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The Crystal and Molecular Structure of Bis(N,N-dimethyl-β-mercaptoethylamine)nickel(II)

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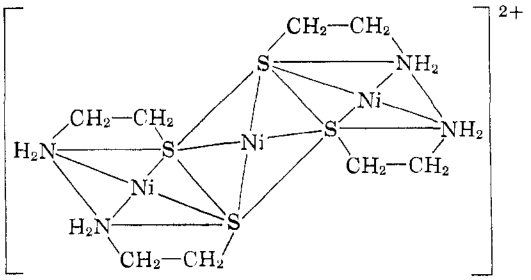
Received May 22, 1967

The crystal structure of bis(N,N-dimethyl-β-mercaptoethylamine)nickel(II), $Ni[SC_2H_2N(CH_3)_2]_2$, has been determined from 604 intensities manually collected by counter means at room temperature. Unit cell constants are: $a = 8.89$, $b = 11.94$, $c = 5.56$, all ±0.01 A, and $\beta = 94.4 \pm 0.1°$. The space group is $P2_1/n$ with two molecules per cell. The observed and calculated densities were found to be 1.50 and 1.51 g cm^{-3}, respectively. The structure was refined by least squares to a conventional R of 0.072. The structure is made up of discrete molecular units of *trans* configuration with a planar NiN_2S_2 entity, separated by ordinary van der Waals distances. The Ni–N and Ni–S distances were found to be 1.974 ± 0.010 and 2.198 ± 0.003 A, respectively, with an N–Ni–S angle of 87.9 ± 0.3°. These distances and angles are explained in terms of nonbonded C–S interactions of the methyl groups on nitrogen. Stereochemically, the methyl groups on the nitrogen are approximately oriented such that one is equatorial and one polar. The polar methyl group effectively blocks the axial Ni(II) position from further chemical attack.

Introduction

Jensen[3] reported the synthesis of a green 1:2 complex between Ni(II) and β-mercaptoethylamine to which he assigned the *cis* structure based only on its color and insolubility in nonpolar solvents. More recently, Busch and Jicha[4-6] have made a detailed study of β-mercaptoethylamine complexes and found that the complex reported by Jensen[1] is diamagnetic and consequently is "square-planar," but the low solubility of this green complex precluded any dipole moment measurements for the elucidation of the stereochemistry. However, they found that this 1:2 complex would react further with $NiCl_2$ to form a trimer whose structure has been shown to be I by X-ray diffraction.[7]



I

When Ni(II) complexes are formed from various N-substituted β-mercaptoethylamines, they can be separated into three groups depending upon their color and solubility properties.[8] These are: (1) brown powders, only slightly soluble in halocarbons or dimethyl sulfoxide, *e.g.*, bis(N,N-diethyl-β-mercaptoethylamine)nickel(II); (2) green solids which are soluble in halocarbons, *e.g.*, bis(N-propyl-β-mercaptoethylamine)nickel(II); (3) maroon crystalline solids appreciably soluble in both polar and nonpolar solvents, *e.g.*, bis(N,N-dimethyl-β-mercaptoethylamine)nickel(II). Magnetic moments, molecular weights, and infrared and visible spectra all indicate that these compounds are "square-planar" nickel(II) complexes. However, only the maroon bis(N-isopropyl-β-mercaptoethylamine) and bis(N,N-dimethyl-β-mercaptoethylamine) complexes are good crystalline complexes suitable for X-ray diffraction studies. The dipole moment measurements of Root and Busch on these two compounds were limited by solubility considerations; nevertheless, they were able to place the dipole moment at a maximum of 3 D. Since the *cis* compound should have a moment of 8–9 D., these data indicate a *trans* configuration. In order to ascertain the configuration of these compounds we decided to investigate the crystal structure of bis(N,N-dimethyl-β-mercaptoethylamine)nickel(II). Further, the effect of the N-methyl groups on the Ni–N bond length and their stereochemical interrelationship is of considerable interest in these types of sulfur chelates.

