bility of a tetrahedral structure. Furthermore, structural investigations on the isoelectronic species ICl_4^-,[27] ClF_4^-,[23,24] and XeF_4[28] have shown that all of them are planar and not tetrahedral.

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Redetermination of the Crystal Structure of Tris(ethylenediamine)copper(II) Sulfate, $Cu(NH_2CH_2CH_2NH_2)_3SO_4$

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The structure of tris(ethylenediamine)copper(II) sulfate, $Cu(NH_2CH_2CH_2NH_2)_3SO_4$, has been redetermined using full three-dimensional X-ray diffraction data and anisotropic thermal parameters. The compound crystallizes in the trigonal space group $P\bar{3}1c$ with hexagonal cell dimensions $a_0 = b_0 = 8.966$ (1) Å and $c_0 = 9.597$ (1) Å. The observed density is 1.69 (1) g/cm^3, while the calculated density is 1.688 g/cm^3 for two molecules in the unit cell. Intensities of 513 independent reflections were measured on a Picker automated four-circle diffractometer. Of these, 29 were considered as unobserved. The structure was refined by full-matrix least squares to a final conventional R factor of 0.034. The complex is isostructural with $Ni(en)_3SO_4$. The copper and sulfur atoms are located at positions of 32 (D_3) symmetry. This site symmetry for the copper atom is in apparent violation of the Jahn–Teller theorem. There is some evidence for the existence of a dynamic Jahn–Teller effect, since the thermal parameters are larger than those in $Ni(en)_3SO_4$ but this difference is small, making it difficult to draw any definite conclusion about the existence of such an effect. The Cu–N, N–C, and C–C bond lengths are 2.150 (2), 1.472 (5), and 1.507 (5) Å, respectively. The oxygen atoms of the sulfate ion are disordered and the apparent SO_4^{2-} tetrahedron is somewhat distorted. The O–S–O angles range from 100 to 119°, while the S–O bond distances range from 1.46 to 1.50 Å.

Introduction

In virtually all six-coordinate copper(II) complexes, the coordination octahedron is distorted, generally having two apical bonds much longer than the four equatorial bonds. This distortion is generally explained by the Jahn–Teller theorem.[1] However several esr studies have shown examples of octahedral (or presumably octahedral) complexes which have isotropic spectra.[2-4] In addition three X-ray structure determinations of copper(II) compounds have been reported, in which the symmetry of the copper coordination polyhedron is higher than allowed by the Jahn–Teller theorem. Two of these, potassium lead hexanitrocuprate(II)[5,6] and tris(ethylenediamine)copper(II) sulfate, $Cu(en)_3SO_4$[7] (en = $NH_2CH_2CH_2NH_2$) were carried out using two-dimensional methods and assuming overall isotropic temperature factors. Three-dimensional methods and anisotropic thermal parameters were used in the structure determination of the third example, tris(octamethylpyrophosphoramide)copper(II) perchlorate, $Cu(OMPA)_3(ClO_4)_2$, which has only recently been reported.[8] A neutron diffraction study has also been recently completed on $K_2PbCu(NO_2)_6$.[9]

The two most general proposals that have been advanced to explain these apparent violations of the Jahn–Teller theorem follow. (1) The complex is oscillating among three equivalent (*e.g.*, tetragonal) distortions so that on a time average the structure appears regular. This is called the dynamic Jahn–Teller effect.[10] (2) Each molecule is trapped in one of several such distortions. Molecules in each of these distortions are distributed at random throughout the crystal, so that on a space average, the structure appears regular.

In most modern X-ray structure determinations, the average of the thermal motion of an atom is approximated by an ellipsoid. If either of the effects postulated above is present, the apparent thermal motion of the atom should be increased. In addition it might be

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expected that the longest axis of the thermal ellipsoid for the donor atoms would be parallel to the copper–donor atom bond. Since the earlier two-dimensional study did not allow this kind of detailed study, the structure of tris(ethylenediamine)copper(II) sulfate has been redetermined using three-dimensional X-ray data and refined with anisotropic thermal parameters.

Experimental Section

Purple, hexagonal, rod-shaped crystals of $Cu(en)_3SO_4$, elongated along the *c* axis, were prepared by the method of Gordon and Birdwhistell.[11] These authors reported their product to be a monohydrate. However Cola, Giuseppetti, and Mazzi,[7] in a similar preparation, found the crystals to be anhydrous. On the basis of the density and the eventual solution of the structure in the present study, the compound is indeed anhydrous. The crystals cleave easily on (001) and those used in this study were cut from larger rods. The crystal used for intensity measurements had the approximate dimensions 0.40 × 0.40 × 0.38 mm in the directions of *a*, *b*, and *c*, respectively. The faces of this crystal were ill defined, with the crystal having an approximately oval cross section when viewed down the *c* axis, which was the axis about which the crystal was mounted.

Oscillation and Weissenberg photographs of crystals mounted along the *c* axis, using Cu Kα radiation, showed trigonal symmetry with systematic absence of reflections of the type $hh\overline{2h}\,l$ when l was odd. This indicated the space group to be either $P\bar{3}1c$ or P31c. The former space group was chosen by the original authors,[7] and the present work has verified this choice.

Cell dimensions were obtained by least-squares refinement of the 2θ values for 12 reflections collected on a Picker manual diffractometer equipped with a General Electric goniostat and pulse height analyzer, using Mo Kα radiation (λ 0.71069 Å). The radiation was filtered by a 0.001-in. thickness of niobium foil. Room temperature is 23°. The cell dimensions (Å) are given below.

	Present work	Original[7]
$a_0 = b_0$	8.966 (1)	8.94 (1)
c_0	9.597 (1)	9.60 (1)

A density of 1.69 (1) g/cm^3 was obtained by the flotation method using a mixture of tetrabromoethane, carbon tetrachloride, and toluene. For two molecules in the unit cell, the calculated density is 1.688 g/cm^3 if the compound is considered anhydrous, whereas it is 1.80 g/cm^3 for a monohydrate. The total number of electrons in the unit cell is 354.

