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Copper(I) and Copper(II) Complexes of Tetramethyldiphosphinedisulfide. II. Isolation and Characterization of a Polymeric Copper(II) Precursor, $(Me_4P_2S_2)CuCl_2$, to the Ultimate Copper(I) Product, $[(Me_4P_2S_2)CuCl]_2$

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It has been found that the reaction of $CuCl_2 \cdot 2H_2O$ with $Me_4P_2S_2$ in ethanol at room temperature affords a small amount of a brown, crystalline product as well as the major, white Cu(I) product, $[(Me_4P_2S_2)CuCl]_2$. The brown compound decomposes to form the white one if left in contact with the reaction mixture for a few hours. X-ray crystallographic investigation has shown that the brown compound has the stoichiometry $(Me_4P_2S_2)CuCl_2$ and that it crystallizes as an infinite polymer in which $CuCl_2$ groups ($\angle$Cl–Cu–Cl = 141.4°) are connected by $Me_4P_2S_2$ molecules. The latter retain their anti rotational configuration and are thus incapable of chelating. The S–Cu–S angle is 137.3°; thus the coordination geometry at copper(II) is a flattened tetrahedron. The mean metal–ligand distances are: Cu–Cl, 2.22 Å and Cu–S = 2.33 Å. The principal crystallographic data are: space group, $P2_1/c$; a = 6.138(1) Å; b = 15.452(5) Å; c = 12.465(7) Å; β = 93.30(40)°; V = 1180.1(8) Å^3; Z = 4.

Introduction

Meek and Nicpon[1,2] have described the reactions of the tetramethyl- and tetraethyldiphosphinedisulfides with various copper(II) salts, the products of which were found to be copper(I) complexes of the $R_4P_2S_2$ ligands. Their observations were that the copper(II) was consistently reduced, rapidly and completely, to copper(I) under the conditions they employed. In contrast to this, it has been reported[3] that the compounds $(Me_4P_2S_2)CuX_2$, X = Cl, Br, can be isolated. However, no details of their preparation were given and only the Cu and X analyses along with their ir spectra were reported.

As reported in the preceding paper,[4] we conducted a reinvestigation of one of the compounds described by Meek and Nicpon,[1,2] *viz.*, the compound of empirical composition $[(CH_3)_4P_2S_2]CuCl$, preparing it under conditions explicitly designed to yield useful single crystals. Under these conditions we obtained, in addition to the desired white cuprous compound, a crystalline brown product. This brown substance was obtained in only about 10% the yield of the white substance and was observed to decompose to produce the white substance if left in contact with the reaction mixture for several hours. These observations led us to hypothesize that the brown compound might be a copper(II) precursor to the final, white copper(I) product, perhaps even the substance formulated as $(Me_4P_2S_2)CuCl_2$ by Beg and his coworkers.[3] Since the brown substance made itself available conveniently in the nature of well-formed single crystals, its identity and structure were investigated by X-ray crystallography.

Experimental

The preparation of the brown compound has been described in the preceding paper.[4]

Collection of X-ray Data

A crystal of approximate dimensions 0.3 × 0.1 × 0.1 mm was placed in a glass capillary and mounted on a Syntex $P\bar{1}$ computer-controlled, four-circle diffractometer, equipped with a graphite-crystal monochromator in the incident beam. The crystal was found to belong to the monoclinic system. Least-squares refinement of fifteen carefully centered reflections produced the orientation matrix required to control data collection and afforded the following unit cell dimensions: a = 6.138(1) Å; b = 15.452(5) Å; c = 12.465(7) Å; β = 93.30(4)°; V = 1180.1(8) Å^3. Assuming a value of Z equal to 4, the reasonable density 1.81 gcm^{-1} can be calculated. Attempts to measure the density were unsuccessful because of the chemical instability of the compound.

Data were collected in the range of $0° < 2\Theta \leqq 30°$ using MoKα radiation. The Θ–2Θ scan technique with a variable scan rate from 4.0 to 24.0 deg/min was used. The scan range was from $2\Theta(\text{Mo K}\alpha_1) - 0.9°$ to $2\Theta(\text{Mo K}\alpha_2) + 0.9°$. In order to check the stability of the measurement three reflections were selected as standards and their intensities were recorded periodically throughout data collection. Data collection beyond $2\Theta = 30°$ failed due to an abrupt decrease of intensities. A total of 583 reflections were collected and the usual data reduction procedures were applied.[5] The parameter p used in the calculation of standard deviations on the intensities ($\sigma(F_o^2)$) was assigned the value 0.05. The linear absorption coefficient was 29.12 cm^{-1} (Mo Kα). As the conditions of the measurement did not permit an accurate determination of crystal dimensions, an absorption correction was not feasible.

