bar{z}$; $^{\mathrm{III}}$½ + x, ½ − y, z;

TABLE III
Equations of least-squares planes of the type.[a]
Ax = By + Cz − D = 0

Plane No.	A	B	C	D*
1	−0.7395	0.1271	−0.6611	−4.1807
2	0.2065	−0.8913	−0.4037	−4.1051
3	−0.7815	0.1023	−0.6155	−4.6150
4	0.4483	−0.7490	−0.4879	−2.2009
5	0.3752	−0.5800	−0.7230	0.9949

*The molecule is located at ½, ½, o.

Deviation of atoms from the least-squares plane (A)

Atom	Plane no. 1	Atom	Plane no. 2
S(1)	−0.001(1)	S(2)	0.001(1)
C(1)	0.003(5)	C(2)	−0.013(5)
N(1)	0.000(5)	N(3)	0.002(4)
N(2)	0.017(4)	N(4)	−0.006(4)
C(3)	0.003(6)	C(5)	−0.001(6)
C(4)	−0.023(6)	C(6)	0.010(6)

Dihedral angles between planes

Plane	Plane	Angles (degrees)
Ni, S(1), S(2)	Ni, S(1), C(1)	87.8(3)
Ni, S(1), S(2)	Ni, S(2), C(2)	1.9(3)
Ni, S(1), C(1)	1 (above)	17.2(3)
Ni, S(2), C(2)	2 (above)	84.7(3)

[a] x, y and z refer to internal orthogonal coordinate system ("International Tables for X-ray Crystallography", Vol. II, The Kynoch Press, Birmingham, England, 1967, p. 61).

correction was not made; with the large crystal size the estimates of error are optimistic and more realistic values would be x2.

SOLUTION AND REFINEMENT OF STRUCTURE

With two molecules of Ni(dmtu)$_4^{+2}$ 2Br$^-$ per unit cell, the Ni^{+2} moieties must lie on centers of symmetry arbitrarily chosen as 0,0,0 and 1/2,1/2,0 in P2$_1$/a. The remainder of the non-hydrogen atoms were located by standard heavy atom techniques.[14]

A full-matrix isotropic least-squares refinement converged to an R of 0.108 and weighted R of 0.159. A full-matrix completely anisotropic (excluding hydrogen atoms) least-squares refinement[15] yielded an R of 0.0466, wR of 0.060 and a standard error of 2.41.[16] On the final cycle of refinement the parameter shifts were all less than 0.1 standard deviation and the final parameters are listed in Table I. A final difference electron density map was qualitatively featureless.

The function minimized was $\Sigma w(F_o - F_c)^2$ with weights determined by counting statistics.[17] Scattering factors of Ni^{2+}, Br$^-$, and neutral sulfur, carbon, nitrogen and oxygen were from Cromer and Waber.[18] The effects of anomalous dispersion were included in the structure factor calculation by addition to F_c:[19] the values for $\Delta f'$ and $\Delta f''$ for nickel, bromine and sulfur were those given by Cromer.[20] The final tabulation of observed and calculated structure factors are listed elsewhere.[21] Unobserved data were not used in the structure refinement, but are listed with the calculated structure factors. Interatomic distances and angles and their errors[22] were computed using the parameters and variance–covariance matrix from the last cycle of least squares and are listed in Table II.