A Picker automated diffractometer was used to collect intensity data using the θ–2θ scan method. Niobium-filtered Mo Kα radiation was used. The crystal was 18 cm from the X-ray tube and 23 cm from the counter aperture. The takeoff angle was 3.5°. The scan range was calculated from the formula of Alexander and Smith[12]

$$\text{scan range (in deg)} = A + B \tan\theta \qquad (1)$$

A, which is, in part, a function of the mosaicity of the crystal, was determined by measuring the width of several of the most intense reflections. A value of 1.10° was used. B is 1.00°. Background measurements were collected for 20 sec at each end of the scan range. The scan speed was 2°/min.

The intensities of 513 unique reflections were measured out to a 2θ value of 55°. Four standard reflections ($2\bar{1}8$, 500, 004, and 214) were remeasured every 3–4 hr. The intensities of all four standards dropped at the same constant rate, indicating breakdown of the crystal. Group scale factors were calculated relative to the first group, using the weighted average of the intensities of the standards, and applied to the intensities of all the reflections. The maximum factor was 1.24.

A set of reflections ranging from medium to the highest intensity was remeasured with two different X-ray tube currents, the normal data-collection current (14 mA) and a smaller current (6 mA). The plot of the ratio of high-current counts to low-current counts against high-current counts gave a good straight line, corroborating the assumption of constant peak shape, and its slope gave a value of $\tau = 6.36 \times 10^{-8}$ loss per dekacount. Intensities were therefore corrected for coincidence loss[13] by $I_{\text{cor}} = I_{\text{measd}}/(1 - \tau I_{\text{measd}})$. The maximum correction was 1.8%. The standard deviations in the intensities, σ_I, were calculated from the equation

$$\sigma_I = [\sigma^2_{I(\text{counting})} + K^2(\text{total counts})^2]^{1/2} \qquad (2)$$

$$\text{total counts} = S + (T_s/2T_b)(B_1 + B_2)$$

$$\sigma^2_{I(\text{counting})} = S + (T_s/2T_b)^2(B_1 + B_2)$$

S is the scan count collected for time T_s, and B_1 and B_2 are the backgrounds, each measured for time T_b. The first term in eq 2 is the error due to counting statistics, while the second term is an empirical one used to account for other random errors in the data collection. A K value of 0.01 was used. Of the 513 reflections collected, 29 had intensities less than or equal to twice their standard deviation and were considered as unobserved. These were assigned "intensities" equal to $I + 2\sigma_I$. The ratio of minimum to maximum intensity for observed reflections was 1:18000.

The linear absorption coefficient for $Cu(en)_3SO_4$ is 18.67 cm^{-1} for Mo Kα radiation. Transmission factors were calculated using a Fortran IV program based on the analytical method of DeMeulenaer and Tompa,[14] roughly approximating the crystal shape as a hexagonal rod. These factors showed a maximum range of 0.57–0.67 with the majority of values in the range 0.64–0.66. Because of these relatively small differences and the difficulty of accurately defining the crystal faces, no absorption corrections were applied. No dispersion corrections were applied. For Mo Kα radiation, the corrections are $\Delta f' = 0.1$, $\Delta f'' = 0.2$ for sulfur and $\Delta f' = 0.3$, $\Delta f'' = 1.4$ for copper.

Structure Determination and Refinement

All further calculations were done using the "X-Ray 63" crystallographic computing system of Stewart.[15] Intensities were corrected for Lorentz and polarization effects in the usual way. Scattering factors for copper(II) ion and sulfur, carbon, oxygen, and nitrogen atoms were those tabulated by Cromer and Waber,[16] while the hydrogen scattering factors were those of Stewart, Davidson, and Simpson.[17]

For two molecules in a unit cell of space group $P\bar{3}1c$, the copper and sulfur atoms are required to be in special positions. From a sharpened, origin-removed Patterson synthesis, the copper ion was found to be at $^2/_3$, $^1/_3$, $^1/_4$ (the symmetry-related position is $^1/_3$, $^2/_3$, $^3/_4$), while the sulfur atom was at $^1/_3$, $^2/_3$, $^1/_4$ (the symmetry-related position is $^2/_3$, $^1/_3$, $^3/_4$), in agreement with the choice made by the original authors.[7] A structure facture calculation, based on the copper and sulfur atom positions, yielded a conventional R factor of 0.283.

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TABLE I[a]

