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The Crystal Structure of Thiocyanatotriethylenetetraminecopper(II) Thiocyanate

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Crystals of [Cu(trien)SCN]NCS (trien = triethylenetetramine, $C_6N_4H_{18}$) are orthorhombic. The space group is $P2_12_12_1$ with four molecules in the unit cell of dimensions $a = 10.803$ (1), $b = 9.381$ (1), and $c = 13.815$ (2) Å. A total of 1836 independent reflections was measured with a Picker automatic diffractometer using Mo Kα radiation. The structure was refined by full-matrix least squares to a conventional R factor of 0.040% for the 1506 observed reflections. The coordination around the central copper atom is square pyramidal with the copper atom about 0.4 Å above the plane of the four nitrogen atoms of the ligand molecule. The Cu–N basal plane bond length has a mean value of 2.016 (4) Å. The fifth, apical, position is occupied by the sulfur atom of a thiocyanate group; the Cu–S bond length is 2.607 (2) Å.

Introduction

In two recent papers,[2] the structures of the complexes of copper(II) and zinc(II) with β,β',β''-triaminotriethylamine (tren) have been reported. Both copper(II) and zinc(II) ions were found to be five-coordinate with a trigonal-bipyramidal coordination polyhedron. With the aim of making a comparison of the molecular parameters as the geometry of the ligand changes, we have investigated the crystal structure of Cu(trien)$(NCS)_2$, where trien = triethylenetetramine is the linear isomer of tren.

Experimental Section

[Cu(trien)SCN]NCS was prepared as described by Barbucci, *et al.*[3]

The crystals are blue prisms elongated along c. A crystal of dimensions 0.12 × 0.20 × 0.28 mm parallel to a, b, and c, respectively, was selected and mounted along the c axis. Oscillation and equiinclination Weissenberg photographs showed the crystal to be orthorhombic; systematic absences observed for the odd orders of $h00$, $0k0$, and, $00l$ are consistent with the space group $P2_12_12_1$. The cell constants and their estimated standard deviations were obtained by a least-squares fit of 20 2θ values ($31° \leq 2\theta \leq 45°$) taken on an automatic Picker diffractometer using Mo Kα radiation (λ 0.71069 Å at 24°). The final values, with standard deviations in parentheses, are $a = 10.803$ (1), $b = 9.381$ (1), and $c = 13.815$ (2) Å.

The density, measured by the flotation method, was 1.53 g cm^{-3} and that calculated on the basis of four molecules in the cell is 1.545 g cm^{-3}.

The crystal was mounted with the c axis parallel to the ϕ axis of an automatic Picker diffractometer, equipped with a pulse height analyzer. The data were collected with Nb-filtered Mo Kα radiation using the ω–2θ scan (2θ scan rate 2°/min); the scan rate was calculated using the formula of Alexander and Smith,[4] $A + B \tan \theta$, with A set equal to 0.90 and B equal to 1.00. A background count was taken at each end of the scan range for 22 sec. Four standard reflections were measured every 5 hr to check the alignment of the crystal as well as the long-range stability of the apparatus. All reflections in one octant of the reciprocal lattice out to $2\theta = 55°$ were measured. The intensity of each reflection was calculated as

$$I = k(C_S - t'C_B - 0.45)$$

and the standard deviation of this intensity was calculated as

$$\sigma_I = k\{(1/10)(C_S + t'^2C_B) + 0.25 + k'^2(C_S + t'C_B)^2\}^{1/2}$$

where k is the scaling factor with respect to the standard reflections, C_S is the total recorded dekacounts in a scan of t seconds duration, C_B is the total recorded dekacounts per x seconds at background, $t' = t/x$, and k' is the estimated stability constant of the instrument.

The factor $^1/_{10}$ in the expression for σ_I arises from the fact that the measurements were recorded in dekacounts (and the variance in counts is equal to counts) and the terms 0.45 in I and 0.25 in σ_I arise from the fact that the recorded dekacounts are obtained by truncation.

In order to estimate the value of k' a set of eight reflections, covering the intensity range, was selected and the intensity of each was measured 25 times. A value of k' was calculated for each reflection so that the calculated σ_I was equal to the empirical value evaluated from the 25 measurements. The mean value of the eight determinations ($k' = 0.07$) was used in the general formula to calculate the standard deviations of the intensities for all of the reflections.

Of the total of 1847 reflections measured, 340 were coded unobserved, as their respective intensities were less than twice their estimated standard deviations, and assigned effective intensities of $2\sigma_I$.

Lorentz and polarization factors were applied to all intensities and the structure factor and its standard deviation were calculated for each reflection. The linear absorption coefficient for Mo Kα radiation is 18.9 cm^{-1} which gives transmission factors ranging from 0.72 to 0.85; no correction was applied for absorption effects.

Structure Determination and Refinement

The copper position was readily found from an unsharpened three-dimensional Patterson function. All of the remaining nonhydrogen atoms were located by a series of three-dimensional Fourier syntheses. All calculations were done on an IBM 7094, using the programs written or adapted by Stewart.[5] The atomic scattering factors used were those of Cromer and Waber[6] for Cu^{2+}, S, N, and C and those of Stewart, Davidson, and Simpson[7] for hydrogen.

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TABLE I

Positional Parameters ($\times 10^4$) and Thermal Parameters ($\times 10^2$)