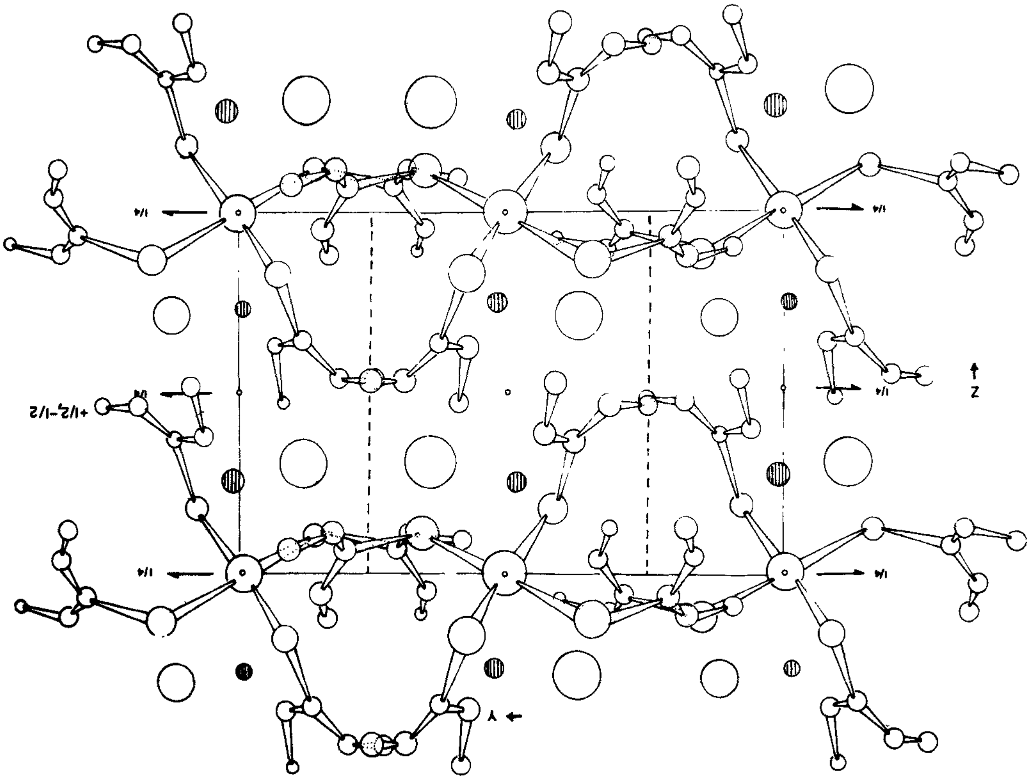


FIGURE 2 A perspective of the contents of the unit cell of Ni[SC(NHCH$_3$)$_2$]$_4^{+2}$ 2Br$^-$. 2H$_2$O looking down a*. The unit cell is outlined in a solid line and the symmetry operations are the conventional symbols. The isolated open circles are Br$^-$ ions and the ruled circles are oxygens of waters of hydration.

TABLE IV
RMS components of thermal displacement along principal axes (A) [esd in parentheses]

	Axis 1	Axis 2	Axis 3
Ni	0.143(2)	0.1617(2)	0.172(2)
Br	0.183(1)	0.219(1)	0.254(1)
S(1)	0.153(3)	0.169(3)	0.201(3)
S(2)	0.169(3)	0.172(3)	0.221(3)
C(1)	0.149(11)	0.164(12)	0.197(11)
C(2)	0.157(12)	0.181(17)	0.200(11)
C(3)	0.149(13)	0.207(12)	0.281(12)
C(4)	0.157(14)	0.236(12)	0.282(12)
C(5)	0.172(13)	0.218(12)	0.266(12)
C(6)	0.150(13)	0.215(12)	0.250(11)
N(1)	0.158(10)	0.202(10)	0.267(10)
N(2)	0.177(10)	0.185(9)	0.219(9)
N(3)	0.162(10)	0.189(10)	0.213(9)
N(4)	0.177(10)	0.191(10)	0.216(9)
O	0.190(9)	0.217(9)	0.301(9)

The dihedral angles between normals to planes and their errors, and the equations of the least-squares planes[23] were computed from the parameters of the last cycle of least-squares refinement and are listed in Table III. Root-mean-square displacements of the thermal ellipsoids are listed in Table IV.

RESULTS AND DISCUSSION

The structure consists of Ni(dmtu)$_4^{2+}$ molecular units (Figure 1) separated by van der Waals interactions (Figure 2). The Ni^{+2} and the four sulfur atoms bound to it define an approximate square planar coordination geometry. Two bromide ions and two waters of hydration are associated with each Ni(dmtu)$_4^{2+}$ molecular unit. The waters of hydration and the bromide ions are involved in hydrogen bonding with the hydrogen atoms on the nitrogens.

