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The Crystal and Molecular Structure of Tetrakis(Thioacetamide)Ni^{II}Bromide

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The crystal structure of tetrakis(thioacetamide)nickel(II) bromide has been determined from three dimensional counter data at ambient room temperature. With $\lambda = 0.71068$*A the cell constants are*: $a = 15.530 \pm 0.004$*A*, $b = 14.989 \pm 0.004$*A*, $c = 9.310 \pm 0.002$*A*, $\gamma = 118.9 \pm 0.1°$, $D_c = D_m = 1.82$ *g* cm^{-3} *B2/b, Z = 4. Solution of the structure was achieved by standard heavy atom techniques and refinement by full matrix least squares with anisotropic temperature factors resulted in a final R of 0.068. The structure is composed of* $Ni(SCNH_2CH_3)_4^{2+}$ *molecular ions and bromide ions. The Ni atom is on a crystallographic center of symmetry requiring the Ni and its four sulfur neighbors to lie in the same plane. The bromide ions are essentially in axial positions with long Ni–Br distances of 3.599±0.004A. The two crystallographically independent Ni–S distances are 2.216 and 2.222 both ±0.009A, while the S–Ni–S angle is 87.3±0.4°. From the Ni–S–C angles of 112(1)° Av. it is clear that the sulfur atom uses an* sp^2 *lone pair of electrons to form the metal-sulfur sigma bond. The geometry of the complex is such that the Ni, Br and thioacetamide groups related by a center of symmetry are almost coplanar,* i.e., *when the molecule* $Ni(SCNH_2CH_3)_4Br_2$ *is viewed down the Ni–Br axis. all atoms lie in one of two planes related by a 90° rotation about this axis. This orientation arises from a combination of hydrogen bonding and electronic effects.*

Introduction

Thiourea, $[SC(NH_2)_2 = tu]$, is a ligand molecule ideally suited to the role of a probe of the interaction of empty π ligand orbitals with appropriate metal orbitals. This ligand is planar, including hydrogen, when it is complexed with a metal ion as well as when it exists as an isolated molecule. In addition, the geometry of the ligand clearly specifies the direction of the donor orbitals. The sp^2 sulfur non-bonding electron pairs are in the molecular plane with the maximum electron density making an angle of somewhat less than 120° with the S–C bond while the π orbitals are obviously normal to the molecular plane. The nitrogen lone-pair electrons are delocalized over the entire molecule. The precise orientation of this ligand molecule relative to a metal ion or a metal ion and its nearest neighbors can be readily found by single crystal X-ray structure studies. From studies of metal complexes of this ligand, we have shown that thiourea can behave as a π-donor in $Cutu_2Cl$,[2] $Agtu_2Cl$,[3] $Cu_4tu_9(NO_3)_4$,[4] $Cotu_4(NO_3)_2$, $Cotu_4(NO_3)_2 \cdot H_2O$,[5] $Cu_2tu_6(BF_4)_2$[6] and as a sulfur sp^2 electron donor in $Pdtu_4Cl_2$,[7] $Pttu_4Cl_2$,[8] $Cotu_4Cl_2$[9] and $Nitu_6Br_2$.[10] Others have also shown this molecule to be a sulfur sp^2 electron donor in $Nitu_4Cl_2$,[11] $Nitu_4S_2O_3$[12] and $Zntu_2(CH_3CO)_2$.[13] From a careful examination of the twist (M—S—C; S—C—N—N dihedral angles) and the tilt (in appropriate cases MS_4; M—S—C dihedral angles) angles in the transition metal complexes of thiourea, we have concluded that rather than the lowest empty molecular orbital of thiourea behaving as an electron acceptor, the empty sulfur d orbitals orthogonal to the ligand π orbitals are the π acceptors from the ligand. The energy levels of thiourea are: a_1, -2.23β; b_1, -1.50β; a_1', -0.81β; and a_1'', $+1.03\beta$. With the six π electrons, two from each nitrogen and one from carbon and sulfur, these are filled through a_1'.

The lowest π antibonding level of the ligand could be made more accessible by substitution of groups for H on the ligand or going to other variations of thiourea, *e.g.*, thioacetamide (tac) with π levels and energies: a, -1.96β; a′, -0.91β and a″ $+0.86\beta$. These levels would then be filled through a′ with the two electrons from nitrogen and one each from carbon and sulfur. In addition, this ligand retains the above mentioned convenient probe features of thiourea. With these principles in mind we decided to examine the crystal structures of some transition metal thioacetamide complexes.