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	2101 (1)	−48 (1)	1071 (1)	237 (2)	314 (3)	271 (2)	11 (4)	1 (3)	9 (4)
S(1)	1111 (2)	−202 (3)	−646 (1)	552 (8)	739 (13)	352 (8)	94 (12)	−131 (7)	−61 (10)
S(2)	2013 (2)	3892 (2)	4033 (2)	378 (8)	578 (10)	604 (11)	68 (9)	−15 (11)	76 (10)
N(1)	3492 (7)	−341 (9)	−1458 (4)	971 (44)	776 (51)	443 (30)	−89 (44)	254 (31)	−113 (33)
N(2)	1432 (6)	6783 (7)	4085 (6)	750 (41)	488 (31)	656 (41)	−87 (32)	−199 (38)	−132 (33)
N(3)	1019 (6)	−1511 (7)	1721 (5)	280 (28)	431 (29)	367 (32)	2 (23)	7 (24)	1 (23)
N(4)	3395 (5)	−1617 (6)	1070 (5)	294 (22)	429 (27)	480 (32)	−9 (20)	32 (25)	4 (27)
N(5)	3548 (5)	1240 (6)	789 (5)	346 (24)	352 (24)	453 (33)	−0 (21)	9 (22)	56 (24)
N(6)	1295 (7)	1722 (7)	1589 (6)	370 (32)	428 (30)	375 (31)	22 (25)	16 (27)	42 (23)
C(1)	2497 (7)	−283 (8)	−1137 (4)	877 (45)	395 (39)	211 (23)	23 (33)	17 (30)	−9 (27)
C(2)	1664 (6)	5589 (8)	4079 (6)	310 (29)	685 (43)	342 (35)	−91 (28)	−64 (27)	−153 (33)
C(3)	1602 (8)	−2935 (9)	1578 (7)	489 (41)	396 (36)	416 (40)	−31 (30)	−16 (34)	−28 (32)
C(4)	2947 (10)	−2745 (8)	1721 (6)	467 (38)	367 (32)	641 (50)	106 (39)	77 (45)	80 (33)
C(5)	4550 (7)	−892 (9)	1405 (6)	279 (29)	659 (47)	747 (54)	32 (33)	−68 (31)	175 (41)
C(6)	4731 (6)	427 (9)	813 (7)	300 (30)	608 (47)	834 (56)	−43 (28)	−1 (34)	77 (39)
C(7)	3413 (9)	2458 (9)	1467 (7)	524 (47)	539 (48)	497 (47)	−154 (39)	−29 (36)	66 (38)
C(8)	2081 (13)	2961 (9)	1398 (8)	705 (51)	341 (31)	635 (51)	46 (46)	157 (50)	24 (33)
Positional Parameters ($\times 10^3$) and Thermal Parameters ($\times 10$)									
H(331)	100 (6)	−133 (6)	259 (5)	54 (17)					
H(332)	35 (6)	−149 (8)	153 (6)	61 (25)					
H(31)	116 (8)	−375 (9)	192 (7)	98 (31)					
H(32)	149 (5)	−326 (6)	93 (4)	32 (14)					
H(41)	319 (6)	−245 (6)	252 (4)	60 (17)					
H(42)	340 (5)	−372 (6)	159 (4)	50 (15)					
H(441)	340 (8)	−180 (7)	23 (6)	80 (26)					
H(51)	442 (6)	−59 (6)	219 (4)	70 (19)					
H(52)	518 (6)	−175 (7)	149 (5)	52 (18)					
H(61)	540 (5)	113 (5)	118 (4)	41 (13)					
H(62)	491 (7)	−14 (10)	14 (5)	119 (26)					
H(551)	351 (9)	178 (9)	30 (6)	84 (33)					
H(71)	365 (5)	211 (5)	211 (4)	24 (12)					
H(72)	391 (5)	333 (7)	112 (5)	61 (17)					
H(81)	185 (7)	378 (7)	198 (5)	66 (18)					
H(82)	194 (10)	340 (9)	70 (7)	112 (33)					
H(661)	57 (6)	182 (8)	145 (6)	39 (23)					
H(662)	113 (5)	154 (5)	220 (4)	10 (12)					

Refinement was carried out by full-matrix least-squares, assigning unit weight to all the reflections (unobserved reflections with $F_c < F_o$ were given zero weight). The function minimized in the least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$ and the discrepancy factors quoted are $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$. Two cycles of least-squares refinement with individual isotropic temperature factors reduced R_1 to 0.083 and one cycle anisotropic to 0.054.

A three-dimensional Fourier synthesis calculated at this stage revealed the positions of the hydrogen atoms, whose peak heights ranged between 0.63 and 0.39 $e^-/\text{Å}^3$. When the hydrogen atoms were included in the F_c calculation, assigning to each hydrogen atom an isotropic temperature factor equal to that of the atom to which it is bonded, R_1 dropped from 0.054 to 0.046.

A total of 226 parameters, including anisotropic temperature factors of nonhydrogen atoms, isotropic temperature factors of hydrogen atoms, and the scale factor, were finally to be adjusted. Because of the limitations of core size on the computer, all of these variables could not be refined simultaneously. Refinement was completed by four successive cycles of least squares, where the weights were assigned values equal to $1/\sigma^2$. In the first cycle all parameters of all nonhydrogen atoms were varied while the parameters of the hydrogen atoms were held constant and in the final three cycles all of the parameters of the atoms (both hydrogen and nonhydrogen) of the organic ligand were allowed to vary while the parameters of the copper and thiocyanate ions were held constant. The final values of R_1 and R_2 are 0.040 and 0.032, with the average shift-to-error ratio of 0.2σ and the maximum ratio of 0.60σ.

The final atomic parameters and their standard deviations are given in Table I. The final values of observed and calculated structure factors are given in Table II.

Discussion

The crystal structure consists of five-coordinate $Cu(trien)SCN^+$ cations, with a distorted square-pyramidal configuration, and SCN^- anions, connected by a network of N–H···N and N–H····S hydrogen bonds.

A perspective drawing of the $Cu(trien)SCN^+$ group is shown in Figure 1. The square-pyramidal coordination polyhedron of the Cu^{2+} ion consists of the nitrogen atoms of trien below the Cu^{2+} ion in the basal positions and the sulfur atom of a thiocyanate group on the

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS (COLUMNS ARE l, $10F_o$, AND $10\,|F_c|$)