LIST OF OBSERVED AND CALCULATED STRUCTURE FACTORS FOR TRIS(ETHYLENEDIAMINE)COPPER(II) SULFATE

10,-5,L		
2	217	219
4	137	139
6	144	137
11,-5,L		
1	105	94
2	101	103
3	45	46
8,-4,L		
2	351	349
4	250	250
6	170	173
8	154	157
9,-4,L		
1	79	81
2	61	60
3	62	63
4	98	102
5	62	62
6	152	152
7	73	68
10,-4,L		
1	43	52
2	132	129
3	40	33
4	73	72
5	59	60
6	51	53
11,-4,L		
1	29*	12
2	169	170
3	25*	3
6,-3,L		
2	512	512
4	453	453
6	272	275
8	219	220
10	202	209
7,-3,L		
1	166	187
2	272	273
3	204	217
4	157	154
5	61	63
6	72	69
7	25	18
8	71	74
9	43	40
8,-3,L		
1	74	75
2	155	153
3	88	90
4	173	172
5	108	106
6	109	112
7	80	78
8	65	69
9,-3,L		
1	67	70
2	208	211
3	63	65
4	216	223
5	35	34
6	214	217
7	66	63
10,-3,L		
1	53	51
2	64	66
3	59	58
4	69	73
5	48	50
11,-3,L		
1	40	38
2	70	67
4,-2,L		
2	349	353
4	538	576
6	458	478
8	241	236
10	166	168
5,-2,L		
1	168	175
2	194	202
3	162	159
4	272	275
5	92	95
6	250	251
7	67	76
8	181	185
9	73	69
10	98	106
11	64	58
6,-2,L		
1	184	198
2	204	201
3	185	193
4	209	210
5	82	85
6	135	141
7	82	85
8	85	88
9	102	101
10	87	88
7,-2,L		
1	137	135
2	342	338
3	21*	6
4	342	344
5	78	75
6	277	282
7	48	40
8	199	205
9	20*	4
8,-2,L		
1	24	7
2	127	126
3	87	92
4	109	117
5	156	148
6	114	110
7	86	79
8	79	78
9,-2,L		
1	82	81
2	121	122
3	46	46
4	104	104
5	58	48
6	75	78
7	38	32
10,-2,L		
1	21	18
2	184	186
3	21*	0
4	158	158
5	24*	17
2,-1,L		
2	422	417
4	580	608
6	570	580
8	384	375
10	219	219
12	157	168
3,-1,L		
1	23	15
2	170	174
3	136	114
4	351	364
5	242	233
6	287	296
7	96	108
8	130	131
9	23	9
10	84	97
11	61	55
4,-1,L		
1	195	198
2	132	140
3	162	149
4	259	271
5	135	131
6	292	293
7	53	93
8	179	175
9	45	45
10	73	76
11	54	51
5,-1,L		
1	16*	9
2	435	437
3	23	25
4	370	377
5	16*	1
6	391	392
7	22*	12
8	324	328
9	27	25
10	161	187
11	20*	0
6,-1,L		
1	198	215
2	262	253
3	67	70
4	112	138
5	49	40
6	96	93
7	85	85
8	136	134
9	80	79
10	109	107
7,-1,L		
1	31	33
2	92	85
3	69	75
4	154	159
5	114	111
6	180	186
7	90	94
8	122	124
9	60	55
8,-1,L		
1	50	53
2	223	221
3	37	32
4	254	259
5	41	39
6	229	232
7	25*	1
8	152	149
9,-1,L		
1	57	55
2	143	146
3	41	39
4	108	106
5	59	53
6	62	53
10,-1,L		
1	70	63
2	68	67
3	56	51
0,0,L		
2	1049E	1303
4	290	287
6	89	84
8	451	453
10	333	313
12	172	167
1,0,L		
0	622	603
1	292	285
2	391	352
3	31	22
4	206	209
5	141	149
6	243	239
7	192	206
8	251	235
9	123	135
10	145	137
11	46	45
12	66	69
2,0,L		
0	720	730
1	395	410
2	489	491
3	333	315
4	193	204
5	437	435
6	125	121
7	196	207
8	155	136
9	64	74
10	144	133
11	42	45
12	105	104
3,0,L		
0	316	316
1	128	130
2	476	518
3	88	90
4	591	630
5	44	44
6	500	505
7	87	92
8	329	325
9	33	39
10	216	225
11	32	21
4,0,L		
0	343	349
1	206	202
2	278	282
3	31	23
4	175	181
5	111	116
6	160	167
7	207	215
8	144	146
9	125	126
10	110	112
11	29*	15
5,0,L		
0	403	403
1	406	423
2	267	263
3	43	40
4	124	125
5	52	46
6	119	117
7	70	72
8	133	131
9	103	98
10	99	94
6,0,L		
0	575	568
1	31*	24
2	439	421
3	25*	15
4	255	246
5	18*	15
6	203	205
7	19*	7
8	215	219
9	25*	4
7,0,L		
0	38*	9
1	74	86
2	107	105
3	82	86
4	217	213
5	86	79
6	168	157
7	68	63
8	94	88
8,0,L		
0	174	173
1	18*	8
2	123	121
3	105	104
4	72	71
5	117	109
6	83	85
7	55	44
9,0,L		
0	179	180
1	47	45
2	170	172
3	28*	10
4	168	167
5	31*	28
10,0,L		
0	88	91
1	66	60
1,1,L		
0	752	719
2	955	994
4	604	612
6	366	357
8	357	343
10	301	297
12	171	177
2,1,L		
0	199	192
1	540	521
2	487	503
3	519	497
4	326	332
5	66	65
6	134	137
7	55	40
8	121	118
9	79	81
10	149	150
11	122	111
3,1,L		
0	235	233
1	380	363
2	323	338
3	278	260
4	236	247
5	73	77
6	181	174
7	46	46
8	164	158
9	98	80
10	130	127
11	86	77
4,1,L		
0	539	542
1	125	124
2	411	414
3	37	31
4	342	346
5	80	79
6	384	375
7	60	54
8	328	324
9	26*	18
10	196	199
11	24	24
5,1,L		
0	315	320
1	218	229
2	134	174
3	65	68
4	139	132
5	28	29
6	154	154
7	87	87
8	126	129
9	99	95
10	71	71
6,1,L		
0	120	114
1	72	83
2	177	180
3	126	133
4	169	169
5	100	100
6	133	134
7	63	58
8	114	113
9	57	54
7,1,L		
0	262	256
1	74	71
2	339	334
3	20	8
4	281	275
5	44	41
6	162	165
7	26*	10
8	132	132
8,1,L		
0	126	126
1	100	97
2	105	100
3	82	83
4	92	88
5	36	35
6	71	72
9,1,L		
0	85	86
1	41	28
2	95	97
3	24	16
2,2,L		
0	583	592
2	952	1001
4	546	546
6	170	153
8	182	179
10	286	290
3,2,L		
0	38	41
1	211	206
2	79	85
3	197	185
4	272	270
5	133	140
6	297	292
7	78	82
8	171	172
9	65	61
10	77	86
11	62	55
4,2,L		
0	225	219
1	42	34
2	290	286
3	21*	9
4	217	212
5	202	209
6	99	99
7	194	193
8	77	77
9	55	51
10	102	102
5,2,L		
0	321	306
1	94	96
2	334	324
3	36	34
4	343	341
5	63	65
6	282	286
7	23	21
8	214	214
9	22*	3
6,2,L		
0	200	195
1	41	49
2	209	199
3	133	138
4	115	113
5	102	102
6	62	64
7	43	43
8	81	82
7,2,L		
0	146	145
1	144	148
2	152	149
3	121	113
4	102	98
5	24	17
6	55	52
7	32	10
8,2,L		
0	193	197
1	21*	7
2	179	174
3	27	21
4	162	158
5	24	4
3,3,L		
0	316	308
2	315	319
4	499	479
6	404	391
8	202	202
10	134	138
4,3,L		
0	261	252
1	62	66
2	170	157
3	110	111
4	143	136
5	128	122
6	131	128
7	47	50
8	99	97
9	19	12
5,3,L		
0	95	91
1	65	70
2	147	146
3	63	67
4	191	187
5	74	68
6	130	128
8	61	62
6,3,L		
0	255	247
1	18*	8
2	270	267
3	21*	14
4	217	217
5	19*	0
6	172	175
7	28	19
7,3,L		
0	130	131
1	45	42
2	133	131
3	58	51
4	83	80
5	61	61
8,3,L		
0	50	47
1	31	28
2	57	61
4,4,L		
0	375	360
2	334	321
4	274	270
6	215	216
8	169	167
5,4,L		
0	100	96
1	76	77
2	118	117
3	64	60
4	107	110
5	71	63
6	126	124
7	61	64
6,4,L		
0	122	121
1	95	86
2	76	75
3	64	57
4	80	81
5	29	31
6	100	99
7,4,L		
0	147	146
1	48	38
2	129	133
3	25	24
5,5,L		
0	286	282
2	228	225
4	145	156
6	143	148
6,5,L		
0	113	111
1	90	81
2	99	95
3	35	29

