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The Crystal Chemistry of Tri-μ-thiocyanato-triamminecopper(I)copper(II)

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The crystal structure of $Cu_2(NCS)_3(NH_3)_3$ has been determined. The material crystallizes in the monoclinic system, in the form of black needles which become dark green when powdered. The space group is $P2_1/c$ with $a = 8.40$ (1), $b = 7.17$ (1), $c = 19.52$ (2) Å, $\beta = 97.3°$. The measured density is 2.04 g cm^{-3}, and the calculated value, assuming $Z = 4$, is 2.01 g cm^{-3}. A total of 1146 photometrically estimated intensities were collected and the structure was refined by least-squares methods with the block-diagonal approximation to give a conventional $R = 0.111$ value. The structure is polymeric and consists of sheets of copper(I) tetrahedra cross-linked by pairs of copper(II) octahedra. The copper(II) is linked by approximately coplanar bonds to three ammonia molecules and the nitrogen atom of a thiocyanate group (1.99–2.06 ± 0.02 Å). The environment of the copper(II) is completed by two thiocyanate sulfur atoms at greater distances (2.946 and 3.286 ± 0.009 Å, respectively). The copper(I) has a tetrahedral configuration consisting of two nitrogen (2.00 ± 0.02 Å) and two sulfur (2.376 and 2.470 ± 0.008 Å) atoms of four different thiocyanate groups. All the thiocyanate groups are involved in bridges.

Introduction

Although a number of mixed-valence copper(I)copper(II) compounds have been prepared, the structure determinations of only two such materials, formulated as $Cu_3(CN)_4(NH_3)_3$[1] and $Na_4\{Cu(NH_3)_4\}\{Cu(S_2O_3)_2\}_2$,[2] have been published. The results of an X-ray analysis of tri-μ-thiocyanato-triamminecopper(I)copper(II) are now reported and discussed.

The present work was undertaken as part of a study of the stereochemistry of thiocyanate as a ligand and an investigation of the relationships between the composition, structure, and redox processes of copper(II) complexes in solution.

The conditions for the preparation of a series of copper(II) thiocyanate complexes have been reported.[3,4] The composition of these materials may be expressed by the general formula $Cu(NCS)_2(NH_3)_2 \cdot nCu(NCS)(NH_3)$. The crystal structure of the first member (where $n = 0$) has been determined[5] and some of the basic structural data for the second compound ($n = 1$) are also known.[6] Since the monoclinic crystals of a third material ($n = 2$) decompose in the X-ray beam, this structure has not been investigated.

Experimental Section

The Unit Cell and the Space Group.—Crystals of $Cu_2(NCS)_3(NH_3)_3$ belong to the monoclinic system. The density of the material, measured by a flotation technique, was found to be 2.04 g cm^{-3}. Assuming four formula units per cell, the calculated value is 2.01 g cm^{-3}. The lattice parameters are: $a = 8.40 \pm 0.01$, $b = 7.17 \pm 0.01$, $c = 19.52 \pm 0.02$ Å, $\beta = 97.3°$. These parameters were obtained from rotation and Weissenberg photographs calibrated with gold. All photographs were taken with unfiltered Cu Kα radiation (1.5405 Å). The unit cell volume is $V = 1166$ Å^3. The ratio of the lattice parameters is $a:b:c = 1.172:1.000:2.722$.

The following systematic absences were observed: for F_{h0l}, $l = 2n + 1$; for F_{0k0}, $k = 2n + 1$. These correspond to space group $P2_1/c$ (no. 14).

X-Ray Collection.—Three-dimensional intensities for $Cu_2(NCS)_3(NH_3)_3$ were obtained by Weissenberg equiinclination photography, using the multiple-film technique. A single crystal, measuring 0.15 × 0.2 × 0.15 mm, was rotated about the monoclinic axis and I_{h0l} through I_{h4l} intensities were obtained. A second crystal was ground to a sphere of 0.06-mm diameter and used for additional $hk0$ and $hk1$ reflections. Intensities were estimated photometrically with a calibrated scale and were corrected for Lorentz-polarization factors. No absorption corrections were applied ($\mu R = 1.37$ and 0.55, respectively).

The Lorentz-polarization corrections and all calculations in the projections were made with a ZRA 1 computer, using programs written by Bähr, *et al.*[7] The interatomic distances and all three-dimensional calculations were carried out with an Elliot 803 B computer using the programs of Daly, Stephens, and Wheatley.[8]

A total of 1146 independent nonzero reflections were used for the crystal structure analysis. The structure factors were calculated from the atomic factor values according to Ibers.[9]

Solution and Refinement of the Structure.—The crystal structure has been determined by the heavy-atom method. The positions of copper atoms were obtained from Patterson syntheses in both projections. The approximate coordinates of the sulfur atoms were determined by the minimization method.

The atomic positions were first refined in both projections by differential Fourier syntheses. The positions thus obtained were used for determination of a scale factor for each layer. The scaled intensities were then used for the least-squares refinement of the structure. The weighting scheme of Cruickshank, *et al.*,[10] was adopted for the least-squares method, and the matrix inversion involved the block-diagonal approximation. Refinement of the atomic positions, individual isotropic temperature coefficients, and over-all scale factor yielded an R value of 0.111 for observed reflections and 0.122 for all reflections listed in Table I. In the latter R value calculation, unobserved reflections were given half the calculated values. The unobserved reflections were not used in the refinement. A difference Fourier based on this refinement revealed electron density as high as

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TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS (×10) FOR $Cu_2(NCS)_3(NH_3)_3$