Refinement of X-ray Data

Systematic extinctions of $l = 2n+1$ for h0l and $k = 2n+1$ for 0k0 are consistent with space group $P2_1/c$. The copper atom was immediately located in a three-dimensional Patterson map. The solution and the refinement of the structure was carried out by the usual sequence of difference Fourier syntheses and full-matrix least-squares refinements. In the refinement only those 386 reflections were used for which $F_o^2 > 3\sigma(F_o^2)$ and the quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, and $w = 4F_o^2/\sigma^2(F_o^2)$.

Because of the small data set no attempt was made to locate the hydrogen atoms. The Cu, 2Cl, 2S and 2P atoms were refined anisotropically and the four carbon atoms isotropically (a total of 80 varied parameters). Final discrepancy indices of $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.039$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2} = 0.049$ were reached at convergence. No parameter changed by more than 0.01 times its standard deviation in the final cycle of refinement. The error in an observation of unit weight was 1.47 and the final difference Fourier map had no peak with an electron density greater than 0.38 eA^{-3}, which may be compared with the peak densities of the carbon atoms which were in the range of 3.0 to 3.3 eA^{-3}.

A list of the observed and final calculated structure factors is given in Table I.

TABLE I. Observed and Final Calculated Structure Factors, $10|F_o|$ and $10|F_c|$, for $[(CH_3)_4P_2S_2CuCl_2]_n$.

L = -8

K	H	FOBS	FCALC
-4	-1	378	393
-3	-1	256	275
-2	-1	512	485
-1	-1	543	520

L = -7

K	H	FOBS	FCALC
-6	-1	610	625
-4	-1	309	311
-3	-1	544	573
-2	-2	202	182
-2	-1	421	436
-1	-2	182	185

L = -6

K	H	FOBS	FCALC
-7	-1	255	247
-6	-1	268	277
-5	-2	261	254
-4	-1	709	702
-3	-2	162	122
-3	-1	553	531
-2	-1	472	432
-1	-2	728	725
0	-3	412	403
0	-2	1193	1184
0	-1	1353	1355

L = -5

K	H	FOBS	FCALC
-8	-1	313	357
-7	-2	704	725
-6	-2	1060	1115
-6	-1	1101	1075
-5	-2	919	[illegible]
-4	-2	259	253
-4	-1	245	240
-3	-2	334	367
-3	-1	962	955
-2	-3	140	150
-2	-2	483	514
-2	-1	1451	1449
-1	-3	867	[illegible]
-1	-2	483	[illegible]

L = -4

K	H	FOBS	FCALC
-9	-1	445	412
-8	-2	244	258
-8	-1	1540	1524
-7	-2	275	[illegible]
-7	-1	253	254
-6	-1	151	174
-5	-3	575	595
-5	-2	724	702
-4	-3	300	254
-4	-2	657	671
-3	-3	273	229
-3	-2	318	367
-3	-1	302	311
-2	-3	155	137
-2	-2	165	133
-2	-1	175	234
-1	-3	492	469
-1	-2	1210	1232
-1	-1	203	177
0	-3	954	[illegible]
0	-2	1636	[illegible]
0	-1	1570	1615

L = -3

K	H	FOBS	FCALC
-10	-1	575	575
-9	-2	280	273
-9	-1	423	413
-8	-2	200	176
-7	-3	574	566
-7	-2	1140	1128
-7	-1	293	330
-6	-3	371	372
-6	-2	505	[illegible]
-6	-1	209	217
-5	-3	394	411
-5	-2	270	266
-4	-3	172	212
-4	-1	231	271
-3	-3	416	399
-3	-2	155	155
-3	-1	626	605
-2	-3	647	673
-2	-2	330	279
-2	-1	471	496
-1	-3	1148	1116
-1	-2	605	617

L = -2

K	H	FOBS	FCALC
-9	-2	324	306
-9	-1	179	168
-8	-2	811	781
-8	-1	984	957
-7	-2	406	424
-7	-1	433	436
-6	-3	293	310
-5	-3	885	889
-5	-2	220	259
-4	-2	433	*425
-4	-1	1310	1239
-3	-2	331	304
-2	-2	216	191
-1	-3	459	467
-1	-2	871	859
0	-3	1170	1145
0	-1	332	342