Experimental Section

Single crystals of bis(N,N-dimethyl-β-mercaptoethylamine)nickel(II), $Ni[SC_2H_4N(CH_3)_2]_2$, suitable for single-crystal X-ray diffraction were generously supplied to us by Professor D. H. Busch of The Ohio State University. Preliminary Weissenberg and precession photographs ($hk0 \cdots hk5$, $h0l$, $0kl$) gave the systematic absences: for $h0l$, $h + l = 2n + 1$; for $0k0$, $k = 2n + 1$ yielding $P2_1/n$ as the space group. From calibrated precession photographs at room temperature the cell constants were found to be: $a = 8.89$, $b = 11.94$, $c = 5.56$, all ±0.01 A, and $\beta = 94.4 \pm 0.10°$. The density measured by flotation [1.50 (3)] in a carbon tetrachloride–bromoform mixture is in good agreement with the calculated value of 1.51 g cm^{-3}, assuming two molecules per cell.

A single needle crystal, 0.08 × 0.12 × 0.84 mm, mounted about the long direction was used to collect 604 independent pieces of hkl intensity data with Zr-filtered Mo Kα radiation on a Picker diffractometer equipped with a GE single-crystal orienter by a scan technique. The takeoff angle was set at 3.5° and the receiving aperature was 6 × 8 mm high. The counting rate never exceeded 5000 counts/sec. The mosaic spread of a reflection was satisfyingly low. Backgrounds were measured by stationary counting for 40 sec at ±1.67° 2θ of the peak maxima. The peak

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[3] K. A. Jensen, *Z. Anorg. Allgem. Chem.*, **229**, 265 (1936).
[4] D. C. Jicha and D. H. Busch, *Inorg. Chem.*, **1**, 872 (1962).
[5] D. C. Jicha and D. H. Busch, *ibid.*, **1**, 878 (1962).
[6] D. H. Busch and D. C. Jicha, *ibid.*, **1**, 884 (1962).
[7] L. Dahl, private communication.
[8] C. A. Root and D. H. Busch, private communication, submitted for publication.

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS[a]