H	L	FOBS	FCAL
	K = 0		
0	2	450	581
0	4	682	792
0	6	180	204
0	8	224	240
0	10	644	637
0	12	1439	1372
0	14	150	163
0	16	-	6
0	18	835	878
0	20	200	172
0	22	536	472
0	24	267	304
1	22	596	635
1	20	366	414
1	18	-	133
1	16	1087	970
1	14	-	143
1	12	423	414
1	10	-	19
1	8	-	25
1	6	871	621
1	4	2230	2082
1	2	496	600
1	0	612	567
1	-2	993	1085
1	-4	885	599
1	-6	203	182
1	-8	676	634
1	-10	982	921
1	-12	-	107
1	-14	654	582
1	-16	1074	1008
1	-18	490	464
1	-20	-	7
1	-22	119	122
1	-24	197	175
2	22	464	555
2	20	524	596
2	18	750	744
2	16	556	520
2	14	192	219
2	12	778	881
2	10	1320	1366
2	8	173	224
2	6	1399	1596
2	4	597	682
2	2	573	538
2	0	1786	2092
2	-2	797	885
2	-4	1239	1150
2	-6	164	177
2	-8	313	449
2	-10	614	549
2	-12	3004	2616
2	-14	743	585
2	-16	-	115
2	-18	383	446
2	-20	-	20
2	-22	343	433
2	-24	696	610
3	22	439	464
3	20	-	34
3	18	224	174
3	16	377	385
3	14	1172	1040
3	12	-	40
3	10	1387	1175
3	8	298	308
3	6	1265	1207
3	4	1354	1314
3	2	-	74
3	0	624	555
3	-2	511	383
3	-4	290	372
3	-6	296	368
3	-8	1025	977
3	-10	349	353
3	-12	743	717
3	-14	485	489
3	-16	572	553
3	-18	351	292
3	-20	-	7
3	-22	374	480
4	18	236	244
4	16	-	3
4	14	218	277
4	12	702	736
4	10	1756	1656
4	8	609	534
4	6	1284	1006
4	4	1004	976
4	2	-	83
4	0	1123	1115
4	-2	1608	1564
4	-4	467	429
4	-6	1205	1109
4	-8	1009	919
4	-10	629	633
4	-12	1409	1269
4	-14	1109	931
4	-16	1226	944
4	-20	-	23
4	-22	574	629
4	-24	551	651
5	20	348	350
5	18	156	174
5	16	157	173
5	14	504	525
5	12	558	481
5	10	604	571
5	8	-	96
5	6	554	557
5	4	188	180
5	2	671	726
5	0	-	181
5	-2	530	557
5	-4	-	3
5	-6	1731	1507
5	-8	1262	1081
5	-10	319	436
5	-12	-	121
5	-14	306	443
5	-16	515	473
5	-18	478	485
5	-20	232	207
6	18	-	2
6	16	724	605
6	14	362	286
6	12	384	426
6	10	1480	1366
6	8	403	368
6	6	192	216
6	4	246	250
6	2	528	426
6	0	599	587
6	-2	1900	1677
6	-4	218	197
6	-6	720	639
6	-8	1046	1032
6	-10	166	162
6	-12	441	446
6	-14	548	549
6	-16	153	119
6	-18	401	424
6	-20	428	606
6	-22	343	393
7	16	188	208
7	14	906	910
7	12	517	394
7	10	-	48
7	8	304	313
7	6	-	32
7	4	313	216
7	2	720	665
7	0	261	255
7	-2	525	510
7	-4	444	527
7	-6	818	770
7	-8	285	257
7	-10	104	111
7	-12	157	173
7	-14	-	15
7	-16	-	117
7	-18	1066	981
8	18	-	33
8	16	621	576
8	14	-	120
8	12	-	73
8	10	564	582
8	8	731	829
8	6	-	23
8	4	655	611
8	2	375	434
8	0	114	144
8	-2	1593	1395
8	-4	546	612
8	-6	497	469
8	-8	189	273
8	-10	227	260
8	-14	900	883
8	-16	-	46
8	-18	215	167
9	14	504	532
9	12	462	410
9	10	-	45
9	8	-	78
9	6	216	173
9	4	252	215
9	2	980	998
9	0	307	336
9	-2	152	193
9	-4	154	156
9	-6	230	233
9	-8	123	168
9	-10	191	249
9	-12	-	78
9	-14	-	75
9	-16	543	499
10	8	352	388
10	6	-	14
10	4	957	896
10	2	153	239
10	0	-	19
10	-2	432	381
10	-4	680	691
10	-6	148	112
10	-8	430	450
10	-10	142	152
10	-12	255	348
	K = 1		
0	1	322	269
0	2	653	727
0	3	210	342
0	4	1099	1259
0	5	382	427
0	6	112	30
0	7	207	229
0	8	1258	1188
0	9	264	231
0	10	985	808
0	11	255	249
0	12	375	341
0	13	-	57
0	14	-	128
0	15	563	607
0	16	-	32
0	17	385	346
0	18	306	311
0	19	135	172
0	20	375	421
0	21	348	387
1	20	649	578
1	19	133	159
1	18	308	363
1	17	278	267
1	16	213	168
1	16	428	428
1	14	980	922
1	13	-	84
1	12	647	588
1	11	743	660
1	10	757	704
1	9	634	646
1	8	1509	1515
1	7	872	852
1	6	1222	1016
1	5	343	383
1	4	1558	1627
1	3	-	10
1	2	1230	1475
1	1	325	480
1	0	103	27
1	-1	1424	1225
1	-2	846	573
1	-3	1072	1181
1	-4	1724	1842
1	-5	230	262
1	-6	1246	1176
1	-7	227	229
1	-8	1537	1361
1	-9	403	359
1	-10	987	887
1	-11	1050	835
1	-12	314	272
1	-13	477	329
1	-14	627	582
1	-15	319	280
1	-16	480	479
1	-17	208	173
1	-18	104	220
1	-19	343	319
1	-20	737	616
1	-21	210	259
1	-22	469	514
1	-23	-	81
1	-24	383	329
2	18	375	408
2	17	-	5
2	16	739	626
2	15	772	753
2	14	246	225
2	13	297	456
2	12	1230	1049
2	11	-	25
2	10	492	452
2	8	1044	976
2	9	1052	938
2	7	240	257
2	6	643	748
2	5	144	198
2	4	92	48
2	3	1191	1161
2	2	211	183
2	1	647	689
2	0	92	154
2	-1	205	259
2	-2	1139	1134
2	-3	542	458
2	-4	525	541
2	-5	324	302
2	-6	537	481
2	-7	183	194
2	-8	1561	1375
2	-9	331	325
2	-10	487	390
2	-11	159	141
2	-13	103	151
2	-12	352	272
2	-14	512	490
2	-15	-	32
2	-16	433	320
2	-17	406	356
2	-18	211	87
2	-19	396	436
2	-20	861	892
3	20	421	434
3	19	148	159
3	18	298	382
3	17	113	147
3	16	-	26
3	15	462	485
3	14	1452	1296
3	13	662	662
3	12	415	391
3	11	219	251
3	10	-	12
3	9	-	5
3	8	999	954
3	7	243	296
3	6	757	765
3	5	230	280
3	4	150	248
3	3	843	873
3	2	1665	1795
3	1	-	10
3	0	476	502
3	-1	617	697
3	-2	110	208
3	-3	696	712
3	-4	1307	1438
3	-5	757	773
3	-6	385	454
3	-7	-	10
3	-8	1170	959
3	-9	-	23
3	-10	1116	830
3	-11	345	489
3	-12	214	175
3	-13	655	549
3	-14	859	247
3	-15	939	729
3	-16	1280	1119
3	-17	-	69
3	-18	258	246
3	-19	-	114
3	-20	490	580
3	-21	-	82
3	-22	531	631
3	-23	332	432
4	20	185	224
4	19	-	8
4	18	562	634
4	17	-	12
4	16	166	149
4	15	-	22
4	14	-	22
4	13	161	164
4	12	639	634
4	11	720	680
4	10	-	76
4	9	133	110
4	8	-	68
4	7	-	88
4	6	535	552
4	5	493	462
4	4	920	811
4	3	347	587
4	2	371	406
4	1	124	126
4	0	[illegible]	[illegible]
4	-1	281	323
4	-2	1076	1024
4	-3	711	706
4	-4	308	245
4	-5	530	471
4	-6	506	501
4	-7	104	123
4	-8	345	334
4	-9	361	299
4	-10	-	110
4	-11	402	311
4	-12	-	49
4	-13	300	311
4	-14	516	495
4	-15	220	202
4	-16	-	16
4	-17	-	17
4	-18	586	532
4	-19	-	13
4	-20	513	641
5	17	155	188
5	16	-	28
5	15	134	142
5	14	637	666
5	13	412	401
5	12	415	433
5	11	403	497
5	10	224	210
5	9	351	352
5	8	410	438
5	7	-	47
5	6	817	805
5	5	-	62
5	4	156	146
5	3	466	516
5	2	2056	1864
5	1	720	717
5	0	-	4
5	-1	623	530
5	-2	102	107
5	-3	109	106
5	-4	1036	906
5	-5	516	476
5	-6	871	694
5	-7	286	266
5	-8	550	367
5	-9	462	469
5	-10	1664	1382
5	-11	-	52
5	-13	-	85
5	-12	153	141
5	-14	320	216
5	-15	514	413
5	-16	555	678
5	-17	396	443
5	-18	-	24
5	-19	-	24
5	-20	243	223
5	-21	-	12
5	-22	255	224
6	18	496	572
6	17	288	270
6	16	179	170
6	15	-	73
6	14	387	376
6	13	184	191
6	12	317	262
6	11	142	124
6	10	165	155
6	9	139	114
6	8	-	24
6	7	261	221
6	6	766	729
6	5	271	299
6	4	132	146
6	3	-	6
6	2	419	466
6	1	-	21
6	0	547	594
6	-1	874	845
6	-2	-	33
6	-3	-	85
6	-4	104	116
6	-5	266	270
6	-6	651	661
6	-7	811	732
6	-8	223	254
6	-9	-	25
6	-10	536	515
6	-11	486	389
6	-12	475	573
6	-13	375	379
6	-14	739	735
6	-15	104	135
6	-16	303	344
6	-17	433	396
7	13	-	40
7	12	570	616
7	11	336	312
7	10	405	375
7	9	603	628
7	8	656	571
7	7	251	305
7	6	662	651
7	5	-	102
7	4	208	220
7	3	154	152
7	2	884	880
7	1	732	404
7	0	303	396
7	-1	654	689
7	-2	283	233
7	-3	530	501
7	-4	105	104
7	-5	117	118
7	-6	617	633
7	-7	224	188
7	-8	205	223
7	-9	204	193
7	-10	1330	1199
7	-11	332	376
7	-12	343	331
7	-13	413	444
7	-14	-	102
7	-15	360	428
7	-16	245	244
7	-17	125	125
8	[illegible]	[illegible]	[illegible]
8	12	203	207
8	10	263	185
8	8	336	327
8	7	120	123
8	6	750	741
8	5	193	174
8	4	372	362
8	3	-	48
8	2	331	416
8	1	124	108
8	0	138	133
8	-1	-	52
8	-2	-	163
8	-3	-	46
8	-4	281	311
8	-5	355	361
8	-6	332	339
8	-7	251	219
8	-8	-	9
8	-9	-	85
8	-10	523	623
8	-11	225	203
8	-12	164	185
8	-13	325	396
9	13	-	46
9	12	563	497
9	11	-	70
9	10	373	349
9	9	113	128
9	8	197	138
9	7	281	380
9	6	294	341
9	5	400	409
9	4	122	139
9	3	-	432
9	2	256	265
9	1	-	68
9	0	662	761
9	-1	-	40
9	-2	-	1
9	-3	446	493
9	-4	357	405
9	-5	376	420
9	-6	734	804
9	-7	-	72
9	-8	253	287
9	-9	121	111
9	-10	504	560
9	-11	140	133
9	-12	287	281
9	-13	303	426
9	-14	-	203
9	-15	277	318
10	3	-	51
10	2	-	56
10	1	187	274
10	-1	134	149
10	-2	239	212
10	-3	-	20
10	-4	391	477
10	-5	-	62
10	-6	309	441
10	-7	-	6