[a] Columns are l, $10|F_o|$, and $10|F_c|$. Unobserved reflections are indicated by an asterisk (the values given for F_o for these reflections are the F's obtained from $I + 2\sigma_I$). Reflections suffering from secondary extinction are indicated by an E.

The conventional R factor is defined by $\Sigma|F_o - F_c|/\Sigma|F_o|$. The initial scale factor and the overall temperature factor ($B = 2$) were estimated from the statistics of the normalized structure factors, using the DATFIX program.[15]

F_o Fourier maps gave the positions of the independent nitrogen and carbon atoms. These positions were virtually the same as in the original structure determination. However, no definite oxygen atom peaks could be found, since the SO_4^{2-} ion is disordered. A structure factor calculation based on the copper, sulfur, nitrogen, and carbon atoms gave $R = 0.159$.

Further refinement was carried out using the "X-Ray 63" version of the Oak Ridge full-matrix least-squares program (ORFLS). The function minimized was $\Sigma w|F_o - F_c|^2$. All weights w were set to unity at this stage of refinement. The only exceptions for this and subsequent cycles of refinement were reflections which were coded as unobserved and which calculated less than the "observed" structure factor. These were given zero weight. Three cycles of refinement on the copper, sulfur, carbon, and nitrogen atoms, assuming isotropic temperature factors, decreased R to 0.107. Three cycles of anisotropic least-squares refinement lowered R to 0.104.

The positions of three of the four oxygen atoms were found from difference Fourier syntheses. When these three oxygen positions, as well as three of the four independent hydrogen atom positions also found from difference synthesis, were refined with the other atoms, the conventional R was 0.047. Isotropic temperature factors for oxygen and hydrogen atoms were used throughout.

The fourth oxygen positions was found by comparison with the structure of the isostructural complex, $Ni(en)_3SO_4$.[18] The position chosen corresponded to a peak on several of the Fourier maps of the copper compound which was of much lower electron density than the other three oxygen positions. Three cycles of least-squares refinement with all atoms, including the fourth hydrogen atom position, lowered the conventional R to 0.034 and the weighted R to 0.040. Weighted R is defined as $(\Sigma w|F_o - F_c|^2/\Sigma w|F_o|^2)^{1/2}$. In this final refinement the weight was inversely proportional to the square of the estimated standard deviations for each reflection, with the exceptions mentioned previously. Examination of the data by the method of Housty and Clastre[19] showed the 002 reflection, by far the most intense, to be suffering from secondary extinction, and it was therefore omitted from the final refinement cycle. During the final cycle all shifts were less than one standard deviation except for some of the positional coordinates of O(3) and O(4). However, these parameters appeared to be oscillating slightly from cycle to cycle, so refinement was considered complete.

The final value for the error in an observation of unit weight, the so-called goodness of fit, was 3.73. A final difference synthesis showed only one peak over 0.5 e$^-$/Å^3 in height. A list of the observed and final calculated structure factors is given in Table I. Table II lists the final parameters and Table III tabulates the root-mean-square displacements for the nonhydrogen atoms.

Description of the Structure and Discussion

In general the present structural determination of tris(ethylenediamine)copper(II) sulfate confirms the earlier results. There are discrete $Cu(en)_3^{2+}$ cations and SO_4^{2-} anions alternating in rows parallel to the c axis; *i.e.*, in one row there are copper atoms at $^2/_3$, $^1/_3$, $N + {^1/_4}$ (N is integral) and sulfur atoms at $^2/_3$, $^1/_3$, $N + {^3/_4}$. In the adjacent row the copper atoms are at $^1/_3$, $^2/_3$, $N + {^3/_4}$ and the sulfur atoms are at $^1/_3$, $^2/_3$,

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[18] Mazhar-ul-Haque, C. N. Caughlan, and K. Emerson, to be submitted for publication.

[19] J. Housty and J. Clastre, *Acta Crystallogr.*, **10**, 695 (1957).

TABLE II[a]

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	$^2/_3$	$^1/_3$	$^1/_4$	184 (4)	184 (4)	154 (3)	92 (2)	0	0
S	$^1/_3$	$^2/_3$	$^1/_4$	206 (6)	206 (6)	174 (5)	103 (3)	0	0
N	4560 (3)	1448 (4)	1272 (3)	397 (12)	370 (12)	318 (10)	206 (10)	56 (9)	27 (9)
C	2985 (4)	1440 (4)	1717 (3)	351 (11)	351 (13)	375 (12)	117 (10)	−54 (9)	−11 (10)

Positional Parameters ($\times 10^3$) and Thermal Parameters ($\times 10$)

Atom	x/a	y/b	z/c	B
O(1)	234 (3)	499 (3)	173 (2)	50 (4)
O(2)	492 (3)	682 (4)	314 (2)	48 (3)
O(3)	410 (5)	807 (3)	149 (3)	58 (5)
O(4)	218 (5)	670 (5)	361 (2)	45 (3)
H(1)	191 (5)	40 (5)	134 (4)	45 (8)
H(2)	296 (4)	248 (5)	130 (4)	41 (8)
H(3)	446 (5)	43 (6)	135 (4)	55 (10)
H(4)	471 (5)	165 (5)	32 (4)	41 (7)

[a] Standard deviations for the least significant figure are shown in parentheses. Parameters for which no standard deviations are shown are fixed by symmetry considerations. The temperature factor is defined by: $\exp(-{}^1/_4\Sigma_i\Sigma_j B_{ij}h_ih_ja_i^*a_j^*)$.