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The preparation of $M(tac)_2Cl_2$ ($M = Fe$, Co, Zn and Cd), $M(tac)_4Cl_2$ ($M = Ni$ and Cd) has been reported by Nardelli, *et al.*[14-16] Truter and Rutherford[17] published the results of the crystal structure analysis of $Cu(tac)_4Cl$. Flint and Goodgame[18] reported on the electronic and vibrational spectra for $M(tac)_2X_2$ ($M = Fe$, Co, Zn or Cd, $X = Cl$, Br or I) and $M(tac)_4X_2$ ($M = Ni$, Pd, Pt or Cd and $X = Cl$, Br, NO^{3-} and ClO_4^-). These latter authors reported $Ni(tac)_4Br_2$ as a blue-purple diamagnetic, presumably square planar, complex with a diffuse reflectance absorption maximum at 16,850 cm^{-1}. In attempting a preparation of $Ni(tac)_4Br_2$ by methods similar to those of Flint and Goodgame, we found that three different complexes could be isolated: (1) A green, presumably octahedral $Ni(tac)_6Br_2$, probably structurally similar to the $Ni(tu)_6Br_2$ for which the crystal structure has been reported;[10] (2) a blue $Ni(tac)_4Br_2$ which is no doubt the complex reported by Flint and Goodgame; and (3) a red complex, $Ni(tac)_4Br_2$. We report the preparation and crystal structure of the red $Ni(tac)_4Br_2$ complex in this paper.

Experimental Section

Crystals of the red $Ni(tac)_4Br_2$ were prepared by grinding together 0.01 mole anhydrous $NiBr_2$ and 0.04 mole thioacetamide $[SC(NH_2)CH_3]$ until a green color appeared. Five drops of H_2O were added and grinding continued until the color changed to red. The red product was extracted with wet acetone to give a green solution. Diethyl ether was added and yellow crystals were formed in approximately 30 min. These crystals were removed and the green solution was allowed to stand for approximately four hours, after which dark red crystals of $Ni(tac)_4Br_2$ which looked blue in mass were formed and removed. The crystals were found to be unstable in air and were placed in thin walled glass capillaries for diffraction studies.

Preliminary Weissenberg data showed the monoclinic red crystals to have systematic extinctions: for $hk\ell$, $h+\ell = 2n+1$ and for $hk0$, $k = 2n+1$, indicating space group B2/b or Bb.[19] A crystal 0.1 mm $\times$0.1 mm $\times$0.5mm was placed in a thin-walled glass capillary and mounted about the unique axis (*c*, the needle axis) on a Picker automated diffractometer and aligned by variations of well known methods.[20] The cell constants for the B centered cell, obtained from a least-squares refinement[21] of the χ, Φ and 2θ angles of 14 accurately centered general reflections with MoKα radiation ($\lambda = 0.71068$A) at room temperature, were found to be: $a = 15.530(4)$A, $b = 14.989(4)$A, $c = 9.310(2)$A, and $\gamma = 118.9(1)^\circ$ (here and elsewhere in this paper, the estimated standard deviation of the last significant digit is in parentheses). The calculated density with four molecules of $Ni(tac)_4Br_2$ per cell is 1.82 g cm^{-3} in good agreement with the observed value of 1.93(2) g cm^{-3} measured by flotation in a bromoform-benzene mixture. With Zr-filtered MoKα radiation 1863 independent $hk\ell$ pieces of intensity data were measured.

Backgrounds were measured by stationary counting for 40 seconds at $\pm 0.75^\circ$ 2θ from 2θ of the peak maxima and the peaks were scanned for 90 seconds (1.5° 2θ) by the usual θ–2θ scan. The source to crystal distance was 18 cm while the crystal to counter distance was 26 cm. The take-off angle was 3.7° and the counter aperture was 6 mm by 8 mm high. A random sampling of 18 symmetry related reflections gave agreement to within three standard deviations of the counting statistics (see below) and only two crystallographically independent ($hk\ell$, $\bar{h}k\ell$) octants were measured. The linear absorption coefficient (μ) for MoKα radiation was calculated to be 61.2 cm^{-1}. No corrections were made for absorption because the crystal slowly decomposed and this effect, in addition to the capillary effect, outweighed simple absorption effects. The width of an average peak at half peak height was $\sim 0.3^\circ$ 2θ at the above take-off angle. This is only to indicate that the peak was completely covered in this angular range. The counting rate never exceeded 5000 counts per second and no attenuators were used. A standard reflection was measured after every tenth reflection to monitor the stability of operation and any crystal decomposition that might occur. Once data collection was in progress, it was noticed that the crystal was indeed decomposing. However, the standard peak dropped linearly with time (over a period of two weeks) until at the end of the sixth layer ($\ell = 6$), it had disappeared into the base line. The crystal alignment was checked several times during the period of data collection, and it remained centered. Hence, the decrease in intensity of the standard peak is due to crystal decomposition and not crystal misalignment. If $\sigma[I(Scan)] = [I(scan) + (1.125)^2(B_1+B_2)]^{1/2}$ where I(scan) is the number of counts over the scan range, B_1 and B_2 the background counts, and 1.125 a constant used to scale the total background time to the total scan time, then the standard reflection never varied more than σ from the straight line plotted for its downward trend. The integrated intensity was calculated as $I(net) = I(scan) - 1.125(B_1+B_2)$ and was considered above background when I(net) was greater than $2.0[(1.125)^2(B_1+B_2)]^{1/2}$. I(net) was then scaled by I_o/I_t where I_o is the initial integrated intensity of the standard peak and I_t the integrated intensity of the standard peak taken immediately previous to the general peak. By this criteria 427 non-zero $kh\ell$ reflections were retained. Lorentz polarization corrections were made and the intensities reduced to structure factors.