• H 0 0 •		
4	430	392
6	73	67
8	175	163
10	62	63
12	49	41
• H 1 0 •		
3	223	230
4	64	85
5	282	276
6	70	71
9	189	180
• H 2 0 •		
3	223	233
4	339	347
5	85	73
6	93	96
8	112	110
10	54	44
• H 3 0 •		
2	94	88
3	265	269
4	163	153
5	234	204
6	71	76
7	69	78
8	57	44
9	107	86
10	59	46
• H 4 0 •		
0	167	162
1	207	138
2	322	258
3	133	117
4	131	147
5	95	84
6	234	214
7	63	56
8	99	85
10	41	36
12	39	31
• H 5 0 •		
1	246	240
2	111	121
4	65	58
5	104	115
6	52	65
7	216	195
8	63	55
11	64	59
• H 6 0 •		
1	74	65
2	421	425
3	42	45
4	64	57
5	122	109
7	61	53
8	60	55
12	44	37
• H 7 0 •		
1	157	160
2	59	64
3	283	263
7	147	144
• H 8 0 •		
0	61	40
1	23	20
2	292	231
3	28	22
4	124	114
7	26	22
10	46	52
• H 9 0 •		
1	168	159
3	112	120
6	33	41
7	101	94
8	45	47
• H 10 0 •		
0	140	127
1	139	120
2	173	139
3	27	25
4	78	76
6	107	93
8	48	46
• H 11 0 •		
1	110	103
2	46	40
3	92	93
5	118	118
7	53	53
8	41	43
• H 12 0 •		
0	98	95
1	70	65
2	51	47
3	51	54
4	122	128
• H 0 1 •		
1	159	147
-1	605	610
5	218	225
-5	234	217
7	40	39
9	160	161
-9	156	130
• H 1 1 •		
0	619	658
1	186	105
-1	225	214
3	207	214
-3	120	147
4	189	221
-4	333	362
5	100	89
-5	71	79
6	89	89
-6	73	76
8	164	158
-8	100	88
10	54	50
-10	71	55
• H 2 1 •		
0	359	329
1	149	183
-1	333	360
3	293	297
-3	266	281
4	144	143
-4	85	95
5	286	292
-5	222	247
6	150	149
-6	47	62
7	41	39
-7	60	73
8	83	77
-8	15	41
9	124	120
-9	123	120
10	47	42
-10	62	53
12	46	38
• H 3 1 •		
0	339	350
1	304	287
-1	340	350
2	356	343
-2	96	110
3	212	190
-3	210	227
4	320	298
-4	284	307
5	134	138
-5	69	88
6	144	143
-6	144	155
-7	80	94
8	93	101
-8	102	117
-9	54	44
10	41	42
-10	59	54
• H 4 1 •		
1	315	294
-1	200	200
2	314	280
3	304	282
-3	186	200
4	125	119
-4	99	113
-5	91	107
5	206	208
6	102	109
-6	52	55
7	95	94
-7	153	169
8	75	73
-8	69	69
9	59	56
-9	71	70
10	68	66
11	52	46
• H 5 1 •		
0	148	170
1	247	239
-1	60	74
2	379	336
-2	151	178
3	133	143
-3	121	127
4	86	82
-4	78	75
5	87	84
-5	105	118
6	170	164
-6	147	154
7	44	40
-7	61	62
8	76	69
-8	86	84
• H 6 1 •		
1	173	164
-1	126	141
2	29	38
3	192	195
-3	210	234
4	64	56
5	81	85
-5	46	43
-6	79	80
7	134	131
-7	133	152
8	33	35
11	60	61
-11	60	57
• H 7 1 •		
2	280	292
-2	299	324
3	57	47
-3	40	60
4	37	41
-4	87	98
-5	46	46
6	153	146
-6	119	139
7	25	30
8	53	57
10	48	48
-10	49	45
• H 8 1 •		
1	130	132
-1	165	203
3	174	173
-3	227	232
4	48	46
5	46	46
-5	63	64
6	62	67
7	139	138
-7	111	107
8	49	42
11	50	59
• H 9 1 •		
0	100	104
1	91	91
-1	84	92
2	197	197
-2	237	243
3	58	57
-3	67	72
4	44	40
-4	49	47
-5	76	80
6	119	117
-6	113	114
8	59	61
-10	49	44
• H 10 1 •		
1	110	111
-1	144	143
2	50	54
-2	39	38
3	111	116
-3	73	75
4	79	75
5	53	61
-5	67	79
7	82	91
-7	73	67
8	51	58
• H 11 1 •		
0	80	73
1	98	104
-1	96	93
2	90	96
-2	74	76
-3	49	59
4	90	103
-4	59	66
-5	32	49
6	53	61
-6	79	76
• H 12 1 •		
1	99	74
-1	69	66
3	89	89
-3	40	44
5	71	79
-5	103	93
• H 13 1 •		
0	106	105
0	110	105
-3	50	45
4	64	95
• H 14 1 •		
1	78	86
-1	75	74
• H 15 1 •		
0	88	89
• H 0 2 •		
0	444	416
2	67	57
4	215	203
-4	403	386
6	131	130
-6	50	56
8	127	126
-8	129	112
10	66	68
• H 1 2 •		
1	317	295
-1	239	243
-2	36	33
-3	232	231
-4	104	89
5	311	338
-5	213	210
6	70	78
7	38	35
-7	76	71
-8	63	57
9	127	126
-9	95	89
• H 2 2 •		
0	259	285
1	228	219
-1	164	202
2	213	218
-2	66	95
3	91	84
-3	130	137
4	254	269
-4	326	333
5	163	160