0,0,L		
2	861	584
4	2730	2719
6	692	690
8	249	240
10	409	405
12	157	157
14	313	216
16	72	72
1,0,L		
0	290	0
1	260	248
2	1113	1063
3	251	249
4	739	734
5	599	592
6	563	553
7	145	146
8	94	45
9	60	39
10	214	218
11	175	166
12	280	290
13	233	212
14	54*	44
15	61*	1
16	178	183
17	166	97
2,0,L		
0	1856	1861
1	117	117
2	209	202
3	49	77
4	1362	1339
5	287	285
6	586	582
7	35*	4
8	501	496
9	205	211
10	583	567
11	63*	52
12	45*	12
13	67	56
14	335	305
15	53*	2
16	56	94
17	128	134
3,0,L		
0	95*	0
1	1016	585
2	219	195
3	940	914
4	571	563
5	509	506
6	49	88
7	603	604
8	244	250
9	70	60
10	66	72
11	281	274
12	79	53
13	272	249
14	116	101
15	69*	35
16	60	73
17	166	161
4,0,L		
0	527	513
1	141	143
2	44*	8
3	105	106
4	182	163
5	207	206
6	161	156
7	218	210
8	483	484
9	347	366
10	396	383
11	53*	20
12	174	182
13	181	185
14	247	248
15	72	80
16	63*	33
17	64*	47
5,0,L		
0	54*	0
1	492	485
2	153	146
3	1183	1180
4	247	253
5	200	206
6	53	84
7	752	749
8	185	187
9	239	236
10	56*	11
11	270	270
12	53*	38
13	65	92
14	54*	5
15	117	106
16	54*	12
6,0,L		
0	394	390
1	112	115
2	59	48
3	94	56
4	286	285
5	459	449
6	56	85
7	153	145
8	88	80
9	513	520
10	91	76
11	54*	36
12	90	56
13	256	244
14	54*	25
15	106	117
16	74	82
7,0,L		
0	54*	0
1	438	446
2	261	258
3	776	777
4	229	238
5	42*	20
6	61*	16
7	633	627
8	49*	25
9	203	199
10	63*	20
11	293	289
12	78	78
13	159	150
14	93	92
15	88	86
8,0,L		
0	191	188
1	633	639
2	45*	6
3	229	239
4	238	242
5	485	491
6	106	103
7	66	65
8	209	208
9	190	199
10	186	193
11	71	63
12	63*	41
13	108	104
14	166	129
9,0,L		
0	64*	0
1	304	293
2	60	41
3	260	256
4	64*	34
5	221	215
6	122	128
7	303	295
8	79	79
9	83*	4
10	77	60
11	156	211
12	110	112
13	113	122
10,0,L		
0	388	349
1	201	223
2	96	96
3	115	124
4	217	202
5	191	202
6	191	189
7	40*	14
8	84	39
9	108	105
10	169	154
11	64*	64
12	55*	28
11,0,L		
0	47*	0
1	60*	14
2	153	165
3	67*	42
4	66*	25
5	49*	6
6	152	161
7	76*	44
8	61	87
9	54*	21
10	61	84
11	67	50
12,0,L		
0	345	341
1	68*	15
2	65*	67
3	54*	5
4	253	249
5	54*	40
6	148	150
7	71*	15
8	89	88
9	65	67
13,0,L		
0	76*	0
1	70*	31
2	163	169
3	71*	33
4	78*	64
5	72*	23
6	95	110
14,0,L		
0	151	130
1	73*	49
0,1,L		
0	26*	0
1	146	151
2	1517	1537
3	255	267
4	517	524
5	48	24
6	838	869
7	88	40
8	792	811
9	63*	17
10	178	182
11	107	107
12	578	599
13	89	81
14	195	176
15	71	57
16	188	195
17	78*	48
1,1,L		
0	1499	1459
1	357	337
2	273	260
3	277	294
4	894	836
5	241	251
6	377	367
7	281	285
8	278	279
9	83	57
10	207	220
11	105	97
12	129	124
13	85	73
14	184	189
15	73	46
16	49*	46
17	69	66
2,1,L		
0	180	169
1	161	171
2	707	689
3	671	659
4	703	697
5	743	765
6	427	425
7	120	124
8	634	644
9	293	296
10	128	113
11	298	293
12	374	351
13	142	138
14	60*	40
15	101	87
16	169	154
17	113	105
3,1,L		
0	307	309
1	1066	1026
2	65	76
3	290	288
4	326	324
5	838	840
6	157	142
7	289	290
8	513	512
9	347	339
10	417	425
11	257	246
12	135	144
13	111	120
14	285	272
15	121	119
16	62	43
17	66	50
4,1,L		
0	327	328
1	345	337
2	570	563
3	345	341
4	465	465
5	192	191
6	153	155
7	245	241
8	223	218
9	80	82
10	54	73
11	191	184
12	51*	23
13	59*	35
14	53	72
15	123	135
16	72*	40
17	107	96
5,1,L		
0	223	219
1	388	389
2	40	53
3	341	340
4	332	331
5	731	724
6	129	132
7	135	135
8	210	212
9	682	674
10	169	174
11	252	245
12	57	60
13	271	234
14	134	154
15	215	217
16	53*	24
6,1,L		
0	461	463
1	254	248
2	251	244
3	563	563
4	416	420
5	134	131
6	91	95
7	386	380
8	159	164
9	160	167
10	64	60
11	184	177
12	66*	49
13	73	67
14	91*	27
15	128	115
16	65*	9
7,1,L		
0	199	196
1	805	611
2	101	105
3	272	271
4	125	132
5	595	595
6	108	107
7	45*	23
8	211	217
9	367	363
10	58	56
11	140	132
12	96	92
13	186	191
14	63*	67
15	149	139
8,1,L		
0	133	134
1	369	369
2	401	396
3	387	395
4	278	283
5	171	168
6	177	181
7	363	374
8	224	225
9	87	94
10	45*	25
11	214	221
12	94	90
13	162	166
14	64*	27
9,1,L		
0	51*	20
1	442	447
2	62*	32
3	220	213
4	65	71
5	330	332
6	52*	41
7	111	112
8	123	122
9	120	114
10	66	75
11	76	71
12	112	95
13	56	65
10,1,L		
0	52*	25
1	155	143
2	255	241
3	113	120
4	44	57
5	106	116
6	257	251
7	157	167
8	184	181
9	62*	20
10	101	100
11	148	149
12	196	185
11,1,L		
0	283	294
1	59*	45
2	85	94
3	90	98
4	198	193
5	54	41
6	130	143
7	80	75
8	77	57
9	64	80
10	89	95
11	73*	36
12,1,L		
0	68*	12
1	41*	37
2	267	270
3	85	86
4	68	80
5	63	54
6	193	187
7	55	38
8	119	117
9	45*	27
13,1,L		
0	138	153
1	69	81
2	54*	27
3	64*	32
4	147	157
5	74	54
6	60	61
0,2,L		
0	1053	1053
1	63	70
2	904	937
3	33*	44
4	703	693
5	183	198
6	1053	1101
7	202	215
8	193	189
9	52*	5
10	442	449
11	179	185
12	99	108
13	72	93
14	171	185
15	68*	50
16	63*	47
17	67	25
1,2,L		
0	34	31
1	112	115
2	421	429
3	195	180
4	444	430
5	278	282
6	399	487
7	288	299
8	599	604
9	73	80
10	299	302
11	255	259
12	442	434
13	143*	129
14	48*	19
15	55	27
16	179	174
17	63	62
2,2,L		
0	453	427
1	572	562
2	234	227
3	375	393
4	630	628
5	539	543
6	510	517