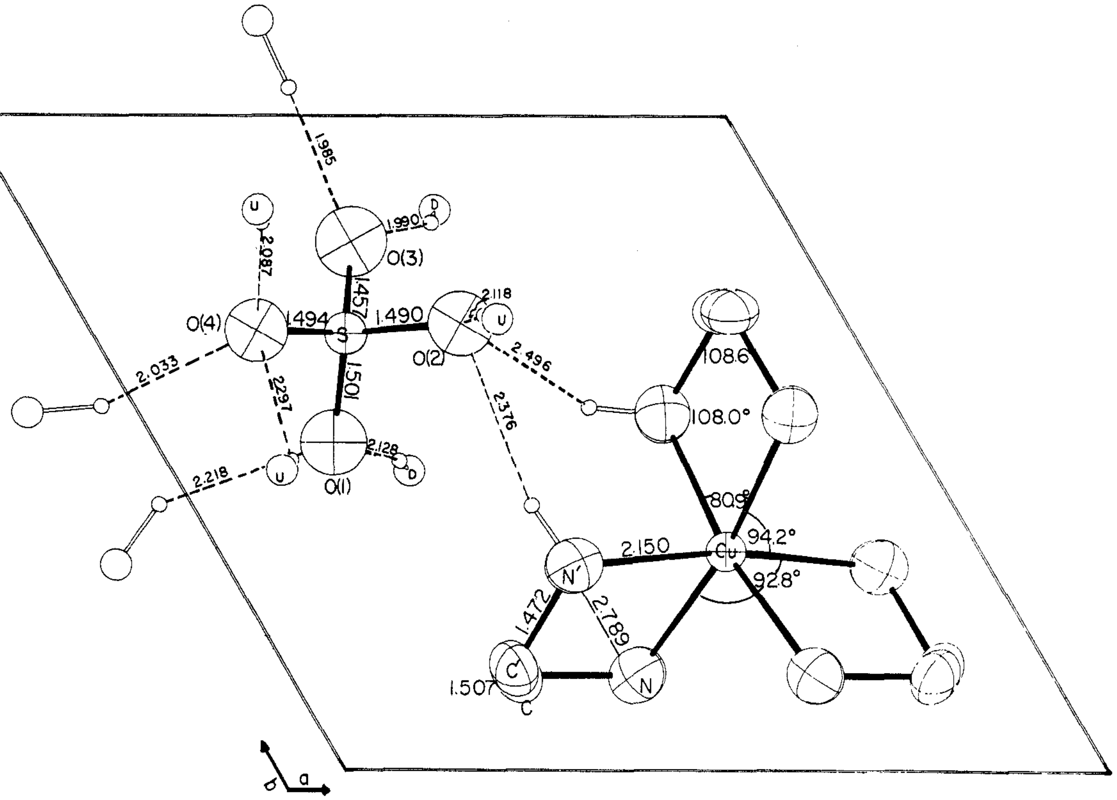

Figure 1.—Tris(ethylenediamine)copper(II) sulfate projection on 001 showing one formula unit and hydrogen bonding. U denotes the nitrogen atom involved in hydrogen bonding is located in the cation above the sulfate ion; D denotes the nitrogen is below the sulfate. Only one of the six possible orientations of the sulfate ion is shown.

TABLE III[a]

ROOT-MEAN-SQUARE DISPLACEMENTS (Å) OF PRINCIPAL AXES OF THERMAL ELLIPSOIDS FOR NONHYDROGEN ATOMS

	Axis 1	Axis 2	Axis 3
Cu	0.140 (1)	0.152 (2)	0.152 (2)
S	0.148 (2)	0.161 (2)	0.161 (2)
N	0.191 (3)	0.211 (4)	0.232 (3)
C	0.168 (4)	0.218 (4)	0.229 (4)
O(1)	0.253 (10)	0.253 (10)	0.253 (10)
O(2)	0.248 (7)	0.248 (7)	0.248 (7)
O(3)	0.272 (12)	0.272 (12)	0.272 (12)
O(4)	0.240 (8)	0.240 (8)	0.240 (8)

[a] Orientation of thermal ellipsoids may be seen by reference to Figure 1.

$N + {}^1/_4$. Figure 1 shows one layer of anions and cations as viewed down the c axis. For later comparison purposes, a similar view of the isostructural complex $Ni(en)_3SO_4$[18] is shown in Figure 2.

The oxygen atoms of the sulfate ion are disordered. The original authors[7] found no evidence for a model in which one of the threefold tetrahedral axes was parallel to the threefold crystal axis but instead found two planes of electron density perpendicular to the z axis, located equidistant above and below the sulfur atom, which would indicate a model in which one of the twofold tetrahedral axes was parallel to the threefold

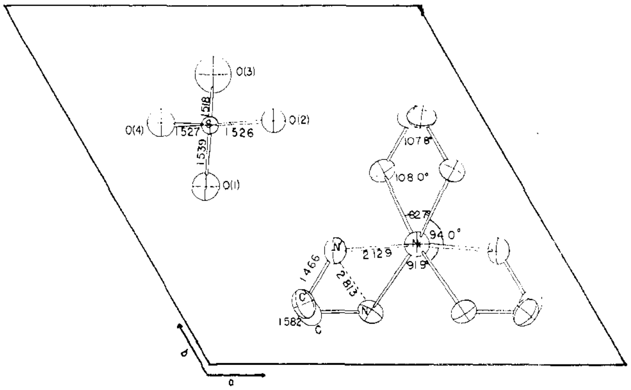

Figure 2.—Tris(ethylenediamine)nickel(II) sulfate projection on 001 showing one formula unit. Only one orientation of the sulfate anion is shown.

crystal axis. They were not able to resolve any definite oxygen peaks and had to assume a statistical model. In the present study the oxygen atoms were not all found in two planes perpendicular to the *z* axis but were in positions which require a model with the twofold axis tipped about 5.5° from the threefold crystal axis.