Structure determination

In space group B2/b there are two possibilities for placing four $Ni(tac)_4Br_2$ entities in the cell. 1) The Ni atom may be placed on one of the four four-fold

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(21) The least-squares fit to compute the lattice dimensions is a program based upon ref. 20 by W. A. Spofford, III for the IBM 1620.

Table Ia. Observed and Calculated Structure Factors for Ni(thioacetamide)$_4$Mr$_2$. First column is h followed by F(obs) and F(calc). F(calc = 10F(calc) absolute.

* H	0	0 *	12	148	121	1	202	-254	3	158	-179	-13	138	125
2	570	605	* H	8	0 *	-3	290	308	-5	501	-491	* H	11	1 *
4	500	-540	0	169	143	-5	226	228	-7	124	-138	-5	220	-228
6	250	-245	2	303	-293	5	345	368	-9	349	349	-9	166	174
8	167	158	-2	756	758	7	188	209	-11	219	232	-11	181	186
10	187	197	-4	374	353	-9	243	-247	* H	6	1 *	* H	12	1 *
12	234	228	6	226	218	11	138	-138	-1	406	411	-1	228	225
* H	2	0 *	8	211	183	* H	2	1 *	1	193	222	-13	174	184
0	186	181	-14	264	273	1	529	527	-3	364	338	* H	13	1 *
-2	675	661	* H	10	0 *	-1	264	247	5	162	192	-7	203	-203
2	740	-705	-2	143	-138	-3	116	-109	-5	121	122	* H	14	1 *
4	195	-222	4	299	289	5	135	141	-7	169	154	-7	166	174
-4	1086	1062	-6	508	527	-5	153	189	-13	186	198	* H	16	1 *
-6	676	654	6	200	200	-7	534	531	-15	165	167	-9	148	157
6	449	469	-8	488	496	7	233	249	* H	7	1 *	* H	0	2 *
8	423	435	-12	160	-179	13	138	136	1	197	-214	0	95	104
-8	132	-121	* H	12	0 *	* H	3	1 *	-3	231	242	4	367	373
-10	235	-216	0	333	304	-1	335	-302	-5	148	139	6	430	474
-14	217	222	-2	189	163	3	332	348	-7	176	-173	14	146	131
* H	4	0 *	2	155	140	-5	264	223	-9	229	-235	* H	1	2 *
0	246	-238	-4	192	-200	-7	263	256	-13	170	178	0	249	316
2	227	270	-8	302	315	7	163	-174	* H	8	1 *	-2	112	-89
-2	647	-662	-10	230	237	-9	114	109	-1	224	244	2	433	488
4	547	578	* H	14	0 *	-11	135	-154	-3	116	100	-4	402	-413
-4	143	-110	-2	294	283	-13	136	-144	-5	152	163	6	350	-361
-6	924	904	-4	170	182	* H	4	1 *	-7	403	405	-6	225	-234
6	430	447	-12	149	167	-1	263	265	-9	270	287	8	224	-236
-8	634	665	-14	148	161	1	372	386	* H	9	1 *	-8	116	127
10	222	-219	* H	16	0 *	-3	146	107	-1	235	-211	-10	239	243
* H	6	0 *	-6	168	163	5	223	263	-3	148	-137	12	152	146
0	813	799	-8	148	160	-7	259	243	-5	138	157	* H	2	2 *
-2	398	404	* H	0	1 *	7	230	265	-7	270	286	0	700	699
2	442	430	1	427	458	-9	143	159	-11	233	-241	2	238	292
-4	556	-553	5	185	202	-11	131	142	-13	160	-162	-4	282	-259
-6	333	-340	7	277	297	-13	152	154	* H	10	1 *	6	133	159
-8	193	215	13	174	140	* H	5	1 *	-1	225	224	-6	303	306
-10	417	431	* H	1	1 *	-1	503	471	-7	178	206	-8	394	383
-12	186	216	-1	141	-134	1	116	143	-9	296	317	12	176	164