10	-8	253	378
10	-9	-	49
10	-10	309	301
	K = 2		
0	1	560	580
0	2	540	618
0	3	453	518
0	4	776	779
0	5	767	849
0	6	1561	1581
0	7	1324	1201
0	8	115	86
0	9	1042	1021
0	10	465	364
0	11	1183	986
0	12	430	431
0	13	-	87
0	14	132	154
0	15	-	7
0	16	-	75
0	17	485	464
0	18	661	539
0	19	631	631
0	20	361	284
0	21	364	325
0	22	249	264
1	23	314	458
1	22	620	575
1	21	-	35
1	20	-	19
1	19	273	285
1	18	306	245
1	17	-	58
1	16	319	230
1	15	427	401
1	14	362	352
1	13	146	134
1	12	211	186
1	11	315	347
1	10	748	721
1	9	286	355
1	8	243	274
1	7	170	214
1	6	485	531
1	5	261	321
1	4	627	771
1	3	984	938
1	2	-	94
1	1	193	258
1	0	412	420
1	-1	571	538
1	-2	1109	1364
1	-3	2035	2078
1	-4	1071	1069
1	-5	-	67
1	-6	273	247
1	-7	359	322
1	-8	837	888
1	-9	1559	1385
1	-10	[illegible]	[illegible]
1	-11	[illegible]	[illegible]
1	-12	[illegible]	[illegible]
1	-13	[illegible]	[illegible]
1	-14	366	[illegible]
1	-15	118	125
1	-16	506	462
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2	22	341	342
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2	20	423	286
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2	18	431	525
2	17	924	897
2	16	355	269
2	15	422	455
2	14	221	236
2	13	345	374
2	12	845	780
2	11	164	205
2	10	696	724
2	9	290	317
2	8	654	562
2	7	1314	1278
2	6	1016	966
2	5	764	879
2	4	409	468
2	3	384	352
2	2	118	230
2	1	123	100
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2	-2	314	388
2	-3	975	1073
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2	-6	1016	966
2	-7	966	844
2	-8	801	692
2	-9	394	382
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2	-11	666	604
2	-12	998	916
2	-13	629	508
2	-14	295	274
2	-15	353	386
2	-16	-	34
2	-17	174	202
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2	-19	417	439
2	-20	-	21
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2	-22	232	166
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3	21	502	547
3	20	-	92
3	19	551	496
3	18	-	14
3	17	306	261
3	16	552	523
3	15	113	121
3	14	359	232
3	13	286	274
3	12	769	664
3	11	412	416
3	10	903	867
3	9	-	78
3	8	308	378
3	7	391	446
3	6	454	527
3	5	315	379
3	4	581	660
3	3	324	371
3	2	508	558
3	1	210	212
3	0	608	679
3	-1	311	340
3	-2	556	647
3	-3	216	241
3	-4	-	121
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3	-18	363	296
3	-19	183	165
3	-20	475	476
3	-21	423	426
3	-22	127	133
3	-23	382	398
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4	18	305	311
4	17	354	601
4	17	547	601
4	16	446	415
4	15	259	311
4	14	428	322
4	13	539	562
4	12	217	196
4	11	-	40
4	10	665	607
4	9	282	282
4	8	459	467
4	7	971	751
4	6		
4	7	144	171
4	6	971	751
4	5	1077	1030
4	4	660	737
4	3	1189	1093
4	2	371	467
4	1	384	441
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4	-6	1257	997
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4	-13	302	283
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4	-16	407	337
4	-17	257	279
4	-18	403	307
4	-19	534	452
4	-20	400	427
4	-21	291	152
4	-22	208	214
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5	17	318	328
5	16	-	34
5	15	-	67
5	14	431	377
5	13	347	358
5	12	498	350
5	11	248	209
5	10	237	183
5	9	435	459
5	8	170	159
5	7	730	736
5	6	379	349
5	5	411	304
5	4	395	425
5	3	207	141
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6	-15	114	129
6	-16	282	307
6	-17	473	578
6	-18	-	51
6	-19	599	578
6	-20	342	370
6	-21	320	316
7	14	376	365
7	13	205	157
7	12	317	253
7	11	329	346
7	10	140	142
7	9	363	283
7	8	366	412
7	7	402	445
7	6	400	379
7	5	456	490
7	4	-	26
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7	0	258	220
7	-1	163	176
7	-2	-	3
7	-3	-	47
7	-4	219	200
7	-5	594	446
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8	2	214	210
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8	-2	433	410
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8	-5	-	96
8	-7	402	248
8	-6	-	90
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8	-12	-	66
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9	-7	378	312
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9	-12	-	94
9	-13	274	253
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10	0	-	97
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0	13	103	246
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0	17	-	44
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0	19	428	460
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0	21	-	26
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0	23	184	197
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1	21	185	324
1	20	236	175
1	19	215	194
1	18	991	998
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1	16	519	471
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1	14	706	667
1	13	495	434
1	12	179	230
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1	10	237	209
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1	1	747	915
1	0	551	754
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1	-4	305	412
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2	21	-	32
2	20	-	68
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2	18	587	591
2	17	-	68
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2	14	-	34
2	13	-	3
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2	11	222	277
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2	8	214	168
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2	6	481	490
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2	3	291	261
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2	-11	129	175
2	-12	467	446
2	-13	592	607
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3	19	188	262
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3	-4	244	263
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3	-6	573	1008
3	-7	509	443
3	-8	407	343
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3	-10	650	618
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3	-12	338	348
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4	19	-	90
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4	17	204	156
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4	6	954	856
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5	-11	270	221
5	-12	-	70
5	-13	551	438
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5	-17	299	263
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6	16	100	139
6	15	145	136
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6	13	360	344
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6	8	330	750
6	7	406	340
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6	-8	215	130
6	-9	-	31
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6	-11	110	121
6	-12	406	421
6	-13	-	163
6	-14	160	163
6	-15	100	101
6	-16	-	0
6	-17	-	70
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6	-19	176	105
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7	13	383	354
7	12	424	421
7	11	231	264
7	10	502	379
7	9	422	431
7	8	-	67
7	7	311	386
7	6	180	170
7	5	343	334
7	4	356	408
7	3	357	331
7	2	-	5
7	1	565	454
7	0	149	111
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7	-2	629	577
7	-3	473	365
7	-4	517	470
7	-5	696	666
7	-6	197	178
7	-7	243	301
7	-8	760	681
7	-9	415	355
7	-10	373	389
7	-11	294	285
7	-12	214	164
7	-13	529	486
7	-14	-	7
7	-15	331	226
7	-16	791	810
7	-17	414	462
8	10	326	369
8	9	296	346
8	8	417	[illegible]
8	7	[illegible]	[illegible]
8	6	[illegible]	[illegible]
8	5	[illegible]	[illegible]
8	4	[illegible]	[illegible]
8	3	-	117
8	2	304	320