-5	31	31
-6	70	68
-7	77	79
8	97	102
-8	106	103
10	60	63
-10	47	42
• H 3 2 •		
0	71	62
1	212	229
-1	262	251
2	34	37
-2	123	158
3	210	211
-3	139	167
-4	73	74
5	195	204
-5	125	136
6	65	66
-6	56	61
7	46	54
-7	107	97
8	81	80
-8	72	73
9	59	71
-9	91	31
-10	53	46
11	49	44
• H 4 2 •		
0	274	265
1	222	217
-1	288	275
2	329	302
-2	173	190
3	203	186
-3	62	64
4	154	142
-4	97	101
5	42	53
-5	101	98
6	69	67
-6	103	103
7	43	46
-7	39	36
8	88	92
-8	98	89
-10	67	57
10	41	41
• H 5 2 •		
0	40	41
1	204	197
-1	272	289
-2	46	33
3	222	208
-3	79	102
4	46	39
-4	25	27
-5	58	72
6	31	37
-6	85	89
-7	129	127
7	114	133
-9	49	43
10	40	47
-11	58	48
11	51	50
• H 6 2 •		
0	61	62
1	69	80
-1	52	47
2	275	265
-2	246	257
3	123	106
-3	109	101
4	93	96
-4	78	68
-5	63	54
6	109	112
-6	141	146
8	72	54
-10	51	46
• H 7 2 •		
1	57	58
-1	187	169
-2	107	107
3	239	229
-3	180	189
5	55	59
-5	100	102
7	141	159
-7	106	103
• H 8 2 •		
-1	39	35
2	210	193
-2	246	253
3	60	49
-3	58	51
4	78	75
-4	70	74
5	36	37
6	117	124
-6	124	131
8	50	65
• H 9 2 •		
0	52	56
1	94	97
-1	143	140
3	129	116
-3	119	117
4	52	50
-4	42	43
5	46	46
-5	64	73
6	42	44
-6	47	43
7	98	112
-7	79	82
• H 10 2 •		
0	87	86
1	94	93
-1	47	40
-2	127	123
3	50	49
-3	87	82
4	64	53
-4	41	43
-5	43	44
-6	86	86
• H 11 2 •		
1	107	109
-1	81	75
2	28	41
3	81	95
-3	67	62
4	52	60
5	57	68
-5	63	69
6	29	33
• H 12 2 •		
0	101	100
-1	50	52
2	69	71
-2	43	50
3	40	36
-3	40	43
4	78	92
-4	68	71
• H 13 2 •		
-1	65	66
1	96	94
-3	43	48
• H 14 2 •		
0	103	102
• H 0 3 •		
1	293	324
-1	196	210
3	58	61
-3	130	126
5	233	293
-5	232	226
-7	92	92
9	95	108
-9	113	95
• H 1 3 •		
0	326	320
-1	37	48
2	79	69
-4	198	202
4	283	299
-6	46	62
6	55	64
-8	136	113
8	84	96
10	52	52
• H 2 3 •		
-1	113	126
1	237	211
-2	50	32
2	62	62
3	94	91
-5	143	149
5	196	199
-6	40	42
-7	50	48
7	32	37
8	54	62
9	67	82
-9	66	66
• H 3 3 •		
0	168	167
-1	125	126
1	162	155
-2	144	152
-4	146	146
4	152	150
-5	54	57
-7	59	45
-8	72	62
8	64	71
10	55	62
• H 4 3 •		
1	236	224
-1	253	239
2	89	92
3	125	114
-3	138	151
4	49	57
5	59	63
-5	66	63
6	55	57
7	112	115
-7	31	76
9	35	44
• H 5 3 •		
0	155	148
-1	72	62
1	74	65
-2	280	286
2	267	250
-3	113	121
3	62	65
-4	57	59
4	52	54
-6	114	113
6	116	119
-8	68	51
8	73	68
• H 6 3 •		
1	144	133
-1	171	160
-2	73	78
3	207	194
-3	148	159
5	46	45
-5	81	83
6	64	64
7	146	147
-7	121	110
• H 7 3 •		
2	223	206
-2	203	200
4	71	81
-4	49	49
6	112	114
-6	130	129
• H 8 3 •		
1	49	45
-1	73	74
3	160	157
-3	88	95
-5	68	65
7	104	103
-7	60	78
• H 9 3 •		
0	54	59
-2	123	123
2	127	116
3	46	45
4	65	63
-6	92	37
6	77	80
• H 10 3 •		
1	93	96
-1	112	112
3	89	94
-3	50	59
4	54	56
5	56	52
-5	57	66
• H 11 3 •		
0	116	112
-1	46	55
-2	79	70
2	67	55
-4	62	68
4	83	81
• H 12 3 •		
1	73	69
-1	73	72
3	54	56
-3	63	58
• H 13 3 •		
0	95	89
• H 14 3 •		
1	53	53
• H 0 4 •		
0	221	217
2	75	76
4	147	163
-4	99	98
• H 1 4 •		
-1	113	105
1	203	196
-3	74	70
3	101	99
• H 2 4 •		
0	196	174
-1	53	40
1	99	87
-2	110	113
2	103	109
-3	62	62
3	60	55
• H 3 4 •		
-1	154	143
1	163	165
2	97	103
-3	177	179
3	107	107
• H 4 4 •		
0	150	141
-1	95	92
1	104	101
-2	186	176
2	100	96
-3	78	77
• H 0 5 •		
-1	84	104
1	188	194
-3	93	86
• H 1 5 •		
0	176	169
2	81	83
-2	63	62
• H 2 5 •		
-1	65	58
1	127	118
-3	101	100
3	70	77
• H 3 5 •		
0	87	73
1	61	48
2	58	63
-2	84	73
• H 4 5 •		
-1	91	79
1	67	58