7	414	415
9	199	211
10	482	485
11	105	94
12	83	86
13	117	120
14	283	264
15	53*	13
16	55	47
17	88	93
3,2,L		
0	144	147
1	630	613
2	636	624
3	574	558
4	401	395
5	263	255
6	209	208
7	517	512
8	241	243
9	57	53
10	71	53
11	318	315
12	95	89
13	168	165
14	68	38
15	68	72
16	120	103
17	117	108
4,2,L		
0	594	576
1	555	546
2	102	114
3	519	516
4	527	520
5	449	449
6	89	102
7	78	87
8	381	375
9	432	452
10	306	310
11	188	184
12	110	95
13	199	206
14	225	228
15	158	155
16	89	84
5,2,L		
0	261	256
1	683	673
2	603	596
3	813	813
4	225	226
5	126	113
6	232	240
7	398	397
8	121	109
9	234	230
10	118	124
12	59*	16
13	154	139
14	69	55
15	136	118
16	64*	38
6,2,L		
0	263	261
1	268	248
2	187	205
3	366	370
4	185	184
5	302	302
6	47	78
7	203	207
8	130	136
9	381	381
10	51	47
11	161	151
12	81	75
13	227	222
14	51*	33
15	191	190
7,2,L		
0	349	363
1	384	383
2	188	190
3	494	511
4	313	314
5	54	60
6	71	70
7	395	398
8	96	88
9	172	181
10	88	79
11	205	198
12	53*	39
13	184	167
14	71	77
15	86	79
8,2,L		
0	117	116
1	471	478
2	51*	43
3	272	278
4	257	268
5	353	365
6	56	54
7	133	124
8	183	185
9	169	162
10	119	129
11	60	70
12	50*	10
13	93	95
14	107	98
9,2,L		
0	242	246
1	121	128
2	214	216
3	130	141
4	156	163
5	170	173
6	204	197
7	240	264
8	132	124
9	92	88
10	94	84
11	196	201
12	80	102
13	102	106
10,2,L		
0	312	328
1	200	210
2	121	124
3	138	149
4	215	227
5	173	185
6	193	196
7	82	84
8	83	86
9	126	131
10	130	116
11	78*	62
12	65*	33
11,2,L		
0	64	60
1	58	86
2	244	245
3	72	73
4	96	89
5	101	97
6	222	224
7	54	63
8	146	149
9	76*	64
10	96	102
12,2,L		
0	258	265
1	57	39
2	69	73
3	61	75
4	223	226
5	70*	39
6	144	146
7	64	56
8	102	109
13,2,L		
0	65	67
1	72	59
2	174	181
3	67	43
4	101	92
5	54*	31
6	126	123
0,3,L		
0	40*	0
1	510	522
2	214	225
3	350	357
4	66	60
5	319	321
6	425	437
7	135	129
8	291	285
9	120	101
10	308	322
11	69	58
12	345	356
13	52*	32
14	47*	11
15	62*	4
16	137	138
17	53*	22
1,3,L		
0	1408	1404
1	344	346
2	378	371
3	384	394
4	983	991
5	376	371
6	362	382
7	219	217
8	350	339
9	169	167
10	350	352
11	50	46
12	114	116
13	70	48
14	194	200
15	69	39
16	50*	5
17	56*	43
2,3,L		
0	33*	18
1	373	367
2	604	593
3	545	544
4	178	181
5	396	405
6	364	362
7	613	629
8	229	246
9	136	175
10	106	110
11	358	361
12	180	180
13	153	150
14	68*	12
15	36	47
16	142	130
17	92	85
3,3,L		
0	830	827
1	675	663
2	300	299
3	51	43
4	706	703
5	624	615
6	103	107
7	190	192
8	404	411
9	286	285
10	342	340
11	109	107
12	60	73
13	130	128
14	263	261
15	63*	43
16	94	80
4,3,L		
0	119	129
1	816	811
2	940	929
3	937	932
4	324	320
5	220	210
6	143	145
7	521	522
8	158	169
9	165	171
10	95	108
11	235	233
12	32*	34
13	143	143
14	49*	25
15	100	111
16	58	52
5,3,L		
0	358	345
1	344	342
2	318	324
3	482	480
4	309	309
5	343	348
6	126	127
7	236	227
8	187	186
9	392	384
10	153	156
11	138	139
12	66*	45
13	188	165
14	119	112
15	169	178
16	73*	25
6,3,L		
0	138	144
1	506	517
2	117	120
3	597	605
4	71	70
5	107	111
6	208	200
7	388	391
8	114	115
9	126	113
10	68	63
11	172	173
12	82	72
13	132	114
14	71*	38
15	68	101
7,3,L		
0	95	109
1	290	290
2	236	260
3	196	211
4	119	116
5	324	320
6	168	166
7	78	91
8	106	104
9	257	264
10	51	53
11	61*	35
12	74	65
13	160	157
14	65	76
8,3,L		
0	59	53
1	156	151
2	342	330
3	268	266
4	68	85
5	123	127
6	172	190
7	362	351
8	79	45
9	70	64
10	106	109
11	226	219
12	70*	38
13	107	104
14	65*	10
9,3,L		
0	295	308
1	199	202
2	162	173
3	46*	22
4	223	236
5	239	246
6	159	158
7	71	62
8	114	115
9	142	136
10	127	115
11	52*	14
12	72*	48
13	80*	75
10,3,L		
0	58*	37
1	125	135
2	211	221
3	87	98
4	60	82
5	121	131
6	216	223
7	177	183
8	151	156
9	63*	25
10	88	111
11	122	137
11,3,L		
0	336	361
1	76	86
2	134	148
3	96	99
4	255	255
5	103	97
6	247	247
7	54*	31
8	71	84
9	83	86
10	188	192
12,3,L		
0	69*	18
1	103	104
2	166	170
3	80	79
4	77*	64
5	94	83
6	140	145
7	64*	13
8	96	111
13,3,L		
0	177	188
1	72*	22
2	55*	49
3	58	35
4	169	163
5	56*	0
0,4,L		
0	659	670
1	32*	37
2	165	170
3	177	180
4	483	479
5	137	147
6	202	214
7	46*	18
8	206	216
9	51*	4
10	105	120
11	59*	4
12	124	121
13	83	83
14	116	122
15	69*	47
16	58*	35
1,4,L		
0	283	277
1	136	146
2	685	692
3	180	185
4	192	191
5	167	174
6	590	616
7	233	240
8	385	408
9	103	97
10	218	222
11	165	170
12	365	360
13	60*	53
14	67*	47
15	54*	20
16	150	152
2,4,L		
0	639	625
1	683	682
2	139	136
3	146	145
4	564	562
5	729	737
6	180	180
7	320	327
8	308	324
9	249	256
10	193	205
11	121	118
12	91	95
13	86	77
14	192	192
15	49*	19
16	64*	19
3,4,L		
0	247	254
1	138	134
2	936	930
3	309	310
4	341	345
5	88	91
6	266	275
7	323	324
8	272	265
9	101	105
10	49	42
11	223	231
12	144	139
13	117	111
14	62*	25
15	94	85
16	102	97
4,4,L		
0	364	365
1	625	622
2	151	154
3	271	270
4	292	297
5	694	696
6	92	104
7	63	85
8	197	191
9	454	447
10	237	240
11	220	220
12	52*	20
13	146	161
14	172	178
15	155	157
16	64*	58
5,4,L		
0	37*	6
1	345	347
2	284	282
3	428	423
4	224	229
5	87	83