H	L	FCAL	FOBS
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8	-1	398	332
8	-2	-	61
8	-3	398	264
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8	-9	263	230
8	-10	107	124
8	-11	146	244
8	-12	475	468
9	7	234	295
9	6	120	131
9	5	369	362
9	4	490	515
9	3	-	71
9	2	-	91
9	1	539	397
9	0	381	391
9	-1	244	207
9	-2	362	433
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9	-5	308	310
9	-6	204	298
9	-7	244	239
9	-8	-	99
9	-9	334	313
9	-10	-	61
9	-11	289	307
9	-12	96	44
9	-13	300	290
10	0	175	167
10	1	-	47
10	2	444	552
10	3	214	157

K	L	FOBC	FCAL
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4	3	570	503
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4	8	783	777
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4	17	170	163
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4	20	344	315
4	18	-	42
4	19	296	167
4	20	344	315
4	21	-	95
5	1	379	337
5	2	347	355
5	3	412	328
5	4	873	867
5	5	90	86
5	6	352	266
5	7	160	166
5	8	-	37
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5	10	727	569
5	11	359	238
5	12	604	510
5	13	131	142
5	14	363	339
5	15	338	385
5	16	322	393
5	17	417	486
5	18	381	297
5	19	233	230
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6	2	139	120
6	3	539	410
6	4	1341	1276
6	5	-	67
6	6	343	201
6	7	414	359
6	8	782	835
6	9	-	145
6	10	-	86
6	11	-	79
6	12	338	310
6	13	-	73
6	14	680	704
6	15	364	381
6	16	412	374
7	1	-	26
7	2	-	80
7	3	143	102
7	4	580	543
7	5	-	105
7	6	-	80
7	7	313	419
7	8	285	303
7	9	-	161
7	10	-	21
7	11	373	443
8	0	-	34
8	1	180	183
8	2	90	127
8	3	471	571
8	4	-	46
8	5	101	107
8	6	376	429
8	7	299	278
8	8	302	290
8	9	220	211
8	10	263	238
8	11	186	255
9	1	350	164
9	2	192	346
9	3	266	349