The nickel of the molecular ion sits on a center of symmetry. The two crystallographically independent Ni–S distances of 2.230(2)Å and 2.204(2)Å (Table II) are significantly shorter than the sum of the single bond covalent radii [2.43Å].[24a] However, this distance is what is expected for square planar

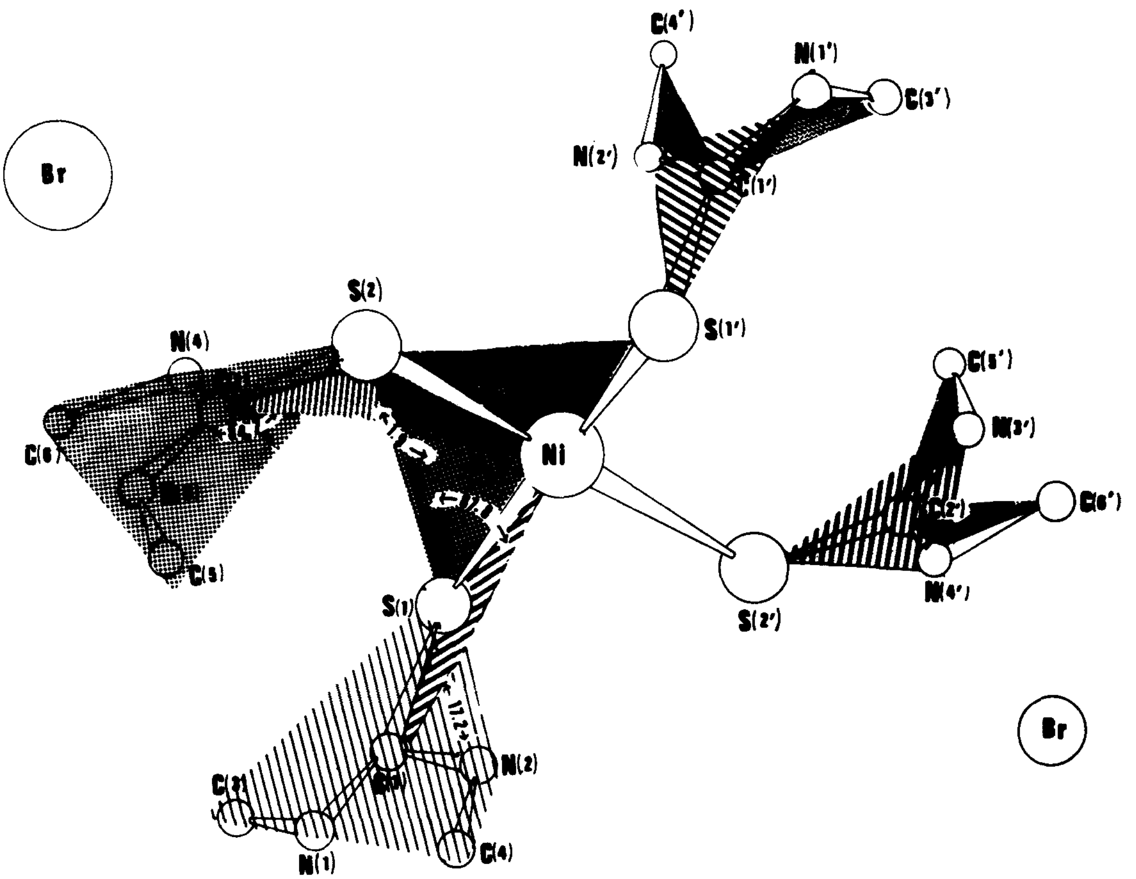


FIGURE 3 A perspective view of the $Ni[SC(NHCH_3)_2]_4^{+2}$ molecular ion showing relevant dihedral angles between planes that are important in specifying the nature of the Ni-S bonding. Notation as in Figure 1.