6	86	78
7	226	230
8	183	181
9	103	109
10	119	127
11	117	126
13	112	90
14	63	60
15	123	105
6,4,L		
0	117	114
1	396	406
2	181	183
3	364	365
4	159	170
5	472	469
6	229	233
7	169	166
8	91	100
9	426	422
10	70	81
11	129	122
12	65*	39
13	187	189
14	52*	33
15	185	164
7,4,L		
0	62	71
1	191	194
2	328	323
3	268	272
4	112	121
5	126	120
6	99	114
7	274	284
8	78	65
9	58*	6
10	71	83
11	163	174
12	54*	30
13	64	63
14	64*	15
8,4,L		
0	55	68
1	338	333
2	185	189
3	113	113
4	84*	65
5	374	363
6	58	58
7	65*	36
8	73*	69
9	230	216
10	47	65
11	49*	41
12	51*	26
13	105	103
9,4,L		
0	72	65
1	57	39
2	361	359
3	113	116
4	160	161
5	84	83
6	214	219
7	211	212
8	198	198
9	50*	25
10	58	40
11	167	167
12	135	117
10,4,L		
0	209	210
1	162	155
2	93	92
3	52	68
4	135	147
5	155	168
6	136	131
7	104	95
8	63	64
9	103	56
10	76	84
11	66	64
11,4,L		
0	53*	20
1	102	94
2	269	265
3	118	110
4	136	130
5	50*	18
6	181	190
7	45	63
8	189	184
9	54*	22
12,4,L		
0	150	158
1	70	70
2	70*	45
3	100	76
4	121	126
5	64*	21
6	91	98
7	65*	39
13,4,L		
0	55*	8
1	55*	35
2	184	182
3	74	57
0,5,L		
0	74*	0
1	160	162
2	45*	54
3	39*	0
4	49*	29
5	58*	36
6	303	305
7	51*	51
8	255	267
9	65	66
10	231	242
11	58	61
12	307	307
13	54*	17
14	61*	6
15	64*	33
16	166	147
1,5,L		
0	838	861
1	258	253
2	280	289
3	57	56
4	600	607
5	176	172
6	536	545
7	117	115
8	232	246
9	84	72
10	380	394
11	59*	41
12	59	52
13	59	77
14	207	209
15	52*	28
16	55*	24
2,5,L		
0	189	195
1	227	222
2	248	270
3	223	219
4	229	217
5	183	178
6	249	272
7	263	257
8	213	223
9	53*	45
10	136	151
11	174	180
12	170	175
13	130	139
14	54*	38
15	53*	40
16	90	105
3,5,L		
0	422	429
1	291	291
2	135	135
3	149	156
4	458	464
5	252	259
6	357	351
7	133	140
8	315	304
9	144	145
10	348	353
11	87	95
12	66*	47
13	89	81
14	155	188
15	43*	44
4,5,L		
0	175	170
1	342	344
2	212	215
3	542	555
4	321	317
5	43	57
6	54	44
7	395	403
8	187	185
9	210	211
10	108	96
11	205	196
12	49*	36
13	168	160
14	77*	57
15	101	97
5,5,L		
0	127	120
1	72	71
2	131	134
3	150	157
4	148	150
5	193	200
6	141	144
7	58	107
8	67	67
9	303	299
10	128	129
11	63	67
12	68*	21
13	185	176
14	60	75
15	112	107
6,5,L		
0	81	79
1	426	436
2	64	72
3	585	586
4	98	92
5	135	138
6	58	122
7	403	407
8	72	55
9	155	158
10	94	110
11	196	188
12	50*	18
13	128	120
14	57	62
7,5,L		
0	54*	10
1	202	201
2	85	92
3	182	188
4	90	101
5	184	191
6	81	81
7	95	88
8	120	109
9	200	209
10	114	114
11	55	35
12	55*	26
13	129	139
8,5,L		
0	45*	23
1	250	247
2	80	79
3	281	289
4	114	112
5	120	126
6	84	77
7	289	282
8	86	84
9	75	70
10	50*	18
11	176	174
12	72*	46
9,5,L		
0	248	247
1	202	210
2	100	100
3	131	121
4	187	189
5	164	174
6	179	173
7	88	96
8	86	89
9	88	92
10	132	132
11	65	71
10,5,L		
0	60*	0
1	121	111
2	121	126
3	119	116
4	61*	29
5	85	81
6	130	126
7	110	114
8	83	77
9	51*	15
10	75	62
11,5,L		
0	281	283
1	119	107
2	109	103
3	69*	63
4	186	192
5	107	112
6	145	158
7	56	51
8	80*	52
12,5,L		
0	63*	25
1	56	54
2	105	115
3	66	54
4	72*	29
5	73*	36
0,6,L		
0	791	802
1	315	307
2	172	175
3	245	245
4	508	513
5	61*	40
6	281	289
7	46*	20
8	143	147
9	50	49
10	231	221
11	75	66
12	52*	24
13	62*	13
14	173	161
15	51*	6
1,6,L		
0	51	55
1	431	442
2	546	561
3	42	39
4	190	197
5	452	456
6	384	393
7	121	122
8	302	315
9	158	161
10	141	134
11	58	58
12	275	279
13	69*	59
14	54*	44
15	53*	12
2,6,L		
0	411	416
1	382	385
2	123	130
3	260	259
4	383	394
5	174	184
6	291	283
7	57*	26
8	264	277
9	51	18
10	244	243
11	53	57
12	116	119
13	64	35
14	138	147
15	67	41
3,6,L		
0	207	203
1	264	266
2	385	389
3	214	215
4	359	355
5	206	221
6	205	212
7	160	150
8	261	261
9	137	135
10	65	64
11	113	111
12	116	125
13	85	92
14	64*	17
15	81	75
4,6,L		
0	47*	34
1	311	313
2	263	261
3	165	162
4	134	134
5	340	342
6	122	125
7	76	67
8	218	212
9	250	241
10	142	137
11	111	121
12	107	103
13	92	103
14	90	95
5,6,L		
0	42*	14
1	211	212
2	118	124
3	333	331
4	108	106
5	61	76
6	103	103
7	284	274
8	102	92
9	48*	38
10	61*	15
11	145	154
12	62*	18
13	72*	96
14	64*	32
6,6,L		
0	64	70
1	314	313
2	308	309
3	186	173
4	142	132
5	390	385
6	61	64
7	53	32
8	84	90
9	306	307
10	67	60
11	89	100
12	71*	32
13	141	143
7,6,L		
0	119	109
1	193	191
2	81	60
3	261	264
4	186	190
5	51	60
6	51	35
7	230	244
8	118	120
9	60	67
10	51*	24
11	174	168
12	72*	31
8,6,L		
0	65*	36
1	293	279
2	68	70
3	120	119
4	54*	40
5	260	262
6	71	82
7	61	48
8	109	96
9	175	166
10	94	78
11	71	87
9,6,L		
0	98	96
1	154	146
2	192	193
4	126	111
5	112	109
6	114	119
7	132	147
8	123	122
9	71*	49
10	61	34
10,6,L		
0	180	171
1	153	150
2	69*	32
3	90	82
4	119	126
5	144	145
6	57	54
7	71*	25
8	74	59
11,6,L		
0	63*	22
1	63	75
2	160	168
3	96	77
4	65	45
5	79*	63
6	119	119
12,6,L		
0	119	127
1	65*	6
2	73*	38
0,7,L		
0	72*	0
1	58	61
2	550	560
3	43*	8
4	44	29
5	58*	34
6	340	338
7	54*	7
8	160	158
9	54*	4
10	103	94
11	74*	54
12	221	203
13	55	38
14	54*	28
1,7,L		
0	692	713
1	186	185
2	132	141
3	240	252
4	490	495
5	69	75
6	183	196