0.9 e/Å^3. No hydrogen atoms were included in the calculations.

All of the atoms occupy general positions in the $P2_1/c$ space group. The refined atomic positions of the independent part of the unit cell are listed in Table II, and some important interatomic distances and valence angles are given in Tables III and IV, respectively. The observed and all final calculated structure factors are listed in Table I.

Discussion

The basic units of the $Cu_2(NCS)_3(NH_3)_3$ structure are copper(I) tetrahedra. These tetrahedra are mutually linked by bridging thiocyanate groups, thus forming infinite sheets which are lying essentially parallel to (001) at $Z = {}^1/_4$ and ${}^3/_4$. The distance between neighboring sheets is 9.83 Å (half of the lattice parameter). The sheets are cross-linked by pairs of copper(II) octahedra, arranged alternately on the left and on the right. Each copper(I) tetrahedron has a common point with one copper(II) octahedron.

The copper atoms in the structure have two coordinations, octahedral and tetrahedral. The strongly distorted octahedral environment of the ligands corresponds to the bivalent copper, which is coordinated in the crystal studied by three ammonia molecules and the

TABLE II

FRACTIONAL COORDINATES ($\times 10^4$) AND ISOTROPIC TEMPERATURE FACTORS FOR THE INDEPENDENT PART OF THE ATOMS OF $Cu_2(NSC)_3(NH_3)_3$[a]

Atom	x	y	z	B, Å²
Cu(1)	2049 (3)	7609 (6)	749 (1)	1.08
Cu(2)	2532 (3)	3424 (6)	2543 (1)	1.42
S(1)	3347 (7)	1565 (14)	236 (3)	1.27
S(2)	920 (6)	4260 (11)	1457 (2)	0.29
S(3)	2832 (6)	6022 (13)	3302 (3)	1.06
N(1)	4337 (21)	6995 (39)	1129 (9)	1.09
N(2)	−1409 (21)	6415 (39)	2007 (9)	1.16
N(3)	1896 (22)	9141 (39)	1806 (9)	1.02
N(4)	−228 (20)	8440 (37)	435 (9)	0.68
N(5)	2359 (20)	6476 (37)	−138 (9)	0.76
N(7)	4577 (21)	2687 (39)	2206 (9)	1.08
C(1)	1540 (22)	1813 (45)	−159 (10)	0.48
C(2)	−478 (22)	5623 (43)	1773 (10)	0.38
C(5)	5612 (23)	1980 (43)	2001 (10)	0.41

[a] Figures in parentheses after numbers are standard deviations ($\times 10^4$).