[a] First column is H followed by $|F_o|$ and $|F_c|$. $|F_c| = |10F(\text{calcd})|$. $F(\text{calcd})_{\text{absolute}} = F(\text{calcd})/\text{scale factor}$. Scale factor = 0.6216 ± 0.002. Unobserved reflections not listed and were not included in the refinement.

was then scanned for 100 sec by the usual θ–2θ method and the net integrated intensity was calculated, assuming a linear variation in background, from the function $I(\text{net}) = I(\text{scan}) - 1.25(B_1 + B_2)$, where B_1 and B_2 are the background counts. A standard reflection was measured every hour to ensure stability of operation.

The linear absorption coefficient (μ) for this crystal with Mo Kα radiation is 13.2 cm^{-1}. No absorption corrections were made but it has been shown[9] that atomic position parameters are not significantly affected by absorption corrections and our estimates of error of thermal parameters may be somewhat optimistic. The upper limit to the variation of intensity due to absorption might be estimated to be 20%.

Structure Determination

The space group $P2_1/n$ demands that with two molecules of bis(N,N-dimethyl-β-mercaptoethylamine)-nickel(II) per cell the Ni atoms must lie on centers of symmetry, and, hence, the configuration of this complex must be *trans*. We placed the Ni atoms at 0, 0, 0 and $^1/_2$, $^1/_2$, $^1/_2$ and all of the other atoms into the general positions $\pm(x, y, z;\ ^1/_2 + x,\ ^1/_2 - y,\ ^1/_2 + z)$. We could have proceeded to find the other atoms based on the Ni phases (all positive) by Fourier refinement, but we decided that it would be more efficient to glean as much information as possible from the Patterson function. From an unsharpened three-dimensional Patterson[10] we located all but one of the carbon atoms, which was subsequently found from a three-dimensional Fourier based on phases calculated from the other atoms.

The structure was refined by complete-matrix least squares[11] including anisotropic temperature factors by minimizing the function $\Sigma w(F_o - F_c)^2$ with equal weights.[12] Scattering factors for Ni^{2+}, C, N, and S were taken from the compilation of Ibers[13] and a real correction for anomalous dispersion for Ni(II) was taken from the data of Cromer.[14] The imaginary correction term was small and was neglected. The final coordinate shifts of the atoms were less than 3×10^{-4} ($<^1/_{10}\sigma$) of a cell edge. The final R,[15] weighted R, and standard error were found to be 0.072, 0.086, and 1.29, respectively. A final difference map was qualitatively featureless and showed no indication of the hydrogen atoms. Final observed and calculated structure factors are listed in Table I. (Unobserved reflections were not included in the refinement and are not included in this table.) Table II contains the final coordinates, temperature factors, and the respective esd's. Distances, angles, thermal parameters, and estimated errors were calculated and are arranged in Tables III and IV.[16]

Results and Discussions

The crystal structure is made up of molecules of *trans*-bis(N,N-dimethyl-β-mercaptoethylamine)nickel(II) separated by ordinary van der Waals distances (Table III).

A perspective view of the *trans*-bis(N,N-dimethyl-β-mercaptoethylamine)nickel(II) molecule is shown in Figure 1 with the most important distances. The Ni atom and its four nearest neighbors are planar by space group requirements but the angles with the metal as vertex are significantly different from the

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(9) R. C. Srivastava and E. C. Lingafelter, *Acta Cryst.*, **20**, 918 (1966).

(10) Patterson and electron density calculations were made with a local variation of a program due to Baenziger on the IBM 7040.