* H	3	2 *	-10	201	185	11	175	180	-7	120	111	0	150	-169
0	115	-129	* H	8	2 *	13	139	118	* H	6	3 *	2	243	-250
-2	892	714	0	166	124	* H	1	3 *	1	487	510	-2	292	284
2	528	-549	2	177	163	1	300	306	-3	204	-201	4	110	103
-4	299	305	-6	343	347	-5	293	-297	3	138	119	-4	202	192
4	319	-342	-8	422	428	7	155	-165	-5	315	-301	6	298	306
-6	288	-284	* H	9	2 *	-9	136	153	-7	136	188	-8	172	-183
8	174	174	-2	327	334	13	137	70	-9	379	374	10	173	-163
-8	308	-304	2	154	-163	* H	2	3 *	-11	199	197	* H	2	4 *
* H	4	2 *	-4	187	174	-1	520	467	* H	7	3 *	0	264	266
0	597	588	-6	146	-163	1	179	-201	-3	125	-161	-2	205	202
-2	472	465	-8	209	-197	-3	894	806	-5	272	-264	4	124	134
6	192	179	-12	134	130	3	371	-386	-9	184	207	-4	112	84
8	219	214	* H	10	2 *	5	230	250	* H	8	3 *	-6	186	173
-10	179	189	0	217	207	-5	514	465	-1	388	374	6	197	207
-12	172	177	-2	296	287	7	544	457	-3	401	471	8	134	130
* H	5	2 *	-8	228	233	-9	178	-183	-5	121	155	-8	150	148
0	508	-521	-10	228	230	9	141	123	-13	267	279	* H	3	4 *
-2	228	-189	-12	159	165	-13	223	222	-15	164	161	-2	176	-135
4	266	271	* H	11	2 *	* H	3	3 *	* H	9	3 *	2	268	290
6	211	220	0	229	-198	1	163	-169	-1	204	211	4	171	188
-6	231	226	-4	190	195	-1	287	250	-3	158	153	6	136	-104
-8	125	140	-6	189	191	-3	433	387	* H	10	3 *	-6	190	198
-10	129	-125	* H	12	2 *	3	226	-255	-5	285	277	-8	267	269
-12	174	-170	-2	197	191	-7	186	-186	-7	305	354	8	231	-183
* H	6	2 *	-14	195	200	* H	4	3 *	-11	149	-172	-12	236	-250
-2	329	342	* H	13	2 *	1	169	174	* H	12	3 *	* H	4	4 *
4	159	152	-4	188	-173	-1	125	-142	-5	141	-154	0	318	324
-4	272	251	-10	185	161	3	226	244	-7	159	153	-2	249	241
-6	406	371	-14	142	-105	-3	220	-223	-9	371	357	-6	176	162
6	247	261	* H	14	2 *	-5	372	267	* H	14	3 *	6	141	170
-14	230	235	-8	192	209	5	333	355	-13	173	159	-8	193	187
* H	7	2 *	* H	16	2 *	-7	735	707	* H	16	3 *	* H	5	4 *
0	293	268	-10	149	147	-9	262	259	-15	160	141	0	138	124
2	260	287	* H	0	3 *	* H	5	3 *	* H	0	4 *	-2	248	260
-4	502	-489	1	852	859	-1	207	-187	0	274	252	-4	257	-260
-6	241	-232	5	165	-172	1	286	-299	6	213	204	-6	293	-285
-8	294	297	7	117	110	5	173	192	* H	1	4 *	-8	182	173