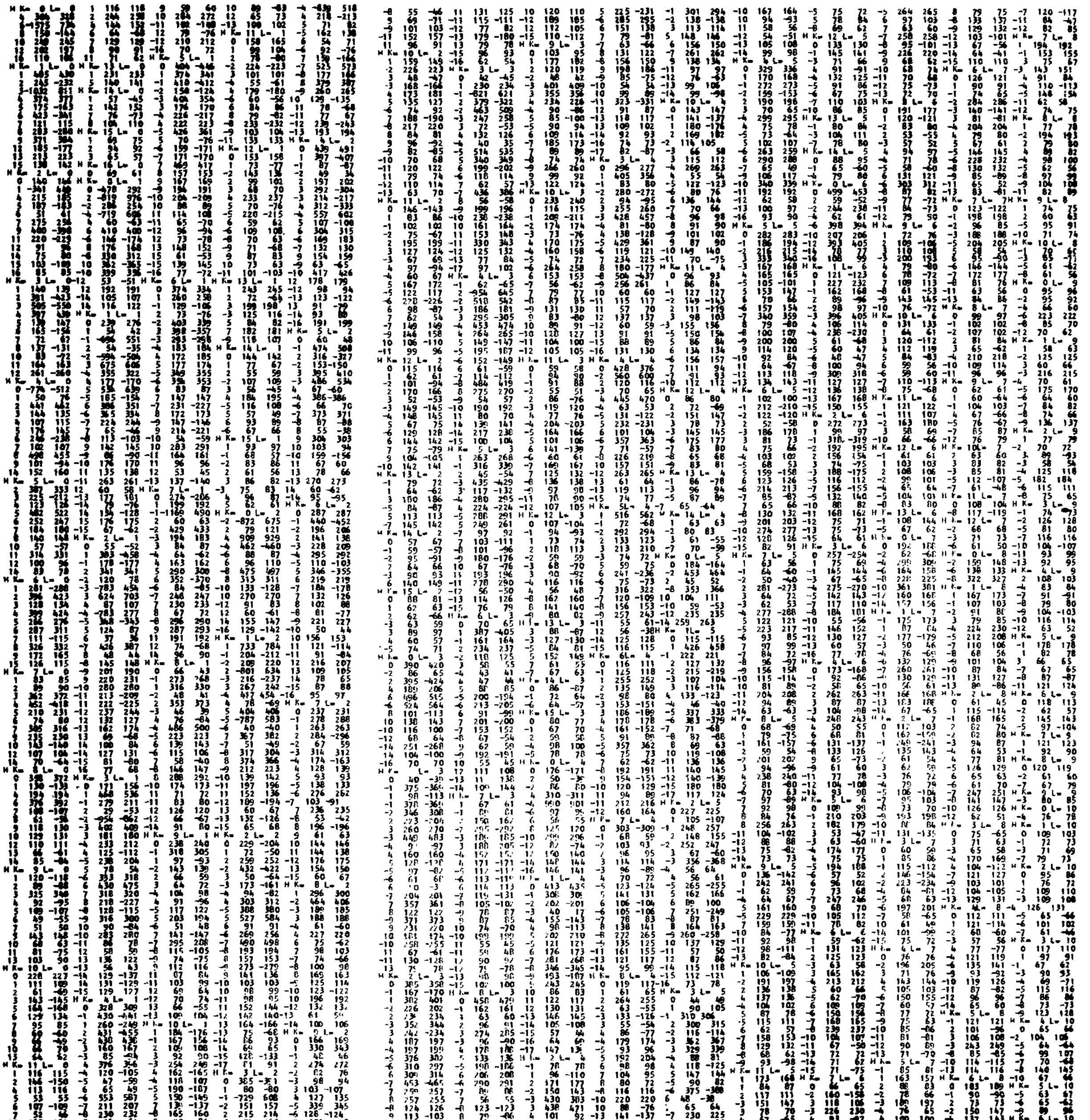
NiS_4^{+2}, e.g. in $Ni(tac)_4Br_2$ (tac = thioacetamide)[25] the Ni—S distances are 2.216(9) and 2.222(9)A, whereas in octahedral NiS_6^{+2}, $[Nitu_6Br_2]$[6], the Ni—S distances are 2.503(6), 2.517(6) and 2.498(6)A.

Although the S—C distances are significantly shorter than a "normal" single bond (1.81Å),[24b] only the S(1)—C(1) distance compares well with free thiourea, 1.720(9)Å by x-ray diffraction[26] and 1.746(9)Å by neutron diffraction.[27]

Both crystallographically independent dmtu groups are planar except for methyl hydrogens and the distances and angles within the groups are those expected. Although the S—C—N angles in thiourea are equal, they are not in this complex. The differences seem to occur due to unequal atomic environments from one side of the ligand to the other.

The normal single bond distance for Ni—Br is 2.50A;[24] this makes the bromine atoms definitely ionic with a Ni—Br distance of 4.566A (Figure 1). Moreover, the Ni—Br distance in $Ni(tac)_4Br_2$ is approximately 1A shorter at 3.599(4)A, and this bromine is considered essentially ionic. The distances and angles indicated in Table II and Figure 1 show possible hydrogen bonding interactions of the type Br——H—N and O——H—N.