(11) Least-squares calculations were performed with a local version of the ORFLS program of W. Busing, K. O. Martin, and H. Levy on the IBM 7040.

(12) Essentially the same results were obtained when the data were weighted on counting statistics and a 4% intensity factor: S. W. Peterson and H. A. Levy, *Acta Cryst.*, **10**, 70 (1957).

(13) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 202, 204.

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

(15) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; weighted $R = \Sigma w(F_o - F_c)^2/\Sigma wF_o^2$; standard error $= [\Sigma w(F_o - F_c)^2/(NO - NV)]^{1/2}$, where $NO = 604$ and $NV = 61$.

(16) These calculations performed with a local modification of ORFFE due to W. Busing, K. O. Martin, and H. Levy on the IBM 7040.

TABLE II

Atom Positional and Temperature Parameters and Errors; $\sigma' = 10^4\sigma$

Atom	x	$\sigma'(x)$	y	$\sigma'(y)$	z	$\sigma'(z)$
Ni	0.0000	...[a]	0.0000	...[a]	0.0000	...[a]
S	0.2262	4	0.0695	3	−0.0163	8
N	0.0925	11	−0.1259	9	0.1860	20
C_1	−0.0015	18	−0.1803	13	0.3617	30
C_2	0.1311	20	−0.2111	12	0.0074	29
C_3	0.2667	16	0.4123	13	0.1657	30
C_4	0.1637	17	0.4712	13	0.3258	37

Thermal Parameters and Standard Deviations; Anisotropic Temperature Factors of the Form
$\exp-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$

Atom	β_{11}	σ'	β_{22}	σ'	β_{33}	σ'	β_{12}	σ'	β_{13}	σ'	β_{23}	σ'
Ni	0.0090	2	0.0042	1	0.0226	9	0.0001	2	−0.0019	4	0.0002	4
S	0.0103	4	0.0068	3	0.0513	21	−0.0013	3	−0.0034	7	0.0030	6
N	0.0109	14	0.0062	8	0.0266	47	0.0002	9	−0.0010	21	0.0030	17
C_1	0.0197	25	0.0097	15	0.0354	73	0.0038	15	0.0075	37	0.0096	28
C_2	0.0271	31	0.0056	10	0.0285	66	0.0041	15	−0.0055	38	−0.0039	23
C_3	0.0127	19	0.0088	12	0.0468	81	0.0001	13	−0.0113	33	−0.0023	26
C_4	0.0138	20	0.0090	16	0.0762	101	−0.0001	13	−0.0150	39	−0.0077	31

[a] Constrained by symmetry requirements.

TABLE III

INTERATOMIC DISTANCES, ANGLES, AND ERRORS

Bonding interatomic distances and angles			
Distance, A		Angle, deg	
Ni–S	2.198 (3)	S–Ni–N	87.9 (3)
Ni–N	1.974 (10)	S–Ni–N[a]	92.1 (3)
N–C_1	1.491 (19)	Ni–N–C_1	116.3 (8)
N–C_2	1.485 (18)	Ni–N–C_2	106.7 (8)
N–C_3	1.519 (17)	Ni–N–C_3	110.3 (8)
C_3–C_4	1.510 (24)	C_1–N–C_2	108.1 (1.2)
C_4–S	1.821 (15)	C_1–N–C_3	105.2 (1.2)
		C_2–N–C_3	110.1 (1.1)
		N–C_3–C_4	109.9 (1.2)
		C_3–C_4–S	108.6 (1.0)
		Ni–S–C_4	100.8 (5)

Nonbonded distances, A			
C_1–S[a]	2.978 (15)	C_3–S[b]	2.711 (17)
C_1–S[b]	4.273 (16)	C_2–S[a]	3.624 (17)
C_1–C_2	2.410 (24)	C_2–S[b]	3.478 (16)
C_1–C_3	2.392 (23)	C_1–Ni[b]	2.955 (15)
C_1–C_4[b]	3.748 (24)	C_2–Ni[b]	2.790 (14)
C_2–C_3	2.461 (22)	C_3–Ni[b]	2.879 (14)
C_2–C_4[b]	2.956 (23)	C_4–Ni[b]	3.105 (14)
N–C_4	2.479 (20)	C_1–C_2[c]	3.689 (24)
N–S[b]	2.901 (11)	C_2–C_1[c]	3.706 (22)
N–S[a]	3.007 (10)	All others >3.9 A	

Dihedral angles between various planes, deg	
Ni–N–C_3 and Ni–N–S	30.8 ± 0.9
Ni–S–C_4 and Ni–S–N	5.14 ± 0.8
Ni–N–S and Ni–C_2–N	91.2 ± 0.9
Ni–N–S and Ni–C_1–N	29.4 ± 1.04

[a] To opposite ring in the same molecule. [b] Across five-membered ring. [c] Between molecules.