Because of the D_3 site symmetry of the sulfur atom, each independent oxygen position generates five other positions. Therefore the model involves disorder among six different orientations for the sulfate ion. These are shown in Figure 3. In addition there is a centrosymmetrically related set of six orientations which are not shown.

The apparent SO_4^{2-} tetrahedron is distorted. Two of the angles, O(2)–S–O(3) and O(3)–S–O(4), differ significantly from the ideal tetrahedral angle of 109.5°. These deviations are considerably larger than the range found in a recent tabulation of sulfate bond lengths and angles.[20] Since O(3) was the oxygen atom which was difficult to locate, it was decided to observe the effect of using a position for O(3) which was the ideal tetrahedral position. A structure factor calculation in which this substitution was made had a conventional R of 0.039 as compared with the original value of 0.034. Three cycles of refinement on this position caused it to refine to essentially the same position originally obtained.

The four S–O bond lengths are 1.50 (2) 1.49 (2), 1.46 (2), and 1.49 (3) Å. Since there is only about a two standard deviation difference in the bond lengths, this range is not significant. These lengths agree well with those in the previously mentioned tabulation.[20]

The chelate rings in $Cu(en)_3^{2+}$ have the *gauche* configuration found in all ethylenediamine complexes. The dihedral angle between the plane defined by one nitrogen atom and the two carbon atoms and the plane defined by the carbon atoms and the other nitrogen atom in the chelate ring is 57.5°. Another measure of the *gauche* configuration is the dihedral angle between the plane defined by the metal ion and the two nitrogen atoms and the plane defined by the metal ion and the two carbon atoms, which is 28.7° for this complex. Both types of dihedral angles are somewhat larger than those recently tabulated for other tris-ethylenediamine complexes.[21] A third measure commonly used is the deviation of the carbon atoms from the plane of the metal ion and nitrogen atoms. For $Cu(en)_3^{2+}$ the carbon atoms are located symmetrically 0.37 Å above and below the plane N–M–N′.

Because of the *gauche* conformations, for $M(en)_3$ complexes there are in general four possible isomers for each of the absolute configurations Λ and Δ. These are designated[21] $\Lambda\partial\partial\partial$, $\Lambda\partial\partial\lambda$, $\Lambda\partial\lambda\lambda$, $\Lambda\lambda\lambda\lambda$, $\Delta\partial\partial\partial$, $\Delta\partial\partial\lambda$, $\Delta\partial\lambda\lambda$, and $\Delta\lambda\lambda\lambda$. Because of the threefold site symmetry of the copper atom in $Cu(en)_3SO_4$, only the isomers $\Lambda\partial\partial\partial$, $\Lambda\lambda\lambda\lambda$, $\Delta\partial\partial\partial$, and $\Delta\lambda\lambda\lambda$, are possible in this case.[22] Finally since the space group is centrosymmetric, there is a racemic mixture of one of the two pairs of enantiomorphs, either ($\Lambda\partial\partial\partial$, $\Delta\lambda\lambda\lambda$) or ($\Lambda\lambda\lambda\lambda$, $\Delta\partial\partial\partial$). In this case the first set was found. Almost all $M(en)_3$ cations have the $\Lambda\partial\partial\partial$ (or $\Delta\lambda\lambda\lambda$) configuration. This is explained by Corey and Bailar,[22] who have calculated that this isomer should be more stable than $\Lambda\lambda\lambda\lambda$ by 1.8 kcal/mol. Only recently have other conformations, including $\Lambda\lambda\lambda\lambda$, been reported.[21,23,24] Hydrogen bonding is believed to be the reason for these exceptions.

The Cu–N bond length is 2.150 (2) Å, slightly shorter than the originally reported distance, 2.17 Å, but still considerably longer than the equatorial bonds in statically distorted octahedral complexes of copper(II); *e.g.*, Cu–N is 2.00 (1) Å in $Cu(en)_2(SCN)_2$.[25] This lengthening of the Cu–N bond distance in $Cu(en)_3SO_4$ may be due to steric effects arising from clustering six ligand atoms at equal distances around the metal ion rather than the more usual four. In $Cu(OMPA)_3(ClO_4)_2$,[8] which is also an apparent violation of the Jahn–Teller theorem, a similar effect is found. The Cu–O bond length in this compound is 2.068 (1) Å. In statically distorted complexes, the average Cu–O equatorial distance is 1.93 Å.

Other bond lengths in the ethylenediamine ligand agree fairly well with previous results. Although the C–C distance of 1.507 (5) Å is significantly shorter than the paraffin C–C single-bond distance of 1.54 Å, it is in agreement with the C–C distances in other ethylenediamine structures, including the recently reported structures of $[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$[23] and $[Cr(en)_3][Co(CN)_6]\cdot 6H_2O$.[24] The N–N separation in the chelate ring, the so-called bite distance, is 2.790 (6) Å. Important bond lengths and angles are shown in Figure 1, and a complete list is given in Table IV.

The polyhedron around the copper(II) ion is not truly octahedral in symmetry, even though all six Cu–N bond lengths are equal. The copper ion site symmetry is 32 (D_3). This distortion is reflected in

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[20] G. D. Andreetti, L. Cavalca, and A. Musatti, *Acta Crystallogr., Sect. B*, **24**, 683 (1968).

[21] K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, **7**, 842 (1968).

[22] E. C. Corey and J. C. Bailar, *J. Amer. Chem. Soc.*, **81**, 2620 (1959).

[23] K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, **7**, 1362 (1968).

[24] K. N. Raymond and J. A. Ibers, *ibid.*, **7**, 2333 (1968).

[25] B. W. Brown and E. C. Lingafelter, *Acta Crystallogr.*, **17**, 254 (1964).