7	191	190
8	144	137
9	106	115
10	191	189
11	79	62
12	61*	35
13	99	88
14	123	131
2,7,L		
0	142	142
1	179	187
2	466	480
3	62	79
4	122	126
5	201	194
6	321	316
7	104	108
8	179	180
9	51	69
10	120	107
11	98	90
12	156	137
13	95	77
14	69	24
3,7,L		
0	241	252
1	251	238
2	218	216
3	212	207
4	303	305
5	209	202
6	110	108
7	51	56
8	142	202
9	108	124
10	150	159
11	54*	24
12	75	62
13	78	62
14	90	108
4,7,L		
0	73	73
1	180	177
2	178	163
3	248	256
4	164	145
5	68	61
6	155	143
7	237	238
8	120	128
9	60	64
10	139	131
11	119	133
12	73	68
13	73	61
5,7,L		
0	44	14
1	218	217
2	44*	26
3	157	154
4	58*	32
5	319	314
6	69	56
7	75	72
8	66	70
9	280	264
10	69*	57
11	70*	69
12	65	52
13	136	114
6,7,L		
0	217	212
1	192	185
2	53*	82
3	338	344
4	170	145
5	53	25
6	71	58
7	278	274
8	73	63
9	56	57
10	70	74
11	121	126
12	53*	25
7,7,L		
0	49*	9
1	238	240
2	51	64
3	166	159
4	53	34
5	273	276
6	68*	27
7	73	51
8	55	55
9	222	208
10	64	42
11	81	67
8,7,L		
0	144	144
1	151	143
2	135	137
4	106	107
5	86	55
6	90	88
7	184	187
8	65	73
9	63*	47
10	64*	33
9,7,L		
0	131	126
1	172	175
2	49*	4
3	108	102
4	100	101
5	156	165
6	57	36
7	62	67
8	58	64
9	116	104
10,7,L		
0	63*	32
1	60	74
2	168	148
3	100	91
4	64*	27
5	80	42
6	120	117
7	108	94
11,7,L		
0	139	144
1	55*	39
2	56*	19
3	55*	30
4	116	104
0,8,L		
0	415	410
1	55	10
2	128	125
3	126	112
4	285	287
5	96	94
6	257	261
7	68*	14
8	118	107
10	193	197
11	68	57
12	55*	26
13	65	63
1,8,L		
0	66	48
1	260	251
2	252	260
3	111	106
4	116	127
5	174	166
6	171	177
7	92	93
8	184	189
9	61	42
10	74	76
11	113	103
12	127	146
13	54*	34
2,8,L		
0	356	356
1	92	97
2	90	84
3	45*	18
4	278	274
5	144	144
6	196	194
7	58	55
8	123	124
9	119	116
10	173	174
11	54*	38
12	72*	47
13	73	61
3,8,L		
0	90	99
1	47	65
2	177	183
3	135	134
4	85	93
5	94	96
6	103	107
7	205	197
8	95	97
9	96	106
10	63	42
11	173	166
12	92	81
4,8,L		
0	160	168
1	108	104
2	57	53
3	58*	33
4	180	185
5	183	186
6	53*	61
7	47*	28
8	119	131
9	177	175
10	114	110
11	64*	58
12	65*	29
5,8,L		
0	87	81
1	281	193
2	98*	35
3	318	313
4	50*	2
5	60*	14
6	53*	35
7	256	242
8	74	77
9	66	81
10	55*	37
11	134	117
6,8,L		
0	53*	15
1	135	143
2	141	129
3	102	102
4	128	122
5	153	161
6	54	47
7	62*	33
8	87	48
9	181	133
10	55*	16
11	58	47
7,8,L		
0	61*	28
2	54*	30
3	274	276
4	68*	29
5	69*	37
6	47*	16
7	205	196
8	59	30
9	73	75
10	55*	11
8,8,L		
0	95	109
1	131	131
2	50*	35
3	90	78
4	105	93
5	122	120
6	57	57
7	52*	12
8	85	77
9,8,L		
0	63*	34
1	119	115
2	83	81
3	156	125
4	71*	11
5	67	55
6	56	69
7	101	118
10,8,L		
0	161	162
1	66	82
2	72*	30
3	72*	37
4	129	125
0,9,L		
0	46*	0
1	133	125
2	188	181
3	75	66
4	200	187
5	88	92
6	169	179
7	54	2
8	202	208
9	56*	54
10	119	108
11	64*	18
12	134	134
1,9,L		
0	119	136
1	58*	47
2	118	120
3	52*	15
4	129	128
5	101	86
6	194	192
7	54	34
8	79	85
9	82	68
10	142	129
11	72*	37
12	57*	41
2,9,L		
0	117	110
1	83	77
2	229	233
3	96	91
4	145	152
5	99	86
6	160	149
7	132	118
8	172	172
9	77*	80
10	57	52
11	136	99
3,9,L		
0	125	127
1	161	148
2	57	74
3	125	114
4	106	119
5	187	179
6	76	80
7	55	35
8	79	90
9	165	144
10	83	80
11	52*	50
4,9,L		
0	52*	16
1	125	114
2	190	186
3	132	128
4	52	67
5	54	62
6	98	106
7	139	126
8	92	84
9	72*	56
10	64*	38
5,9,L		
0	67*	48
1	239	229
2	96	78
3	160	148
4	105	92
5	196	194
6	62*	43
7	54*	12
8	96	72
9	131	126
10	73*	35
6,9,L		
0	61	53
1	164	154
2	51*	36
3	141	144
4	67	64
5	70	59
6	70*	42
7	95	90
8	65	98
9	73*	40
7,9,L		
0	34*	8
1	181	187
2	54*	34
3	108	109
4	63*	8
5	180	174
6	63*	38
7	64*	26
8	36*	17
8,9,L		
0	69	70
1	70	69
2	63	90
3	70	71
4	96	67
5	86	54
6	97	46
9,9,L		
0	73	39
1	115	122
2	53*	18
3	64	66
0,10,L		
0	228	228
1	49*	2
2	59	62
3	69*	19
4	195	193
5	63*	23
6	123	121
7	81	72
8	81	98
9	56*	7
10	100	102
1,10,L		
0	215	125
2	160	164
3	60	64
4	75	76
5	49*	26
6	146	157
7	78	60
8	79	72
9	52*	22
10	80*	65
2,10,L		
0	233	224
1	96	95
2	61	63
3	102	81
4	175	174
5	99	97
6	85	99
7	56	53
8	79	70
9	67	59
3,10,L		
0	149	159
1	116	127
2	148	160
3	137	144
4	104	99
5	98	87
6	113	116
7	111	120
8	56	58
9	64	54
4,10,L		
0	153	138
1	150	135
2	54	54
3	142	122
4	128	110
5	129	115
6	64*	33
7	71*	44
8	72*	55
5,10,L		
0	60	68
1	169	168
2	63	68
3	179	177
4	61	70
5	69	81
6	65	57
7	141	127
6,10,L		
0	51*	16
1	87	103
2	63*	39
3	78	75
4	54*	27
5	96	102
6	69	24
7,10,L		
4	55*	26
3	151	140
2	64*	29
1	111	98
0	64*	22
8,10,L		
0	75	64
0,11,L		
0	69*	0
1	96	83
2	178	176
3	54	34
4	55*	37
5	94	77
6	117	116
7	64*	4
1,11,L		
0	148	140
1	55*	50
2	54*	33
3	54*	38
4	124	117
5	56	59
6	56	47
2,11,L		
0	51*	40
1	82	72
2	163	150
3	62	73
4	64*	50
5	74	61
6	91	90
7	74	56
3,11,L		
0	119	114
1	93	94
2	94	81
3	58	47
4	90	92
5	112	106
6	73	61
4,11,L		
5	64*	44
4	55*	37
3	94	96
2	71	80
1	85	67
0	52	14
5,11,L		
0	55*	38
1	92	85
2	74	75
3	72*	44
4	66	58
6,11,L		
0	56*	17
0,12,L		
0	87	85
1	54*	24
2	55*	16
1,12,L		
0	64*	7
1	55*	30
2	125	100
2,12,L		
0	87	69
1	58	58