-10	267	251	7	292	275	-7	228	235	8	134	-134
* H	6	4 *	* H	1	5 *	7	186	179	-10	158	153
0	217	212	1	259	321	-13	158	116	* H	2	6 *
-2	203	211	-1	230	210	-15	140	124	-2	289	296
-6	248	232	5	128	-98	* H	7	5 *	-4	253	228
-8	201	176	-5	375	-393	-1	158	171	-14	189	124
* H	7	4 *	7	180	-208	-3	130	-112	* H	3	6 *
0	170	-158	-9	153	195	-5	293	-275	-2	403	399
-2	260	270	* H	2	5 *	-9	158	170	2	244	-260
2	208	-218	1	437	493	* H	8	5 *	4	204	-169
-4	239	235	-1	143	157	1	224	212	* H	4	6 *
-6	135	-131	3	357	396	-3	135	-184	-6	328	336
-8	219	-225	-3	338	-307	3	197	215	-8	187	191
-14	178	154	-5	118	-119	-7	336	360	* H	5	6 *
* H	8	4 *	-7	333	346	-9	293	281	0	258	-308
-2	170	170	-9	284	285	* H	9	5 *	-12	146	-110
-6	180	175	* H	3	5 *	-1	232	231	* H	6	6 *
-8	191	194	1	187	-202	-3	255	245	-8	213	231
* H	9	4 *	-1	180	204	-7	159	-161	-10	224	210
0	132	-95	3	280	-306	* H	10	5 *	* H	7	6 *
-8	168	194	-3	359	330	-1	319	295	-4	248	-223
-12	206	-202	-7	202	-170	-3	138	146	-6	182	-148
* H	10	4 *	9	134	109	-5	158	-112	* H	8	6 *
-2	175	158	* H	4	5 *	-9	175	155	-12	191	179
-8	135	132	-1	551	574	-11	178	214			
* H	11	4 *	1	157	188	* H	11	5 *			
-4	213	-184	-3	369	351	-7	161	144			
-6	152	-143	3	162	-111	* H	14	5 *			
-10	208	210	-11	203	177	-9	180	165			
-14	143	-153	* H	5	5 *	* H	0	6 *			
* H	13	4 *	-1	297	-289	0	322	364			
-8	151	-192	1	241	-282	2	198	214			
* H	14	4 *	5	258	267	10	157	168			
-8	163	127	-7	179	167	* H	1	6 *			
* H	0	5 *	* H	6	5 *	0	228	221			
1	162	-186	-3	321	311	2	201	197			
3	179	196	-5	418	389	-4	270	-288			
5	413	424	5	281	280	6	146	-160			

Table Ib. Unobserved Reflections with Calculated Value, greater than F_{min}. First column is h followed by k and F(calc) same scale as part a. $F_{min}=96$. Number of reflections less an $F_{min}=1365$. Unobserved reflections were not included in refinement.

$F_{MIN} \le |F(CALC)| < 2.0 \times F_{MIN}$ (68)

L	=	0	5	3	109	-8	6	134	-5	5	120	2	0	117	-6	13	131	L	=	6
4	6	110	-3	11	116	0	6	101	-1	7	132	4	0	128	-2	13	104	8	0	181
-12	8	97	-3	12	121	0	9	116	-9	8	113	-4	3	102	L	=	5	-6	1	184
-10	8	109	-3	13	160	-4	12	118	-7	8	113	0	3	134	-7	4	101	-12	2	134
4	8	135	-1	14	111	-8	13	137	1	11	142	2	4	105	-5	5	134	-6	2	97
-10	10	145	-7	16	107	-2	13	99	-11	14	101	4	4	121	3	5	151	-4	4	177
0	10	127	L	=	2	-6	14	141	-3	14	179	-12	7	126	1	6	185	-6	5	172
2	10	112	8	0	109	-8	16	128	-1	14	155	-10	7	137	-7	7	99	-4	5	98
-6	12	109	10	0	119	L	=	3	-7	16	120	-10	9	104	-5	11	97	-2	6	96
L	=	1	4	2	111	9	0	134	-5	16	113	-6	9	119	-1	11	126			
11	2	119	-10	6	96	3	1	101	L	=	4	-8	11	153	-7	14	154			

$2.0 \times F_{MIN} \le |F(CALC)|$ (3)

-1	6	3	387	-1	12	3	214	-2	8	6	219

Table II. Atom Positional and Thermal Parameters.

Atom	x	y	z
Ni	0.0000(—*)	0.0000(—*)	0.0000(—*)
Br	−0.0954(03)	−0.1563(03)	−0.3156(04)
S(1)	−0.1482(07)	−0.0154(07)	−0.0316(13)
S(2)	−0.0757(08)	−0.1631(07)	0.0649(10)
C(1)	−0.1710(22)	0.0667(23)	0.0764(36)
C(3)	−0.2687(22)	0.0659(23)	0.0497(37)
N(1)	−0.1082(17)	0.1284(18)	0.1643(32)
C(2)	−0.0754(27)	−0.1716(28)	0.2400(40)
C(4)	−0.1356(29)	−0.2789(30)	0.3031(49)
N(2)	−0.0349(21)	−0.0947(23)	0.3349(37)

Anisotropic Temperature Factors of the Form: $[\exp-(h^2\beta_{11}+k^2\beta_{22}+\ell^2\beta_{33}+2hk\beta_{12}+2h\ell\beta_{13}+2k\ell\beta_{23})]\cdot 10^4$.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	44(4)	42(4)	68(12)	22(4)	−2(05)	0(05)
Br	74(3)	68(3)	79(07)	46(3)	−2(04)	7(04)
S(1)	47(6)	56(7)	201(22)	25(6)	−33(10)	−55(10)
S(2)	82(8)	39(6)	79(19)	27(6)	13(10)	11(09)

Isotropic Temperature Factors for Carbon and Nitrogen.