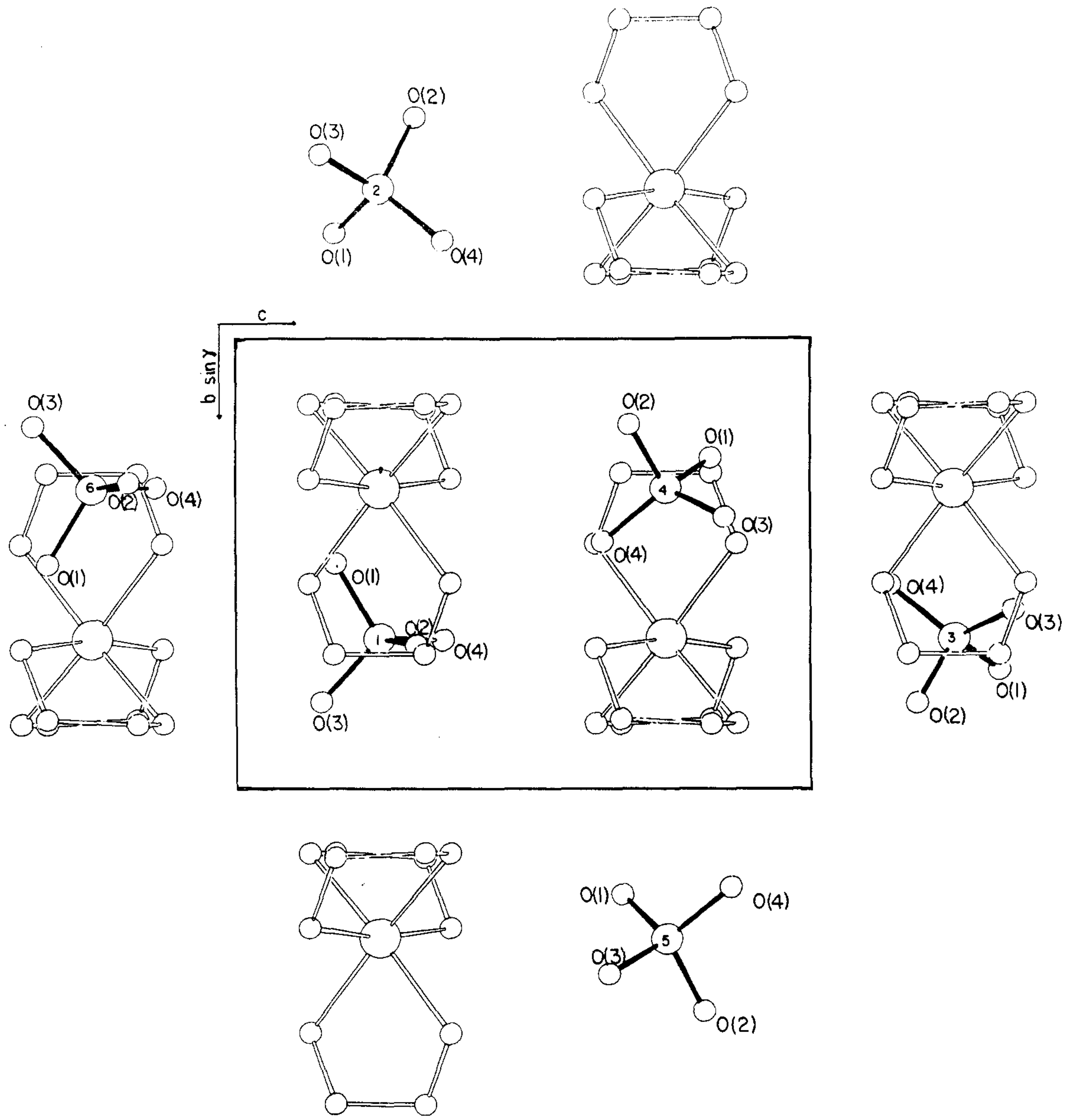

Figure 3.—Tris(ethylenediamine)copper(II) sulfate projection on 110. The six orientations of the sulfate ion are shown. Orientation 1 involves the set of oxygen positions given in Table II.

TABLE IV[a]

BOND LENGTHS (Å) AND ANGLES (DEG)

Cu–N	2.150 (2)	N–Cu–N′	80.9 (1)	N–C–H(2)	110 (2)
N–C	1.472 (5)	N–Cu–N″	92.8 (1)	C′–C–H(1)	113 (2)
C–C′	1.507 (5)	N–Cu–N‴	94.2 (1)	C′–C–H(2)	110 (2)
S–O(1)	1.50 (2)	Cu–N–C	108.0 (2)	H(1)–C–H(2)	105 (3)
S–O(2)	1.49 (2)	Cu–N–H(3)	111 (3)	O(1)–S–O(2)	111 (2)
S–O(3)	1.46 (2)	Cu–N–H(4)	114 (2)	O(1)–S–O(3)	109 (1)
S–O(4)	1.49 (3)	C–N–H(3)	112 (3)	O(1)–S–O(4)	108 (2)
C–H(1)	1.03 (3)	C–N–H(4)	110 (3)	O(2)–S–O(3)	100 (2)
C–H(2)	1.03 (5)	H(3)–N–H(4)	103 (4)	O(2)–S–O(4)	110 (2)
N–H(3)	0.87 (5)	N–C–C′	109 (2)	O(3)–S–O(4)	119 (2)
N–H(4)	0.92 (3)	N–C–H(1)	111 (3)		

[a] The figures in parentheses are standard deviations of least significant digits. Correlation effects have been considered in estimating standard deviations. C′ and N′ are related to C and N by the operation: $x' = x$, $y' = x - y$, $z' = {}^1/_2 - z$. N″ is related to N by the operation: $x'' = 1 - y$, $y'' = x - y$, $z'' = z$. N‴ is related to N by the operation: $x''' = 1 + y - x$, $y''' = y$, $z''' = {}^1/_2 - z$.

the N–M–N′ angles. Instead of the 90° expected for an ideal octahedron, the angle involving two nitrogen atoms in the same chelate ring is 80.9°, the angle involving two nitrogen atoms related by a threefold rotation is 92.8°, and the angle involving two nitrogen atoms neither related by a threefold rotation nor in the same chelate ring (*i.e.*, related by a combination of a threefold and a twofold rotation) is 94.2°. This reduction of O_h symmetry to D_3, which is a trigonal distortion, is not sufficient to remove the Jahn–Teller degeneracy.[26]

Temperature factors in the $Cu(en)_3^{2+}$ cation are all normal, except those of the nitrogen atom, which are suggestive of a dynamic Jahn–Teller effect. Dunitz and Orgel[27] have predicted that the temperature factor of atoms in complexes exhibiting this effect should be larger than normal. In general the thermal parameters in $Cu(en)_3SO_4$ are slightly larger than those in $Ni(en)_3SO_4$,[18] which should not be subject to any Jahn–Teller

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(26) R. A. Palmer and T. S. Piper, *Inorg. Chem.*, **5**, 864 (1966).