The dmtu group [S(2)] which possesses two nitrogen atoms involved in hydrogen bonding has a twist angle of 84.7(3)° and the other dmtu group [S(1)] has a twist angle of 17.1(3)° (Figure 3). The twist angle is defined as the dihedral angle between normals of the least-squares planes of Ni—S—C and the dmtu group. The tilt angle, the dihedral angle between normals of the $Ni—S_4$ plane and the Ni—S—C plane, for the dmtu group [S(2)] is 1.9(3)°, but is 87.8(3)° for the dmtu group [S(1)]. Not only does steric hinderance affect the twist and tilt angles, Observed and calculated structure factors for tetrakis(N,N'-dimethylthiourea)nickel(II) bromide dihydrate. First column is h followed by F(obs) and F(calc). F(calc) = 10.F(calc)$_{\text{absolute}}$.



but also the hydrogen bonding has predetermined the twist and tilt for the dmtu group [S(2)]. These twist and tilt angles, as well as the Ni–S–C angles, are significant in describing the bonding scheme. The Ni–S(1)–C(1) and Ni–S(2)–C(2) angles are not unexpected. The Ni–S(2)–C(2) angle is greater than

Tetrakis(N,N′-dimethylthiourea)nickel(II) bromide dihydrate
Unobserved Reflections with Calculated value Greater than F_{min}. F_{min} is 34. First column is h, followed by k and F(calc) on the same scale as in part a. Unobserved reflections were not included in the refinement.

$F_{min} \leqslant |F(calc)| < 2.0 \times F_{min}$ (234)

L	=	0	−7	13	52	12	0	42	−12	5	41	−5	8	35	−3	11	40	3	2	53
14	0	45	−6	13	45	12	1	47	−5	5	40	−4	8	49	0	11	36	−8	3	45
13	2	44	0	13	38	12	2	40	11	5	50	−9	9	53	−6	12	35	−13	4	63
12	4	41	−4	14	43	−8	3	34	−9	6	38	−3	10	45	−3	12	63	−8	4	41
13	4	49	0	15	54	10	4	43	−10	7	46	−1	10	51	0	12	42	−12	5	41
13	6	37	L	=	2	−14	5	47	1	7	42	3	10	53	L	=	7	−11	5	36
13	7	37	−14	0	34	−10	5	42	−9	8	36	−2	11	49	−12	1	35	−9	5	42
3	8	37	−16	2	45	−12	6	45	−8	9	38	2	12	42	−8	1	50	−7	5	45
11	10	41	9	3	42	−11	6	39	0	9	34	L	=	6	−11	3	39	−10	6	51
12	10	54	−11	4	52	8	6	58	4	9	40	−8	0	44	−9	3	47	1	6	43
3	11	36	−8	4	36	−13	8	37	−9	11	50	−10	1	41	−8	3	40	−2	7	39
10	12	50	10	4	36	−10	8	45	−8	11	43	−14	2	38	−4	4	43	0	7	38
3	13	45	−9	5	36	11	8	39	4	11	54	−4	2	37	−1	4	41	2	7	37
0	14	50	1	5	35	−6	9	49	−4	12	63	−9	3	45	−6	5	40	−3	8	36
3	14	45	−14	6	50	2	10	43	1	12	46	−6	3	42	0	5	45	0	8	40
4	14	45	−6	6	37	3	11	42	−6	14	54	−2	3	41	5	5	35	−8	9	38
5	14	50	9	6	45	−7	12	46	−3	14	39	1	4	40	−12	6	61	−7	9	36
L	=	1	12	7	39	5	12	40	2	14	46	7	4	66	−7	6	40	−1	9	41
−6	2	50	−5	8	36	0	13	49	L	=	5	−9	5	35	−9	7	39	0	9	43
10	2	42	5	8	40	1	13	37	−4	0	50	−9	6	41	1	7	38	L	=	9
−15	4	57	−10	9	43	6	13	38	4	0	35	1	7	40	2	7	41	−9	3	35
−8	5	43	−4	9	43	−4	14	36	8	0	45	−10	8	34	4	7	43	−11	4	41
6	5	34	5	9	43	−3	15	54	−10	1	34	3	8	46	−9	8	34	−6	4	42
−8	6	50	10	9	36	L	=	4	6	1	58	5	8	49	−8	8	47	−5	4	36
9	8	49	−5	10	36	−12	1	34	−12	2	35	−5	9	44	−6	8	44	−2	4	36
10	8	35	8	11	49	−11	1	34	−10	2	51	−2	9	46	−11	9	36	−2	5	42
10	9	38	9	11	35	−10	1	40	−6	2	37	−1	9	37	−10	9	41	1	6	55
−12	10	51	4	12	46	7	1	35	−14	4	52	5	9	38	−4	10	39	0	7	49
−11	10	60	0	13	41	−10	3	42	−8	4	41	−5	10	51	−2	10	44	−6	8	66
11	10	45	3	14	55	9	3	55	1	5	51	−2	10	44	0	10	44	−3	8	46
−10	11	39	4	14	43	−9	4	42	2	5	49	−1	10	40	−5	12	34	L	=	10
−1	11	42	5	14	42	−1	4	42	7	5	45	2	10	42	L	=	8	−6	1	50
−7	12	47	−2	15	42	1	4	42	−14	6	40	−8	11	67	−6	1	39	−5	1	39
−1	12	36	−1	15	37	3	4	34	−13	7	38	−6	11	44	2	1	54	−2	1	52
8	12	41	L	=	3	−13	5	37	4	7	48	−5	11	34	−11	2	57	−1	2	50