TABLE III

DISTANCES (Å) WITH STANDARD DEVIATIONS IN PARENTHESES ($\times 10^3$)

Atoms	Value	Atoms	Value
Distances in the Copper(II) Polyhedron[a]			
Cu(1)–S(1)	3.286 (9)	N(1)–N(3)	2.913 (34)
Cu(1)–S(2)	2.946 (7)	N(1)–N(5)	2.846 (33)
Cu(1)–N(1)	2.024 (25)	N(2)–N(4)	3.570 (33)
Cu(1)–N(3)	2.061 (24)	N(2)–C(2)	1.128 (35)
Cu(1)–N(4)	1.987 (23)	C(2)–C(3)	3.688 (37)
Cu(1)–N(5)	2.048 (23)	N(3)–N(4)	2.923 (32)
Cu(1)–C(2)	3.371 (26)	N(3)–C(2)	3.243 (35)
Cu(1)–C(3)	3.161 (27)	N(4)–N(5)	2.814 (32)
S(1)–C(1)	1.638 (28)	N(4)–C(2)	3.176 (34)
S(2)–N(1)	3.617 (25)	N(5)–N(6)	3.712 (32)
S(2)–N(2)	2.835 (25)	N(5)–C(1)	3.416 (35)
S(2)–N(3)	3.613 (24)	N(6)–C(1)	1.181 (35)
S(2)–N(4)	3.424 (23)	C(2)–C(3)	3.688 (37)
N(2)–N(3)	3.550 (33)		
S(2)–C(2)	1.710 (27)		
Distances in the Copper(I) Tetrahedra[b]			
Cu(2)–S(2)	2.470 (7)	Cu((2)–C(6)	3.051 (29)
Cu(2)–S(3)	2.376 (8)	S(3)–N(9)	2.797 (26)
Cu(2)–N(7)	2.006 (25)	S(3)–C(6)	1.671 (29)
Cu(2)–N(8)	1.996 (24)	N(9)–C(6)	1.127 (38)
Cu(2)–C(4)	3.085 (26)	N(8)–C(4)	1.128 (35)

[a] Nomenclature of atoms as in Figure 2. [b] Nomenclature of atoms as in Figure 3.

TABLE IV

ANGLES (DEG) WITH STANDARD DEVIATIONS IN PARENTHESES

Atoms	Value	Atoms	Value
Angles in the Copper(II) Octahedra[a]			
S(2)–Cu(1)–N(1)	91.5 (0.7)	N(4)–Cu(1)–N(5)	88.4 (0.9)
S(2)–Cu(1)–N(3)	90.6 (0.7)	Cu(1)–N(4)–N(3)	44.8 (0.6)
S(2)–Cu(1)–N(4)	85.6 (0.7)	Cu(1)–N(4)–N(5)	46.7 (0.7)
S(2)–Cu(1)–N(5)	98.9 (0.7)	Cu(1)–N(4)–C(3)	172.3 (2.2)
Cu(1)–S(2)–N(2)	90.6 (0.5)	Cu(1)–N(5)–N(1)	45.3 (0.7)
Cu(1)–S(2)–C(2)	88.7 (0.9)	Cu(1)–N(5)–N(4)	44.9 (0.6)
N(1)–Cu(1)–N(3)	91.0 (1.0)	S(1)–C(1)–N(6)	179.3 (2.5)
N(1)–Cu(1)–N(4)	175.5 (1.0)	Cu(1)–N(2)–S(3)	179.3 (0.7)
N(1)–Cu(1)–N(5)	88.7 (0.9)	S(1)–N(6)–C(1)	0.4 (1.4)
Cu(1)–N(1)–N(3)	45.0 (0.7)	S(2)–C(2)–N(2)	175.1 (2.5)
Cu(1)–N(1)–N(5)	46.0 (0.7)	N(2)–S(2)–C(2)	1.9 (1.0)
N(3)–Cu(1)–N(4)	92.4 (0.9)	N(1)–N(3)–N(4)	86.7 (0.9)
N(3)–Cu(1)–N(5)	170.5 (0.9)	N(1)–N(5)–N(4)	90.2 (0.9)
Cu(1)–N(3)–N(1)	44.0 (0.7)	N(3)–N(4)–N(5)	91.0 (0.9)
Cu(1)–N(3)–N(4)	42.8 (0.6)	N(3)–N(1)–N(5)	90.6 (0.9)
Angles in the Copper(I) Tetrahedra[b]			
Cu(2)–N(7)–C(5)	168.2 (2.4)	Cu(2)–S(3)–N(9)	97.7 (0.9)
S(2)–Cu(2)–S(3)	111.4 (0.3)	N(7)–Cu(2)–N(8)	115.1 (1.0)
S(2)–Cu(2)–N(8)	108.5 (0.7)	N(7)–Cu(2)–C(6)	83.4 (0.9)
S(2)–Cu(2)–N(7)	100.5 (0.7)	Cu(2)–N(7)–S(4)	170.2 (1.2)
Cu(1)–S(2)–Cu(2)	113.8 (0.2)	Cu(2)–N(7)–C(5)	168.2 (2.4)
Cu(2)–S(2)–C(4)	98.3 (0.9)	Cu(2)–N(8)–C(4)	161.0 (2.3)
S(3)–Cu(2)–N(7)	113.2 (0.7)	C(6)–S(3)–N(9)	1.5 (1.1)
S(3)–Cu(2)–N(8)	108.1 (1.1)	S(2)–C(6)–N(9)	176.5 (2.7)
S(3)–Cu(2)–S(4)	104.9 (0.5)		

[a] Nomenclature of atoms as in Figure 2. [b] Nomenclature of atoms as in Figure 3.