Atom	B	Atom	B
C(1)	2.7(10)	C(2)	3.9(14)
C(3)	3.2(12)	C(4)	5.8(16)
N(1)	3.3(09)	N(2)	5.5(12)

* Indicates a fixed parameter.

Table III. Interatomic Distances and Angles.

Donded Distances (Å)		Angles (degrees)	
Ni—S(1)	2.216(9)	S(1)—Ni—C(2)	87.3(4)
Ni—S(2)	2.222(9)	S(1)—Ni—Br	75.2(3)
S(1)—C(1)	1.75(3)	S(2)—Ni—Br	71.0(3)
S(2)—C(2)	1.64(4)	Ni—S(1)—C(1)	114(1)
C(1)—C(3)	1.53(4)	Ni—S(2)—C(2)	110(1)
C(1)—N(1)	1.27(4)	S(1)—C(1)—C(3)	116(2)
C(2)—C(4)	1.53(5)	S(1)—C(1)—N(1)	123(2)
C(2)—N(2)	1.34(4)	C(3)—C(1)—N(1)	121(3)
		S(2)—C(2)—C(4)	116(3)
		S(2)—C(2)—N(2)	127(3)
		C(4)—C(2)—N(2)	116(3)

Non-Bonded Distances (Å)	
Ni—Br	3.599(4)
Br—N(1)	3.30(2)
Br—N(2)	3.30(3)
Br—N(1)*	3.44(3)
Br—N(2)*	3.39(3)

Dihedral Angles Between Various Planes.

Plane 1	Plane 2	Angle(degrees)
S(1)—Ni—S(2)	Ni—S(1)—C(1)	60(1)
S(1)—Ni—S(2)	Ni—S(2)—C(2)	79(2)
Ni—S(1)—C(1)	S(1)—C(1)—C(3)	175(2)
Ni—S(1)—C(1)	S(1)—C(1)—N(1)	0(3)
Ni—S(2)—C(2)	S(2)—C(2)—C(4)	173(2)
Ni—S(2)—C(2)	S(2)—C(2)—N(2)	1(4)

* Atoms on adjacent molecules.

sets of centers of symmetry [(0,0,0; 0,1/2,0; 1/2,0,1/2; 1/2,1/2,1/2), (0,0,1/2; 0,1/2,1/2; 1/2,0,0; 1/2; 1/2,0), (1/4,0,1/4; 3/4,1/2,1/4; 3/4,0,3/4; 1/4, 1/2,3/4), (1/4,1/2,1/4; 3/4,0,1/4; 3/4,1/2,3/4;, 1/4, 0,3/4)] requiring the molecule to have a center of symmetry. 2) The Ni atom may be placed on the four-fold set of the two-fold axis (0,1/4,z; 0,3/4,z; 1/2,1/4,1/2 +z; 1/2,3/4,1/2—z) requiring the molecule to have C_2 symmetry. In space group Bb, four molecules may be placed in general positions in which case no restrictions are imposed on the molecular symmetry.

An unsharpened three-dimensional Patterson function was computed[22] and was readily interpreted in

(22) Patterson and Electron Density Calculations done on IBM 7040 with ERFR-3, a modification of ERFR-2 of Sly-Schoemaker-van den Hende by D. R. Harris.

terms of a Ni atom at the origin and bromine and sulfur atoms in general positions of B2/b. The space group was then assumed to be B2/b and the structure was solved and refined on this basis. A structure factor calculation was made at this point which yielded an R (see below) of 0.21 after two cycles of least-squares varying only the scale factor and atomic coordinates. We assumed the model to be correct and computed a three-dimensional electron density map based on the phase angles from the output parameters from the least-squares. All of the remaining atoms were located from this calculation and subsequent full matrix[23] least-squares refinement with scattering factors from a standard source[24,25] including real and imaginary dispersion corrections for Ni, Br and S atoms,[26] converged with isotropic temperature factors to an R of 0.09 after three cycles. By allowing the Ni, Br and two S atoms to vary anisotropically, the structure converged after three cycles to a final conventional R of 0.068, weighted R of 0.083 and standard error of 2.60.[27] Unit weights were used throughout the refinement. The listing of observed and calculated structure factors is found in Table I. Table II contains the final atomic coordinates and thermal parameters. Interatomic distances, angles, dihedral angles, errors[28] and appropriate least-squares planes[29] are enumerated in Table III and IV.

Table IV. Equations of least square planes of the type * $Ax+By+Cz-D=0$.