L = -1

K	H	FOBS	FCALC
-10	-1	379	352
-9	-2	340	335
-9	-1	233	243
-8	-3	202	192
-8	-2	344	353
-8	-1	244	233
-7	-3	259	220
-7	-2	998	1032
-7	-1	522	517
-6	-3	1021	1350
-6	-2	379	597
-6	-1	403	357
-5	-3	337	343
-5	-2	173	155
-5	-1	650	622
-3	-2	201	172
-2	-3	657	646
-2	-2	1252	1201
-2	-1	1433	1319
-1	-4	277	249
-1	-3	265	277
-1	-2	573	545
-1	-1	745	789

L = 0

K	H	FOBS	FCALC
-10	-2	166	184
-9	-2	259	255
-9	-1	276	330
-8	-3	550	535
-8	-2	1127	1174
-8	-1	1173	1206
-7	-3	165	245
-7	-2	758	810
-7	-1	626	615
-6	-3	307	292
-6	-1	175	187
-5	-3	549	593
-5	-2	174	137
-5	-1	714	682
-4	-3	809	795
-4	-2	270	249
-4	-1	638	681
-3	-2	665	676
-1	-4	445	441
-1	-2	572	547
-1	-1	1023	1063
0	-4	455	451
0	-3	1231	1202
0	-2	1295	1175

L = 1

K	H	FOBS	FCALC
-10	-3	602	636
-10	-2	450	424
-10	-1	432	424
-10	0	634	635
-9	-2	530	549
-9	-1	318	331
-9	0	224	234
-8	-1	236	242
-8	0	337	351
-7	-3	568	582
-7	-2	818	805
-7	-1	832	845
-7	0	517	535
-6	-3	760	780
-6	-1	696	670
-6	0	2028	2019
-5	-3	573	582
-5	-2	169	180
-5	-1	863	856
-5	0	384	374
-4	-1	149	182
-3	-2	936	973
-3	-1	208	271
-3	0	235	204
-2	-3	890	925
-2	-2	400	330
-2	-1	2059	2141
-2	0	547	576
-1	-4	478	492
-1	-2	649	661
-1	-1	1219	1239
-1	0	206	207

L = 2

K	H	FOBS	FCALC
-9	-2	612	651
-9	-1	526	529
-9	0	135	162
-8	-3	346	345
-8	-2	139	144
-8	-1	680	707
-8	0	251	273
-7	-3	193	154
-7	-2	574	569
-7	-1	263	264
-7	0	431	326
-5	-3	690	713
-5	-2	274	276
-5	-1	970	979
-4	-3	737	772
-4	-2	784	812
-4	-1	2180	2051
-4	0	217	127
-3	-3	307	326
-3	-2	1093	1119
-3	-1	344	354
-3	0	222	140
-2	-1	257	274
-1	-4	351	359
-1	-2	559	547
-1	-1	1374	1335
0	-4	579	555
0	-3	189	140
0	0	2321	2374

L = 3

K	H	FOBS	FCALC
-10	-1	255	257
-10	0	396	337
-7	-3	335	335
-7	-2	556	514
-7	-1	727	754
-7	0	845	870
-6	-3	237	262
-6	-2	167	168
-6	-1	467	427
-6	0	656	662
-5	-3	565	597
-5	-1	720	712
-5	0	305	305
-4	-2	160	167
-3	-3	281	315
-3	-2	1438	1434
-3	0	267	287
-2	-3	241	213
-2	-1	333	333
-2	0	219	307
-1	-2	216	240
-1	-1	845	863
-1	0	425	443

L = 4

K	H	FOBS	FCALC
-10	0	208	216
-9	-1	491	504
-9	0	292	285
-8	-1	721	723
-8	0	336	351
-7	-3	209	180
-7	-1	193	243
-7	0	851	807
-6	0	285	262
-5	-3	631	645
-5	-2	232	213
-5	-1	930	855
-5	0	183	172
-4	-3	570	513
-4	-2	399	402
-4	0	238	236
-3	-2	986	963
-3	0	402	390
-2	-2	283	295
-2	-1	198	210
-1	-1	1081	1073
-1	0	506	486
0	-4	410	425
0	-3	505	487
0	-2	354	414
0	-1	1793	1753