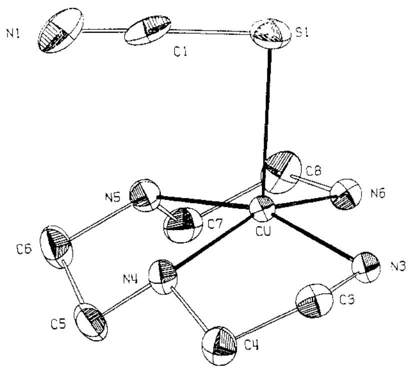

Figure 1.—Perspective drawing of cation showing labeling of atoms.

apical position. The conformation adopted by the trien is quite different from that adopted in the two cobalt(III) compounds β-[Co(trien)(glyglyOEt)]-$(ClO_4)_3 \cdot H_2O$ and β-[Co(trien)Cl(H_2O)]$(ClO_4)_2$, recently reported,[8] in which the four nitrogen atoms occupy one apical position and three equatorial positions of an octahedron. The geometry of the four nitrogen atoms is close to a trapezoid whose sides are: 2.722 Å [N(3)–N(4)], 2.713 Å [N(4)–N(5)], 2.711 Å [N(5)–N(6)], 3.053 Å [N(6)–N(3)]. The Cu–S vector is nearly perpendicular to the basal plane; the angle of 2° with the normal to the plane is hardly significant.

The equation of the basal plane, calculated with reference to the direct cell, is: $4.071x + 0.552y + 12.770z = 2.590$. The copper atom is 0.37 Å above the plane, while the four nitrogen atoms are alternately above and below the plane: N(3), +0.06 Å; N(4), −0.07 Å; N(5), +0.07 Å; N(6), −0.06 Å. Such slight distortion from planar toward tetrahedral has been reported for a number of Cu compounds.

The bond lengths and angles and their standard deviations are given in Table III. The four Cu–N bonds are not significantly different and their mean value of 2.016 (4) Å compares well with the values found in the analogous structures $Cu(en)_2(SCN)_2$[9] and $Cu(en)_2(NO_3)_2$.[10]

The apical Cu–S bond is a long bond, as normally found in five-coordinate copper compounds with square-pyramidal configuration.[11] Its length of 2.607 (2) Å, 0.3–0.6 Å longer than the value reported in copper(II) diethyldithiocarbamate,[12] is definitely in the range of copper–sulfur interaction.

There is no weak coordination of the copper atom below the basal plane; the nearest atom in this direction (N(1) of the symmetry related thiocyanate) is 3.491 Å away.

The intrachelate N–Cu–N bond angles, which are equal to the mean value 84.5° within one standard deviation, agree well with those reported in related structures [84.1° in [Cu(tren)NCS]SCN,[1] 85° in $Cu(en)_2(SCN)_2$,[9] 86° in $Cu(en)_2(NO_3)_2$[10]].