Plane No.	1	2	3	4
A	0.0874	0.9956	0.1119	0.9966
B	0.7036	−0.0913	0.7744	−0.0621
C	−0.7052	−0.0226	−0.6227	−0.0536
D	0.1336	−0.1996	0.1033	−0.0525

Deviation of atoms from least square planes (A).

Plane No. (I) [a]	1	2
S(I)	0.008(7)	−0.009(5)
C(I)	−0.027(22)	0.030(15)
N(I)	0.011(19)	−0.012(12)
C(I+2)	0.009(23)	−0.009(17)
	3	4
S(I−2)	−0.115(7)	0.057(5)
C(I−2)	0.014(22)	0.042(15)
N(I−2)	0.162(19)	0.003(12)
C(I)	−0.036(23)	−0.056(17)
Ni	0.103(**)	−0.052(**)
Br	−0.100(3)	0.007(2)

* Coordinates x, y, z refer to an orthogonal coordinate system (J. S. Rollett, *Computer Methods in Crystallography*, Pergamon Press. New York, p. 22). ** Atom constrained by space group requirements. [a] See figure for notation.

Description and Discussion

The structure of $Ni(tac)_4Br_2$ is made up of molecular ions, $Ni(tac)_4^{2+}$, with two essentially ionic bromine atoms. The Ni atom lies on a crystallographic center of symmetry and this demands that the Ni and four S atoms be coplanar. The two bromine atoms occupy almost axial positions to this plane, but at rather long distances (Figure 1) which imply only van der Waals interactions exist between metal and halogen.

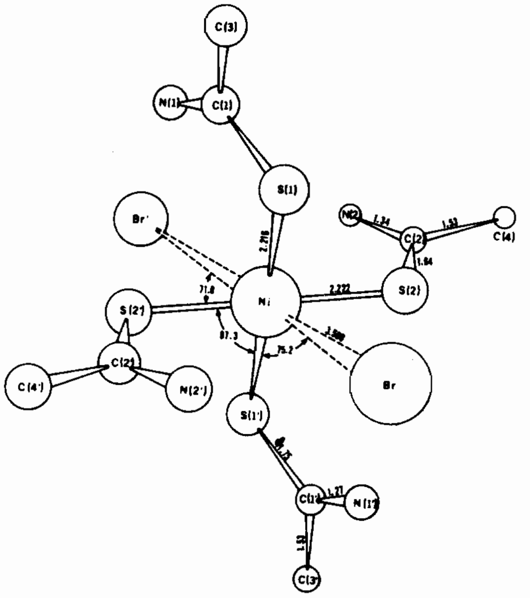

Figure 1. A perspective view of the $NI(thioacetamide)_4Br_2$ unit showing the bonded distances, the Ni-Br distance and the most important angles.

The two crystallographically independent Ni–S distances of 2.216(9)A and 2.222(9)A (not statistically different) are significantly shorter than the 2.498(6)A to 2.517(6)A observed in $Ni(tu)_6Br_2$ [10] and the 2.418(1)A to 2.481(1)A observed in *trans*–$Ni(tac)_4Cl_2$ [30] as well as the 2.43A expected from the sum of single bond covalent radii,[31] but are essentially the same as the 2.200(2)A and 2.225(2)A observed in Ni(N,N'-dimethylthiourea)$_4$Br$_2$ [32] and the 2.198(3)A observed in $Ni[SC_2H_4N(CH_3)_2]_2$ [33] and only slightly longer than the 2.160(2)A and 2.171(2)A reported in $Ni[SC(NH_2)NC(NH_2)S]_2$.[34] On the other hand, the Ni–Br distance of 3.599(4)A is at least 1A larger than a normal single bond distance (sum of single bond covalent radii = 2.50A) and the bromines must be viewed as essentially bromide ions. The orientation of the thioacetamide groups as shown by the Ni–S–C angles of 110(1)° and 114(1)° as well as the dihedral angles between planes defined by Ni–S–C and

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(23) Least-squares refinement performed with ORFLS of W. Busing, K. O. Martin and H. Levy (ORNL-TM-305, 1962) with local modifications including anomalous dispersion.

(24) D T. Cromer and J. T. Waber, *Acta Cryst.*, *18*, 104 (1965).

(25) D. T. Cromer, *Acta Cryst.*, *18*, 17 (1965).

(26) Anomalous dispersion corrections made to F_c, as suggested by J. A. Ibers, and W. C. Hamilton, *Acta Cryst.*, *17*, 781 (1964).

(27) $R = [\Sigma||F_o|-|F_c||]/\Sigma|F_o|$; Weighted $R = [\Sigma w(F_o-F_c)^2]^{1/2}/[\Sigma wF_o^2]^{1/2}$; Standard Error $= \{[\Sigma w(F_o-F_c)^2]/(NO-NV)\}^{1/2}$, where $NO = 427$, $NV = 58$.