L = 5

K	H	FOBS	FCALC
-9	-1	208	187
-9	0	242	229
-8	-1	256	254
-7	-2	135	202
-7	0	643	680
-6	-2	945	925
-6	-1	478	501
-6	0	533	528
-5	-1	932	905
-5	0	194	174
-4	-3	243	241
-4	-1	237	205
-4	0	319	293
-3	-2	1013	1017
-3	0	410	417
-2	-3	1022	1029
-2	-3	1022	1029
-2	-2	814	827
-2	-1	235	292
-2	0	561	630
-1	-3	204	195
-1	-2	161	155
-1	-1	497	533
-1	0	413	393

L = 6

K	H	FOBS	FCALC
-8	-1	355	331
-8	0	409	421
-7	-1	240	273
-7	0	555	551
-6	-1	263	274
-6	0	291	288
-5	-2	173	142
-5	-1	846	816
-5	0	403	425
-4	-3	810	762
-4	-2	1330	1322
-4	0	1765	1742
-3	-3	352	355
-3	-2	848	859
-3	-1	345	323
-3	0	220	223
-2	-2	370	371
-1	-3	214	198
-1	-1	553	553
-1	0	452	360
0	-2	1101	1033
0	-1	224	201
0	0	698	659

L = 7

K	H	FOBS	FCALC
-7	0	593	590
-6	-1	297	273
-6	0	483	445
-5	-1	706	717
-5	0	144	148
-4	0	469	492
-3	-2	338	334
-3	-1	546	520
-3	0	536	639
-2	0	1059	1081
-1	-1	466	510

L = 8

K	H	FOBS	FCALC
-5	-1	629	634
-4	-1	353	309
-4	0	746	729
-3	-1	248	248
-3	0	415	386
-2	0	176	149
-1	-2	267	265
-1	0	512	519
0	-2	280	234
0	-1	942	956

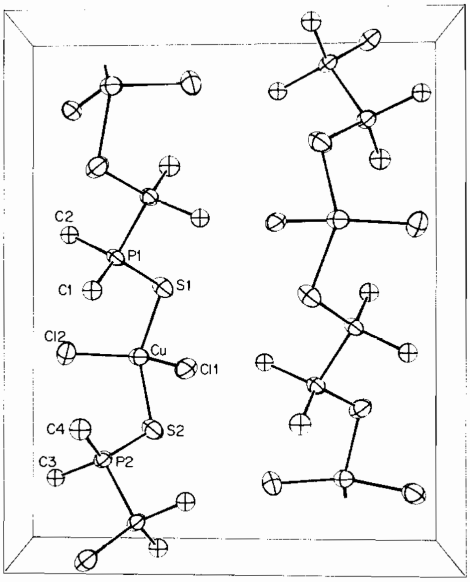

Figure 1. An ORTEP projection of the contents of one unit cell in the x direction (the origin of the unit cell is at the lower left corner, X axis is directed backward, Y axis upward and Z axis to the right, providing a right handed system). The atom numbering scheme used in the tables is shown. Each atom is represented by its thermal vibration ellipsoid scaled to enclose 50% of the electron density.

TABLE II. Positional and Thermal Parameters and their Standard Deviations.[a]
The Form of the Thermal Ellipsoid is $\exp[-(\beta_{11}k^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Atom	x	y	z	B	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.1323(5)	−0.1290(2)	0.2309(2)		0.024(1)	0.0024(2)	0.0043(3)	−0.0001(4)	−0.0013(4)	0.0000(2)
Cl1	−0.1369(9)	−0.1382(4)	0.1038(5)		0.027(3)	0.0032(4)	0.0056(6)	−0.0017(9)	−0.001(1)	0.0002(4)
Cl2	0.1968(9)	−0.1216(4)	0.4067(4)		0.035(3)	0.0035(3)	0.0043(6)	0.001(1)	−0.001(1)	−0.0003(4)
S1	0.216(1)	0.0084(4)	0.1700(5)		0.033(4)	0.0023(4)	0.0041(7)	−0.0012(9)	−0.001(1)	0.0002(3)
S2	0.230(1)	−0.2714(4)	0.1945(5)		0.029(4)	0.0020(4)	0.0060(6)	0.0010(8)	−0.002(1)	−0.0002(4)
P1	0.424(1)	0.0658(4)	0.2766(5)		0.023(3)	0.0018(4)	0.0035(6)	0.0000(9)	−0.001(1)	0.0004(4)
P2	0.439(1)	−0.3212(4)	0.3063(5)		0.019(3)·	0.0022(4)	0.0036(7)	−0.0001(8)	−0.001(1)	−0.0002(4)
C1	0.663(4)	0.002(1)	0.322(2)	2.5(6)						
C2	0.303(3)	0.112(1)	0.393(2)	2.3(5)						
C3	0.323(3)	−0.363(1)	0.425(1)	2.2(5)						
C4	0.679(4)	−0.256(1)	0.348(2)	3.1(6)						

[a] Numbers in parentheses are estimated standard deviations in the last significant digits.