$2.0 \times F_{min} \leqslant |F(calc)| \leqslant 3.0 \times F_{min}$ (6)

L	=	0	0	12	78	−3	1	80	L	=	2	1	12	68
2	2	70	L	=	1	8	1	91	0	0	78			

$3.0 \times F_{min} \leqslant |F(calc)|$ (15)

L = 0		L = 1		L = 4		L = 5		3	1 232	L = 7	
2	0 721	−5	7 166	1	1 298	6	0 310	5	4144	7	5 139
10	2 130	L = 2		0	2 231	7	1 104	8	4 209		
9	3 102	−1	2 973	5	3 113	L = 6		5	5 237		

that of Ni–S(1)–C(1) because hydrogen bonding has "opened" the Ni–S(2)–C(2) bond.

The dmtu group [S(1)] bonding to the nickel can be described as taking place through a non-bonding sp^2 orbital of S(1). In contrast, the dmtu group [S(2)] is bonding through the $p\pi$ molecular orbital of the dmtu group and the sp^2 lobes are not involved in bonding. This bonding scheme is indicated by the twist and tilt angles which place the $p\pi$ MO almost coplanar with the $Ni–S_4$ plane and essentially directed toward the nickel. Also the long S(2)–C(2) bond indicates a withdrawal of electron density from the pπ MO.

This is the first nickel(II)-"thiourea" complex which displays bonding for one ligand through the pπ sulfur orbital. Normally bonding is through the sp^2 sulfur orbital, although "mixed" bonding (partially through the sp^2 sulfur orbital and pπ MO of one thiourea) has been observed.[28,29,30] In $Ni(dmtu)_4Br_2 \cdot 2H_2O$ hydrogen bonding has helped to create a situation where bonding of two ligands are through the pπ MO exclusively. The somewhat unexpected color of this complex is due at least in part to this unusual S–Ni binding mode. Spectroscopic details will be reported elsewhere.