nitrogen atom of a thiocyanate group. The distorted octahedral coordination of the copper(II) atom is completed by two sulfur atoms, the copper–sulfur distances being greater than the four copper–nitrogen bonds (see Figures 1 and 2). The three copper(II)–ammonia bonds (2.024, 2.048, 2.061 Å) are somewhat but probably not significantly longer than the fourth bond to the thiocyanate nitrogen atom (1.987 Å). The difference between the four copper(II)–nitrogen distances and the copper(II)–sulfur bond length is significant (see Table III and Figure 1). Such differences have also been observed in other thiocyanate complexes of copper(II)[5] and are in agreement with predictions based on the ligand field strength series of Orgel and Dunitz.[11] The distances of the two sulfur atoms, which complete the distorted octahedral environment of the copper(II) atom, are not equal. In this respect $Cu_2(NCS)_3(NH_3)_3$ differs from other thiocyanate complexes containing only copper(II) as the central atom.[12–14]

The formation of two nonequivalent Cu(II)–S bonds (2.946 and 3.286 Å) is due to the different function of the two thiocyanate groups. The second Cu–S distance is quite long for any kind of covalent interaction and it seems more reasonable to say that the copper(II) atom has a tetragonal-pyramidal configuration. The four nitrogen atoms are approximately coplanar, and the equation of this plane has the form (in cartesian coordinates): $0.371X + 0.859Y - 0.351Z - 4.813 = 0$. The copper(II) is displaced from this plane by 0.062 Å toward the nearer sulfur atom. The ligand–copper(II)–ligand valency angles are 85.6–92.4° (see Table IV). On the basis of the structural results, the redox stability of bivalent copper in copper thiocyanate systems can be regarded as being due to the planar coordination of copper(II) by four nitrogen ligands.

The copper(I) atom is coordinated by two sulfur atoms and two nitrogen atoms of four different thiocyanate groups. The configuration of the ligands is a distorted tetrahedron. While the copper(I)–nitrogen distances are very similar (1.996 and 2.006 Å), the copper(I)–sulfur bonds have lengths 2.376 and 2.470 Å (Table III, Figure 1). The longer Cu(I)–S bond is weakly bonded to the copper(II) atom (Figures 1 and 3).

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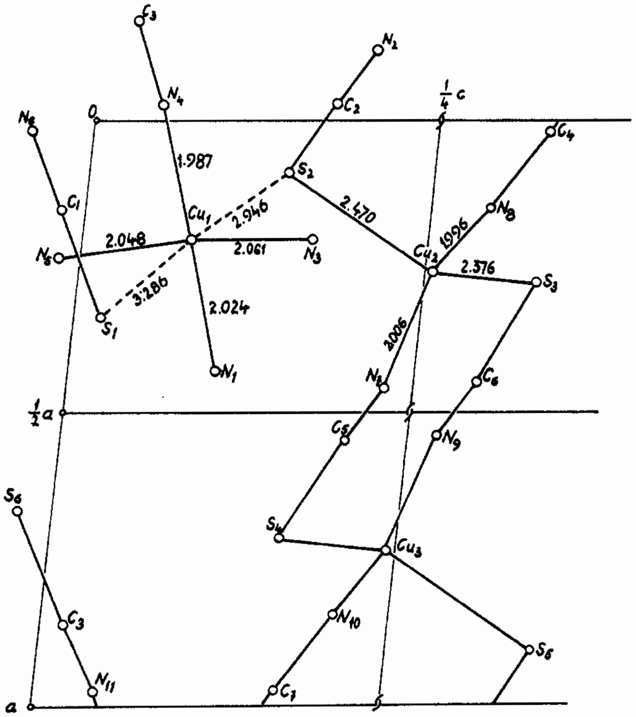

Figure 1.—The (010) projection of $Cu_2(NCS)_3(NH_3)_3$.

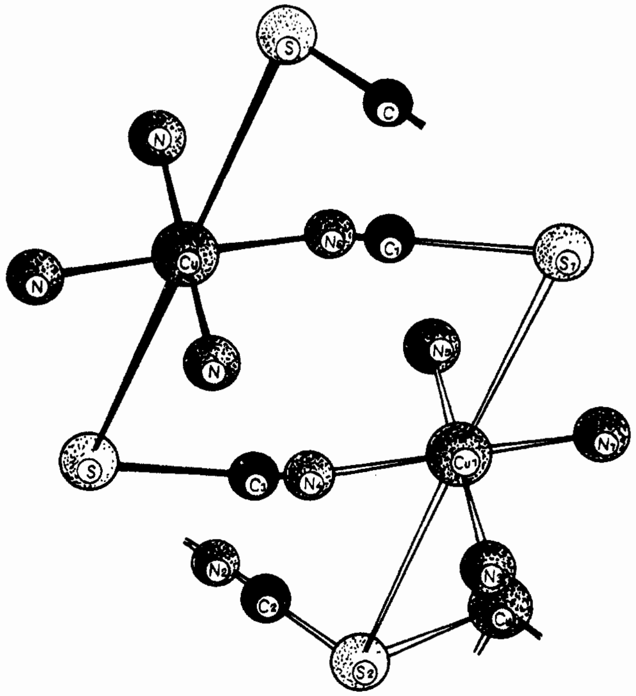

Figure 2.—Coordination of copper(II) and type of the mutual bonding of the distorted octahedra in $Cu_2(NCS)_3(NH_3)_3$.

TABLE V

RELATIONSHIP BETWEEN Cu–NCS–Cu DISTANCES (Å) AND ANGLES (DEG)

No. of SCN group	Cu–N	C–N	C–S	Cu(II)–S	Cu(I)–S	S–N
I	1.987	1.181	1.638	3.286	...	2.819
II	1.996	1.128	1.710	2.946	2.470	2.830
III	2.006	1.127	1.671	...	2.376	2.798

No. of SCN group	S–C–N	Cu–N–C	Cu–S–C
I	179.3	172.3	85.2
II	175.1	162.0	88.7
III	176.3	168.1	96.3

The valence angles in the coordination polyhedron around the copper(I) atom are within the range 100.5–115.8° (see Table IV).