(27) J. D. Dunitz and L. E. Orgel, *J. Phys. Chem. Solids*, **3**, 20 (1957).

distortion. The root-mean-square displacements for the nitrogen atom along the principal axes of the thermal ellipsoid are 0.191 (3), 0.211 (4), and 0.232 (3) Å, while the displacements for the same atom in the nickel complex are 0.105 (10), 0.158 (9), and 0.186 (8) Å.[18] The largest displacement forms an angle of 19.1° with the Cu–N bond in the copper compound, while the largest displacement is in a direction 94.5° from the Ni–N bond in the nickel complex. The difference in orientation of the thermal ellipsoids may be seen in Figures 1 and 2.

The difference in magnitude of the thermal parameters between the nickel and copper complexes is small, and considering the susceptibility of thermal parameters to systematic errors, it is difficult to support the conclusion that the copper complex exhibits a dynamic Jahn–Teller effect or tetragonally distorted cations in different orientations.

However, the fact that the direction of maximum apparent thermal motion of the nitrogen atom is nearly parallel to the metal–nitrogen bond direction in $Cu(en)_3SO_4$, contrary to expectation based on bond stretching and bond bending energies and also contrary to that found in $Ni(en)_3SO_4$, is strongly suggestive of the presence of a Jahn–Teller effect.

Results of X-ray and neutron diffraction studies on other compounds which apparently violate the Jahn–Teller theorem show equally ambiguous results. The oxygen atom thermal ellipsoid in $Cu(OMPA)_3(ClO_4)_2$[8] was reported as essentially isotropic and of the same magnitude as those in the corresponding Mg(II) and Co(II) complexes. The nitrogen atom thermal ellipsoid in the neutron diffraction study of $K_2PbCu(NO_2)_6$[9] was also found to be essentially isotropic and of normal magnitude. However, a three-dimensional X-ray study[28] of $K_2PbCu(NO_2)_6$ shows the thermal parameters for the nitrogen atom are the same magnitude as in the neutron study, but the rms displacement for the principal axis which is parallel to the Cu–N bond is 0.02 Å longer than the other two principal axes. On the basis of the estimated standard deviations, this difference is significant.

Electron spin resonance measurements have given quite definite evidence for the existence of a dynamic Jahn–Teller effect. At room temperature the esr spectra of all of the complexes which are apparent violations of the Jahn–Teller theorem are isotropic.[2–4,8,25,29,30] For those which have been studied at low temperatures, the esr spectra are anisotropic under these conditions. $Cu(en)_3SO_4$ has only been studied at room temperature.[29] This temperature dependence would seem to rule out the possibility of different orientations of tetragonally distorted cations, since the esr measurements should be anisotropic at all temperatures if this were the case.[8] However, the temperature dependence is consistent with the proposal of a dynamic Jahn–Teller effect, since the anisotropic spectra at low temperatures may indicate that the complexes "freeze" into one of the tetragonal distortions.[30]

The disorder of the sulfate ion complicates the hydrogen-bonding scheme. For any single orientation of the sulfate ion there are ten hydrogen atoms within 2.5 Å of an oxygen atom. These are postulated as being hydrogen-bonding distances, even though the N–O distance for one of these is 3.22 Å, longer than the upper limit of 3.17 Å listed by Pimentel and McClellan[31] for N–H···O hydrogen bonds. The hydrogen-bonding scheme is shown in Figure 1. It should be emphasized that this scheme is for one orientation of the sulfate molecule. If the sulfate ion is in another orientation, different nitrogen atoms will be involved in the hydrogen bonding.

A complete list of the hydrogen-bond distances is given in TableV. Also listed are the N–H–O angles.

TABLE V

HYDROGEN BOND LENGTHS AND ANGLES

Oxygen	N–O, Å	H–O, Å	N–H–O, deg	Symmetry operation
	Group A: Hydrogen Bonds of Type N–H(3)···O (N–H = 0.872 Å)			
O(1)	2.98 (2)	2.22 (6)	145 (6)	1
O(2)	3.17 (3)	2.50 (6)	135 (3)	2
O(2)	3.23 (4)	2.38 (7)	165 (4)	3
O(3)	2.86 (3)	1.99 (6)	177 (4)	4
O(4)	2.86 (4)	2.03 (6)	159 (4)	5
	Group B: Hydrogen Bonds of Type N–H(4)···O (N–H = 0.924 Å)			
O(1)	3.03 (2)	2.13 (5)	165 (4)	6
O(2)	3.04 (2)	2.12 (4)	175 (4)	7
O(3)	2.85 (3)	1.99 (5)	155 (5)	8
O(4)	2.93 (3)	2.09 (5)	151 (3)	9
O(4)	3.07 (3)	2.30 (5)	140 (4)	10

Symmetry Operations to Be Applied to Nitrogen and Hydrogen Atoms

No.	x'	y'	z'
1	$-y$	$x - y$	z
2	x	$x - y$	$1/2 - z$
3	$1 + y - x$	$1 - x$	z
4	x	$1 + y$	z
5	$-y$	$1 - x$	$1/2 - z$
6	$x - y$	x	$-z$
7	$1 - x$	$1 + y - x$	$1/2 + z$
8	$1 - x$	$1 - y$	$-z$
9	$x - y$	$1 - y$	$1/2 + z$
10	y	x	$1/2 + z$

These angles range from 134 to 177°. Hydrogen bonds through H(3) (group A in Table V) involve anions and cations in which the copper and sulfur atoms have the same *z* coordinate. Hydrogen bonds through H(4) (group B in Table V) involve anions and cations in which the copper and sulfur atoms are in the same row parallel to the *c* axis.

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(30) H. Elliott, B. J. Hathaway, and R. C. Slade, *Inorg. Chem.*, **5**, 669 (1966).

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