The positional and thermal parameters are listed in Table II.

Results

The structure consists of infinite chains running parallel to the y axis, as shown in Fig. 1. The $Me_4P_2S_2$ ligands are extended in an anti rotational conformation with each sulfur atom bonded to a different copper atom. Each copper atom is surrounded by a very distorted tetrahedral array of two chlorine atoms and two

TABLE III. Important Interatomic Distances and Angles.[a]

1. Distances (Angstroms)		Average values
Cu–Cl(1)	2.225(6)	2.215 ± 0.010
Cu–Cl(2)	2.206(6)	
Cu–S(1)	2.322(7)	2.327 ± 0.005
Cu–S(2)	2.332(7)	
S(1)–P(1)	1.995(9)	1.993 ± 0.002
S(2)–P(2)	1.991(9)	
P(1)–C(1)	1.83(2)	1.82 ± 0.02
P(1)–C(2)	1.81(2)	
P(2)–C(3)	1.80(2)	
P(2)–C(4)	1.84(2)	
P(1)–P(2)	2.220(8)	
2. Angles (Degrees)		
Cl(1)–Cu–Cl(2)	142.4(3)	
S(1)–Cu–S(2)	137.3(2)	
Cl(1)–Cu–S(1)	89.7(2)	
Cl(1)–Cu–S(2)	89.5(3)	
Cl(2)–Cu–S(1)	104.3(3)	
Cl(2)–Cu–S(2)	102.1(3)	
P(1)–S(1)–Cu	109.5(3)	
P(2)–S(2)–Cu	113.1(3)	
Cl–P1–S1	115.9(7)	
Cl–P1–P2	104.2(7)	
C1–P1–C2	108.9(9)	
C2–P1–S1	115.6(8)	
C2–P1–P2	104.3(7)	
S1–P1–P2	106.6(4)	
C3–P2–S2	116.4(7)	
C3–P2–P1	106.1(7)	
C3–P2–C4	108.3(9)	
C4–P2–S2	117.2(7)	
C4–P2–P1	104.3(7)	
S2–P2–P1	103.0(3)	

[a] Numbers in parentheses are estimated standard deviations occurring in the last decimal place listed for each parameter.

sulfur atoms. Interatomic distances and angles of greatest interest are listed in Table III.

Discussion

The structure is a very reasonable one. It allows the tetramethyldiphosphinedisulfide ligand to have a sterically favorable anti rotational conformation. At the same time the copper(II) atom has a coordination geometry which is one of its more common ones, namely, a flattened tetrahedron. The instability of the compound is evidently of chemical rather than structural origin. It can be ascribed to the ability of the phosphine sulfide ligand to reduce Cu(II) to Cu(I). Apparently when equilibrium is reached this reduction is complete and under the normal preparative conditions used by Nicpon[1,2] there was no opportunity to isolate the intermediate cupric complexes. It would be interesting to know the circumstances under which Beg and coworkers obtained the cupric complexes.

Acknowledgement

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References

1 D.W. Meek and P.E. Nicpon, *J. Am. Chem. Soc., 87,* 4951 (1965).

2 P.E. Nicpon, Doctoral Dissertation, The Ohio State University, 1966. We thank Professor Devon W. Meek for providing relevant portions of this dissertation and for discussions thereof.

3 (a) M.A.A. Beg and K.S. Hussain, *Chem. And Ind. (London),* 1966, 1181; (b) M.A.A. Beg and S.H. Khawaja, *Spectrochim. Acta, 24A,* 1031 (1968).

4 F.A. Cotton, B.A. Frenz, D.L. Hunter and Z.C. Mester, *Inorg. Chim. Acta, 8,* 111 (1974).

5 All computer programs employed for data reduction and refinement of the structure and all sources of scattering data are the same as those cited in ref. 4.