There are three types of thiocyanate groups in the structure, with bridging functions and bonding through the nitrogen and sulfur atoms. The first, which mutually bonds the distorted octahedra, forms a strong covalent copper(II)–nitrogen bond of the length 1.987 Å and a very weak copper(II)–sulfur link (interatomic distance 3.286 Å). The second type bonds only the copper(I) tetrahedra (with bond lengths 2.376 and 2.006 Å). The third kind of thiocyanate group forms two covalent bonds Cu(I)–N and Cu(I)–S. The sulfur atom is also bonded to the copper(II). Despite its weakness, the Cu(II)–S bond (2.946 Å) causes a restriction of the temperature oscillations of this sulfur atom (*B* for the sulfur atom S(2) has a particularly low value of 0.29). The same function of the thiocyanate group has been observed in the structure of $Cu(NCS)_2$-Py_2[1](Py = pyridine) and $Cu(NCS)_2(NH_3)_2$.[5]

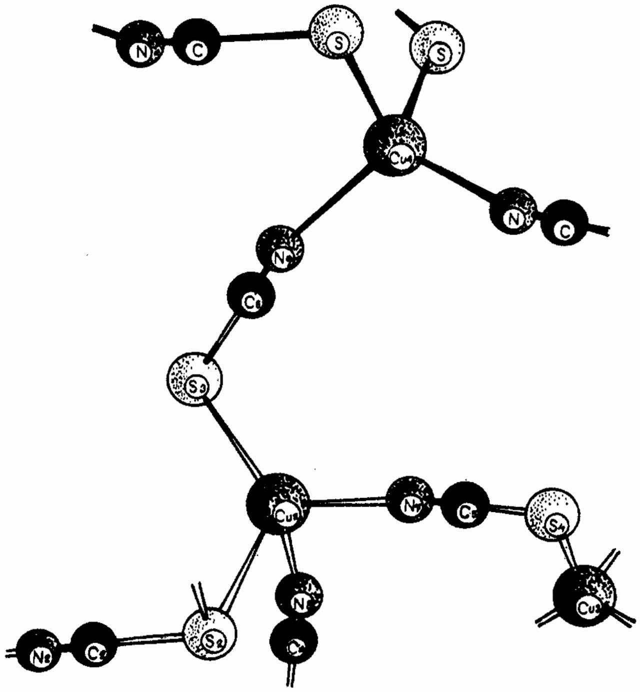

Figure 3.—Coordination of copper(I) and bonding of the tetrahedra by the SCN groups in the crystal of $Cu_2(NCS)_3(NH_3)_3$.

The $Cu(NCS)_2(NH_3)_2$ complex is light-blue while α- and β-Cu(NCS) are yellow-white. The dark color of the $Cu_2(NCS)_3(NH_3)_3$ complex can be explained as a result of the absorption, due to the intervalence transfer through the sulfur S(2) atom. The optically excited electron is assumed to be spread over both the copper atoms and the intervening bridging sulfur atom, in agreement with McConnell and Davidson.[15] This fact might also explain the particularly low *B* factor of sulfur S(2).

The effect of these different functions of the thiocyanate groups on the interatomic distances and on the valence angles is shown in Table V.

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The Crystal and Molecular Structure of the Yellow Form of Dichlorobis(2,6-lutidine N-oxide)copper(II)

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The crystal and molecular structure of dichlorobis(2,6-lutidine N-oxide)copper(II), $(C_7H_9NO)_2CuCl_2$, has been determined by single-crystal X-ray diffraction techniques. The crystals belong to the orthorhombic space group $Pna2_1$ with unit cell dimensions $a = 13.88\ (1)$, $b = 7.677\ (5)$, and $c = 16.23\ (1)$ Å. There are four molecules per unit cell, and the observed and calculated densities are 1.49 and 1.48 g/cm^3, respectively. The equiinclination Weissenberg technique was used to record the intensities of 981 nonzero reflections. Positional and isotropic thermal parameters were refined by least-squares methods to a conventional *R* factor of 8.3%. The molecules are monomeric, and the coordination around the central Cu ion is intermediate between tetrahedral and *cis* square planar. The Cu–Cl distances are 2.221 (4) and 2.247 (4) Å while the Cu–O distances are 1.97 (1) and 1.93 (1) Å.

Introduction

Complexes of Cu(II) compounds and various N-oxide ligands have been the subject of a number of studies. Most of the ligands form complexes in both a 1:1 and a 2:1 ligand-to-metal ratio;[1–7] however, complexes with other ligand-to-metal ratios also occur. Most 1:1 complexes have low magnetic moments at room temperature, and an oxygen-bridged dimeric structure was proposed.[8,9] A single-crystal study of dichloro(pyridine N-oxide)copper(II) showed the structure to be composed basically of oxygen-bridged dimeric units.[10,11] The dimeric units are chlorine bridged to adjacent dimers to form infinite chains, and the geometry around the Cu(II) ion is square pyramidal[12] with the apical chloride bond elongated to 2.836 Å. The two bridging oxygen atoms form an edge of the square base, and the apical chlorides are *trans* with respect to the joined basal planes. The low magnetic moments of the 1:1 complexes are rationalized in terms of a superexchange mechanism.

The structure and properties of the 2:1 complexes have not been studied as extensively as the 1:1 complexes. The 2:1 complexes in general are monomeric and have normal magnetic moments although both low-moment and normal-moment dimeric structures are known. The low-moment dimers are similar to the 1:1 complexes with the extra pyridine N-oxide ligands in the fifth coordination site rather than a bridging chloride ion. The normal-moment dimers are similar except one bridging oxygen is apical and the other basal. If the magnetic electrons are restricted to orbitals of approximately $d_{x^2-y^2}$ symmetry, superexchange does not occur because the orbitals of the magnetic electrons do not overlap significantly at the shared oxygen atoms.

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