REFERENCES

1. a) W. A. Spofford, III and E. L. Amma, *Chem. Comm.*, 405 (1968).
   b) W. A. Spofford, III and E. L. Amma, *Acta Cryst.*, **B26**, 1474 (1970).
2. a) E. A. Vizzini and E. L. Amma, *J. Am. Chem. Soc.*, **88**, 2872 (1966).
   b) E. A. Vizzini, I. F. Taylor, Jr., and E. L. Amma, *Inorg. Chem.*, **7**, 1351 (1968).
3. R. L. Girling and E. L. Amma, *Inorg. Chem.*, **10**, 335 (1971).
4. G. W. Hunt, N. W. Terry, III and E. L. Amma, *Cryst., Struc. Comm.* **3**, 523 (1974).
5. a) M. S. Weininger, I. F. Taylor, Jr. and E. L. Amma, *Inorg. and Nuc. Chem. Letters*, **9**, 737 (1973).
   b) I. F. Taylor, Jr., M. S. Weininger and E. L. Amma, *Inorg. Chem.*, **13**, 2835 (1974).
   c) R. G. Vranka and E. L. Amma, *J. Am. Chem. Soc.*, **88**, 4270 (1966).
6. M. S. Weininger, J. E. O'Conner, and E. L. Amma, *Inorg. Chem.*, **8**, 424 (1969).
7. W. A. Spofford, III, P. Boldrini, E. L. Amma, P. Carfagno and P. S. Gentile, *Chem. Comm.*, 40 (1970).
8. A. Lopez-Castro and M. Truter, *J. Chem. Soc.*, A, 1880 (1968).
9. D. R. Eaton and K. Zaw, *Can. J. Chem.*, **53**, 633 (1975).
10. N. F. M. Henry, and K. Lonsdale, eds., "International Tables for X-Ray Crystallography," Vol. I., The Kynock Press, Birmingham (1969); p. 99.
11. Attempts to cleave crystals perpendicular to the needle axis usually resulted in shattering of the crystal. Since we were primarily interested in the stereochemistry about the Ni^{2+} moiety we decided to proceed in spite of the crystal size.
12. a) W. R. Busing and H. A. Levy, *Acta Cryst.*, **22**, 457 (1967).
    b) K. Knox in "Master Card Programs for Picker Four Angle Programmer," prepared by F. C. Carter, Picker Instruments, Cleveland, Ohio, 1967, p. 11. Local modifications of W. A. Spofford.
13. a) The least-squares program, which computes the lattice dimensions, is based upon ref. 12a, b by W. A. Spofford, for the IBM 1620.
    b) Although it is known that crystals may decompose anisotropically, i.e., different hkl intensities may decrease at different rates, it is always a trade-off of time spent measuring a number of standards against getting the job done and minimizing exposure. This trade-off is particularly significant with the above described slow diffractometer (since revitalized). We have found from experience that one can do almost as well with a single standard (or at least fewer) if it is well chosen as with a larger number. For example, the standard needs to be a general reflection in the middle of the χ, ϕ, 2θ range and of average intensity. Of course, the other extreme is the scaling sets that are needed for protein data collection.
14. Patterson and Electron Density Calculations done on IBM 7040 with ERFR3 program which is a modification of ERFR2 of Sly–Shoemaker–Van den Hende by D. R. Harris.
15. W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, a Fortran Crystallographic Least-Squares Program," Oak Ridge National Laboratory Report ORNL–TM–305 (1962). The version used incorporated modifications by W. A. Spofford.
16. $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$. Weighted $R = \{[\Sigma w(|F_o| - |F_c|)^2]/\Sigma w F_o^2\}^{1/2}$. Standard error $= [\Sigma w(|F_o| - |F_c|)^2]^{1/2}/(NO-NV)$. NO = 1917, NV = 127. The reported R factor does not include unobserved reflections.
17. S. W. Peterson and H. A. Levy, *Acta Cryst.*, **10**, 70 (1957); $w = 1/\sigma^2$; $\sigma^2(F^2) = S/(LP)^2 [I(scan) + (1.5)^2 (B_1 + B_2) + (0.004I(scan))^2]^{1/2}$; $\sigma^2(F) = S/LP$. $1/F\ [I(scan) + (1.5)^2 (B_1 + B_2) + (0.004I(scan))^2]^{1/2}$ where S = a scale factor and Lp is the Lorentz-polarization factor.
18. D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965).
19. J. A. Ibers and W. C. Hamilton, *Acta Cryst.*, **17**, 781 (1964).
20. D. T. Cromer, *Acta Cryst.*, **18**, 17 (1965).
21. A complete listing of calculated and observed structure factors is available from the authors and is deposited on microfilm.
22. W. R. Busing, K. O. Martin and H. A. Leavy, "ORFFE, A Fortran Crystallographic Function and Error Program," Oak Ridge National Laboratory Report ORNL–TM–306 (1964).
23. W. A. Spofford, "Least-Squares Planes and Dihedral Angles Program for IBM 1620," (1969).
24. L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca, (1960); a) p. 246, 249, b) p. 224.
25. W. A. Spofford, III, P. Boldrini and E. L. Amma, *Inorg. Chem. Acta*, **5**, 70 (1971).
26. M. R. Truter, *Acta Cryst.*, **22**, 556 (1967).
27. M. M. Elcombe and J. C. Taylor, *Acta Cryst.*, **A24**, 410 (1968).
28. W. T. Robinson, S. L. Holt, Jr., and G. B. Carpenter, *Inorg. Chem.*, **6**, 605 (1967).
29. L. M. Amzel, S. Baggio, and L. N. Becka, *J. Chem. Soc.*, A, 2066 (1969).
30. H. Lüth and M. R. Truter, *J. Chem. Soc.*, A, 1879 (1968).