Table III

Bond Distances (Å) and Angles (deg)

Coordination Polyhedron around Copper Atom

Bonds

Cu–S(1)	2.607 (2)	Cu–N(5)	2.015 (6)
Cu–N(3)	2.013 (7)		
Cu–N(4)	2.030 (5)	Cu–N(6)	2.008 (7)

Angles

Cu–S(1)–N(1)	89.5 (1)	N(5)–Cu–S(1)	100.1 (2)
N(3)–Cu–S(1)	97.5 (2)	N(6)–Cu–S(1)	101.1 (2)
N(4)–Cu–S(1)	104.0 (2)	N(4)–Cu–N(5)	84.3 (2)
N(3)–Cu–N(6)	98.9 (3)	N(5)–Cu–N(6)	84.7 (3)
N(3)–Cu–N(4)	84.6 (3)		

Thiocyanate Groups

Bonds

S(1)–C(1)	1.646 (8)	S(2)–C(2)	1.637 (8)
N(1)–C(1)	1.164 (10)	N(2)–C(2)	1.147 (10)

Angles

S(1)–C(1)–N(1)	178.0 (6)	S(2)–C(2)–N(2)	178.1 (7)

Organic Ligand

Bonds

N(3)–C(3)	1.490 (11)	N(5)–C(6)	1.489 (9)
N(4)–C(4)	1.470 (10)	N(5)–C(7)	1.484 (11)
N(4)–C(5)	1.495 (9)	N(6)–C(8)	1.463 (12)
C(3)–C(4)	1.478 (14)	C(7)–C(8)	1.518 (16)
C(5)–C(6)	1.497 (12)		

Angles

N(3)–C(3)–C(4)	106.8 (7)	C(5)–C(6)–N(5)	108.9 (6)
C(3)–C(4)–N(4)	109.2 (7)	C(6)–N(5)–C(7)	117.8 (6)
C(4)–N(4)–C(5)	114.4 (7)	N(5)–C(7)–C(8)	107.0 (7)
N(4)–C(5)–C(6)	108.4 (6)	C(7)–C(8)–N(6)	107.0 (7)

Bonds

N(3)–H(331)	1.21 (6)	N(6)–H(661)	0.82 (7)
N(3)–H(332)	0.80 (7)	N(6)–H(662)	0.89 (5)
N(4)–H(441)	1.17 (9)	N(5)–H(551)	0.85 (8)
C(3)–H(31)	1.03 (9)	C(6)–H(61)	1.10 (5)
C(3)–H(32)	0.96 (6)	C(6)–H(62)	1.09 (8)
C(4)–H(41)	1.17 (6)	C(7)–H(71)	0.98 (6)
C(4)–H(42)	1.06 (6)	C(7)–H(72)	1.09 (6)
C(5)–H(51)	1.13 (6)	C(8)–H(81)	1.14 (7)
C(5)–H(52)	1.07 (7)	C(8)–H(82)	1.06 (9)

The bonded thiocyanate group is oriented parallel to the equatorial plane and extends in the direction away from the "open" side; the angle Cu–S(1)–N(1) is 89.5°, which compares with the value of 90° reported in $Cu(NH_3)_4(SCN)_2$.[13]

All three ethylenediamine rings have the *gauche* configuration; the N(3)–C(3)–C(4)–N(4) ring has a k conformation[14] and an almost symmetrical *gauche* form: C(3) is 0.38 Å above the N–Cu–N plane and C(4) is at −0.32 Å. The other two rings have a k′ conformation and an unsymmetrical form, as observed in other copper compounds; C(5), C(6), C(7), and C(8)

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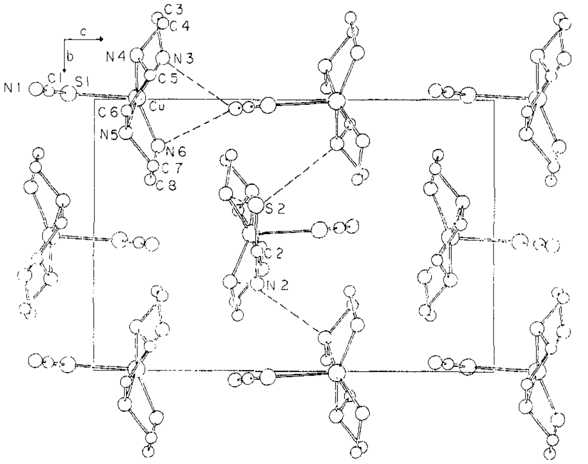

Figure 2.—Projection of structure on (100). Only one of the noncoordinated thiocyanate ions is shown.

are, respectively, at −0.72, −0.11, −0.57, and 0.14 Å from their corresponding N–Cu–N planes. The ethylenediamine conformations may also be described by the dihedral angle made by the two N–C–C planes. These angles are 55° in the terminal ethylenediamine groups and 49° in the central group.

Within the ethylenediamine groups there are no significant differences in bond lengths and angles. The average value for the C–C bond lengths is 1.498 (10) Å and that for C–N bond lengths is 1.482 (5) Å.

No significant differences occur within the two thiocyanate ions, whose average values of S–C bonds (1.641 (8) Å) and N–C bonds (1.156 (10) Å) are within the range reported for other thiocyanates.

In Figures 2 and 3 the projections of the structure along the *b* and *c* axes are shown. The nitrogen atom of the coordinated thiocyanate, N(1), and both the nitrogen and the sulfur atoms of the uncoordinated thiocyanate, N(2) and S(2), accept two hydrogen bonds; they are diagrammatically shown in Figure 2 and listed in Table IV.

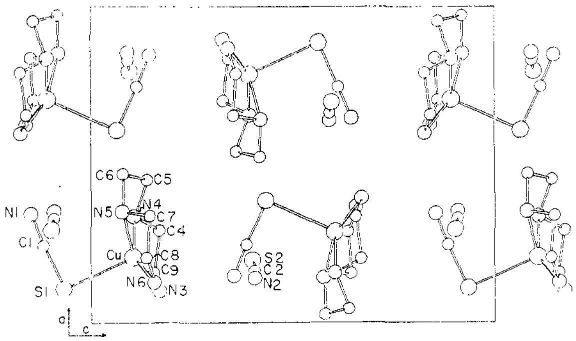

Figure 3.—Projection of structure on (010).

TABLE IV

HYDROGEN BONDS[a]

	Distance, Å	Angle, deg
$N(3^{i})$–$H(331^{i})\cdots N(1)$	3.103	134.9
$N(6^{i})$–$H(662^{i})\cdots N(1)$	3.000	149.9
$N(5^{ii})$–$H(551^{ii})\cdots N(2)$	2.997	174.5
$N(6^{iii})$–$H(661^{iii})\cdots N(2)$	3.091	171.5
$N(3^{iii})$–$H(332^{iii})\cdots S(2)$	3.458	171.9
$N(4^{iv})$–$H(441^{iv})\cdots S(2)$	3.558	138.1

[a] The superscripts have the following significance: (i) $\frac{1}{2} - x, -y, z - \frac{1}{2}$; (ii) $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$; (iii) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (iv) $\frac{1}{2} - x, -y, \frac{1}{2} + z$.

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