TABLE IV

RMS ATOMIC DISPLACEMENTS IN THE DIRECTION OF THE PRINCIPAL AXES (A)[a]

Atom	1	2	3
Ni	0.168 (3)	0.177 (3)	0.209 (3)
S	0.191 (4)	0.217 (4)	0.298 (5)
N	0.177 (18)	0.212 (14)	0.234 (16)
C_1	0.172 (27)	0.247 (20)	0.334 (21)
C_2	0.169 (23)	0.210 (22)	0.353 (20)
C_3	0.170 (22)	0.252 (18)	0.318 (21)
C_4	0.177 (20)	0.253 (21)	0.389 (23)

[a] Values in parentheses are $\sigma' = 10^4\sigma$.

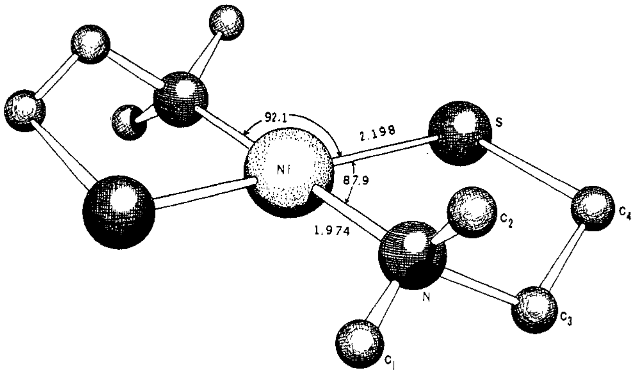

Figure 1.—Perspective view of the *trans*-bis(N,N-dimethyl-β-mercaptoethylamine)nickel(II) molecule with the most important intramolecular distances and angles.

idealized 90° at 87.9° and 92.1°, both ±0.3°. The Ni–N distance is significantly longer at 1.974 ± 0.010 A than the range of 1.82–1.92 A[17] found for rigorously planar Ni(II) chelates and probably is caused by nonbonded repulsions between S and the C_1 methyl group which are separated by 2.978 ± 0.015 A, short compared to the sum of the S and methyl van der Waals radii[18] of 3.85 A. Hence, it is not surprising that the *cis* isomer of this compound is not readily formed since this would require either a substantial molecular distortion from planarity or further elongation of the Ni–N distance due to the van der Waals repulsion between the methyl groups on the nitrogen atom. Further, the Ni–S distance of 2.198 ± 0.003 A is significantly longer than the 2.168 and 2.146 A, both ±0.011 A, observed by Fernando and Wheatley[19] in biacetylbis(mercaptoethylimine)nickel(II) and the

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[17] (a) E. Frasson, C. Panattoni, and I. Sacconi, *J. Phys. Chem.*, **63**, 1908 (1959); (b) R. L. Braun and E. C. Lingafelter, *Acta Cryst.*, **21**, 546 (1966), and references to unpublished data therein; (c) L. Godycki and R. E. Rundle, *ibid.*, **6**, 487 (1953).

[18] L. Pauling, "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

[19] Q. Fernando and P. J. Wheatley, *Inorg. Chem.*, **4**, 1726 (1965).