(28) Distances, angles, dihedral angles, rms displacements and errors computed with ORFFE program of W. Busing, K. O. Martin and H. Levy (ORNL-TM-306, 1964) with local modifications on the IBM 7040.

(29) Least-squares planes calculated on IBM 1620 with program by W. A. Spofford, III

(30) R. L. Girling, J. E. O'Connor, and E. L. Amma, to be published.

(31) L. Pauling, « Nature of the Chemical Bond », 3rd Ed., Cornell University Press, Ithaca, New York, 1960, pages 246, 249.

(32) M. S. Weininger and E. L. Amma, to be published.

(33) R. L. Girling and E L. Amma, *Inorg. Chem.*, 6, 2009 (1967).

(34) H. Lüth, E. A. Hall, W. A. Spofford, III, and E. L. Amma, *Chem. Comm.*, 520 (1969).

S–C–N (twist) of 0(3)° and 1(4)° (Table III) indicate that the sulfur is using an sp^2 lone pair of electrons in bonding to the nickel. The thioacetamide groups are also rotated about the Ni–S bond and tilted out of the square plane by 60(1)° and 79(2)° for the S(1) and S(2) thioacetamide groups, respectively (see Ni–S–C dihedral angles, Table III).

In each thioacetamide group the nitrogen is closest to the bromine with a N–Br distance of 3.30(3)A for both N(1) and N(2). The least-squares planes (Table IV) indicate that the entire S(2) thioacetamide group is approximately coplanar with the Ni, Br and S(2) atoms. In addition, Table IV shows that the S(1) thioacetamide group is close to being coplanar with the Ni, Br and S(1) atoms but not as good a fit as the S(2) thioacetamide group with the Ni, Br and S(2) plane. These facts might indicate that N–H - - Br hydrogen bonding is the factor that dedetermines the orientation of the thioacetamide groups. However, it is germane that the C–N - - - Br angle is 136°(2) for N(1) and N(2). Further, if idealized proton positions are placed upon the nitrogen the N–H - - - Br angles would be 151° and 157° for N(1) and N(2), respectively. Therefore, the amide protons are not in the best locations for hydrogen bonding to the bromide ions. In addition, it is interesting to note that in *trans*–Ni(tac)$_4$Cl$_2$ there are no intramolecular hydrogen bonds (the hydrogens were located), but there still exists a large tilting about the Ni–S bond of from 56.2(3)° to 65.7(3)° and intermolecular hydrogen bonds are formed. Moreover, the dihedral angles between planes defined by Ni–S–C, S–C–C–N vary from 4.6(5)° to 8.5(5)° for *trans*–Ni(tac)$_4$Cl$_2$ and the analogous angle observed in Ni(tac)$_4$Br$_2$ indicate that the bonding in thioacetamide complexes is different from thiourea complexes in which these angles usually vary from 14-35°.[7-13,35]

As indicated earlier in the introduction, there is a significant difference in the π orbital energies between thiourea and thioacetamide. Particularly germane is the fact that the lowest empty orbital of thiourea is at $+1.03\beta$ (a_1'') and the lowest empty orbital of thioacetamide is $+0.86\beta$.[36] We have interpreted the twist angles (dihedral angles between M–S–C and S–C–N planes) for transition metal-thiourea complexes as arising from the fact that it is energetically more expensive to transfer electrons from filled metal d orbitals into a_1'' than to twist the thiourea molecule such that the empty sulfur d orbitals that are orthogonal to the π system can act as electron acceptors. However, with the lower energy thioacetamide π antibonding available at 0.86β it seems that now Ni^{II} finds it profitable to delocalize the b_{2g} (d_{xy}) otherwise non-bonding electrons. This is our explanation for the orientation of the thioacetamide ligands in Ni^{II} complexes.

The thioacetamide groups in Ni(tac)$_4$Br$_2$ are all essentially planar within experimental error (Table IV) and their bond distances and angles do not differ significantly from free thioacetamide.[37] All of the errors are quite large, but in view of the fact that the crystal was decomposing during data collection, they seem quite reasonable.

We were never able to obtain a macroscopic sample of red tetrakis (thioacetamide)Ni(II)bromide completely free of black nickel sulfide. The samples always indicated a small variable residual paramagnetism due to this decomposition product. Presumably the pure red material is diamagnetic.

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(35) M. Nardelli, G. F. Gasparri, G. G. Battistini, and P. Domiano, *Acta Cryst.*, *20*, 349 (1965)

(36) Huckel π calculations performed with program due to B. M. Gimarc, University of South Carolina, Columbia, S. C.

(37) M. R. Truter, *J. Chem. Soc.*, 997 (1960).