2.174 and 2.156 A, both ±0.006 A, observed by Eisenberg and Ibers[20] in di(tetramethylammonium)bis(maleonitrile dithiolate)nickel(II). The 92.1° N–Ni–S angle as well as the elongated Ni–N and Ni–S distances are consistent with a nonnegligible amount of steric hindrance between the C_1 methyl group and sulfur. The N–C_1, N–C_2, and N–C_3 distances are not significantly longer than the expected N–C bonded distance of 1.47 A. The C–C and C–S distances are also, well within experimental error, "normal" single bonds. The C_1–N–C_2 and C_2–N–C_3 angles are within experimental error of the idealized tetrahedral 109° 28′, but C_1–N–C_3 is significantly less at 105.2 ± 1.2°, again probably due to steric repulsion between C_1 and S. The C_4–S–Ni angle of 100.8 ± 0.5° indicates that the sulfur contributes a p orbital to the Ni–S σ bond and to the S–C bond as well. The Ni–S interaction probably includes some $p\pi$–$p\pi$ interaction, but this is not discernible from the bond lengths and angles.

The dihedral angles between particular planes and the perpendicular displacements of the carbon atoms from the Ni–N_2–S_2 plane are particularly interesting. The dihedral angle between the Ni–N–S plane and the Ni–C_2–N plane is 91.2 ± 0.9° and C_2 is 1.192 A above the plane defined by Ni–N_2–S_2. This means that C_2 is in a stereochemically polar position relative to the NiN_2S_2 plane and effectively blocks any axial chemical attack on the Ni(II) species by another ligand. This is in agreement with the fact that this seems to be a particularly stable complex, relatively inert to attack by other ligands. On the other hand, the dihedral angle between the Ni–N–S plane and the Ni–C_1–N plane is 29.4 ± 1.04° and the C_1 atom is 0.652 A below the NiN_2S_2 plane. Therefore, the C_1 methyl group can be considered as being in an essentially equatorial position relative to the NiN_2S_2 plane. C_3 and C_4 are displaced 0.72 (2) and 0.16 (2) A below this same plane conforming to the expected geometry for the β-mercaptoethylamine group in a metal chelate.

Acknowledgment.—We wish to acknowledge financial support from the National Institutes of Health, Grant No. GM-13985-01,02.

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The Crystal and Molecular Structure of Dimethyltin Bis(8-hydroxyquinolinate)

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Received June 19, 1967

The crystal structure of dimethyltin bis(8-hydroxyquinolinate), $(CH_3)_2Sn(C_9H_6NO)_2$, has been determined from three-dimensional X-ray diffraction data. Unit cell constants are a = 9.44 ± 0.02 A, b = 13.28 ± 0.02 A, c = 15.62 ± 0.03 A, and β = 110.0 ± 0.2°. The space group is $P2_1/c$. The density by flotation is 1.57 g/cc. Four molecules in the unit cell give a calculated density of 1.586 g/cc. By visual estimation of film data, the intensities of 1738 independent reflections were obtained. The structure was solved by three-dimensional Patterson and Fourier methods and refined by full-matrix least squares to a final conventional R factor of 7.8%. The arrangement of atoms about the tin atom can be considered to be a highly distorted octahedron with the following bond distances: Sn–C, 2.15 and 2.17 A; Sn–O, 2.10 and 2.11 A; Sn–N, 2.31 and 2.38 A. The bond angles in the distorted octahedron range from 73.4 to 110.7°. The results are discussed in relationship to previous spectroscopic studies of the complex and a qualitative molecular orbital approach to the bonding.

Introduction

In recent chemical literature there have been numerous reports of compounds in which group IV elements are believed to exhibit coordination numbers greater than six. In the case of group IV transition elements the structures of some of these higher coordinate compounds have been determined by X-ray diffraction methods. For example, tetrakis(acetylacetonato)zirconium(IV) has been found to have a square-antiprism structure.[1] However, for the group IV nontransition elements no crystal structures of higher coordinate complexes have been determined. Since a knowledge of the configuration about the metal atoms in higher coordinate group IV complexes could lead to a better understanding of the nature of the bonding, the structures of a number of these compounds will be studied by X-ray diffraction methods.

One of the group IV elements of particular recent interest has been tin. However, even for the lower coordination numbers five and six, crystal structures of tin complexes have not been studied. Before proceeding to a study of the higher coordination numbers, it was considered necessary to examine the configuration about the tin atom in at least one six-coordinate complex. Dimethyltin bis(8-hydroxyquinolinate), $(CH_3)_2Sn(C_9H_6NO)_2$, has been previously studied by spectroscopic techniques,[2-6] and at least two aspects

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