showed a single sharp –CH_2– proton resonance at τ 8.75 whereas the pattern of –CH_2– and –CH– proton resonances for VI was much more complex, consisting of three broad resonances for each type of proton.

Compounds VII and VIII, which have molecular formulas $[C_5H_5Mo(CO)_3S_2C_6H_{10-11}]_x$ and $[C_5H_5MoS_3C_6H_{10-11}]_2$, respectively, on the basis of analytical data could not be assigned structures. VII was not a simple derivative of a $C_5H_5Mo(CO)_3$ group since the infrared spectrum showed bridging carbonyls; unless the latter contains an uncoordinated sulfur atom it is difficult to conceive of a way to use all the possible coordination sites of all sulfur atoms. Lacking further data we regard the molecular structures as only tentatively correct.

The orange crystalline compound $[C_5H_5MoSO]_2$ (IV) appeared not to be formed as a direct product in the reaction since no single band on the original chromatographic column was observed to contain this material. Instead IV appeared in several crude products and was presumably a product of air oxidation of one or several organosulfur molybdenum compounds. This product was exceptionally stable thermally and was also insensitive to oxygen or moisture in the solid state.

A suggestion as to the structure of this compound is seen in the paper of Green and Cousins[17] discussing oxomolybdenum compounds. In this paper a compound of the formula $[C_5H_5MoO_2]_2$ is described; this was obtained with other products on air oxidation of $C_5H_5Mo(CO)_3H$ or $[C_5H_5Mo(CO)_3]_2$. The physical properties and reactivity were not greatly dissimilar from those of IV, and the infrared spectrum appeared rather similar to that of IV, as might be expected if the only difference in these compounds was the presence of two sulfur atoms rather than two oxygen atoms in bridging positions (Figure 2). Specifically the two Mo–O stretching frequencies predicted by Green and Cousins to fall at approximately 920 and 850 or 898 cm^{-1} in the oxo compounds were observed in IV at 920 and 895 cm^{-1}.

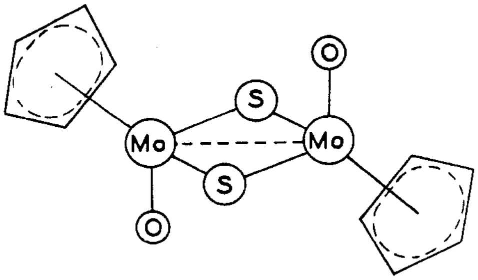

Figure 2.—Structure of $[C_5H_5MoSO]_2$.

The structural formulation of IV in Figure 2 can be seen to fall two electrons short of the inert gas configuration for each molybdenum atom. The sharp C_5H_5 proton resonance indicates this compound is diamagnetic, however.

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[17] M. L. H. Green and M. Cousins, *J. Chem. Soc.*, 1567 (1964).

CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS,
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The Crystal and Molecular Structure of Dichloro(1,10-phenanthroline)zinc

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Crystals of dichloro(1,10-phenanthroline)zinc are monoclinic with four molecules in a unit cell of dimensions $a = 9.73$, $b = 15.67$, $c = 7.97$ A, $\beta = 101° 5'$, space group $P2_1/n$. Three-dimensional data were used, and the structure was solved as a heavy-atom problem. The coordination about the zinc atom is distorted tetrahedral. The 1,10-phenanthroline molecule itself is essentially planar, and the zinc atom departs 0.13 A from this plane. The chlorine atoms are nearly equidistant from the zinc atom. The plane of the zinc and two chlorine atoms makes an angle of 79° with the plane of the 1,10-phenanthroline molecule.

Introduction

The electron paramagnetic resonance technique has provided considerable information about the bonding in paramagnetic transition element complexes.[1] Especially useful data have been obtained when the paramagnetic ion under investigation resides as a substitutional impurity in a diamagnetic lattice. This special utility is a consequence of the fact that magnetic dilution frequently permits the observation of ligand hyperfine structure which can, in turn, be related to bonding parameters. The paramagnetic copper(II) ion has been investigated in a variety of environments and in several instances crystals of the zinc compound have served as the diamagnetic host for these ions. Crystals of copper(II)-doped dichloro(1,10-phenanthroline)zinc (hereafter called $ZnCl_2 \cdot phen$) were obtained and preliminary paramagnetic resonance spectra revealed the presence of abundant hyperfine structure. In order to carry through an analysis of this hyperfine

[1] W. Low, *Solid State Phys. Suppl.*, **2**, 1 (1960).

structure, however, the crystal structure and molecular geometry were required. The present investigation was undertaken to provide this structural information.

Experimental Section

Crystals of $ZnCl_2 \cdot$phen doped with copper(II) were grown in a gelatin medium. Details of the method of preparation are described elsewhere.[2] Chemical analysis indicated that the copper to zinc ratio was 1:100. All calculations throughout this structure determination, however, were carried out ignoring the presence of the small amount of copper impurity.

Unit cell dimensions[3] were determined from precession photographs taken with Mo Kα (λ 0.7107 A) radiation. A summary of the crystal data is given in Table I. The systematic extinctions observed ($h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$) allowed the unambiguous assignment of the space group as $P2_1/n$. The density of $ZnCl_2 \cdot$phen determined by the sink–float method was found to be 1.74 g/cc which corresponds to four molecules per unit cell.

TABLE I

CRYSTAL DATA

$a = 9.73 \pm 0.01$ A	Space group $P2_1/n$
$b = 15.67 \pm 0.02$ A	$Z = 4$
$c = 7.97 \pm 0.01$ A	$\rho_o = 1.74$ g/cc
$\beta = 101° 5' \pm 10'$	$\rho_c = 1.76$ g/cc

Systematic extinctions
$0k0$ $k = 2n + 1$
$h0l$ $h + l = 2n + 1$

For the structure determination, a nearly cylindrical crystal 0.3 mm long with a diameter of 0.1 mm was mounted along the c axis: $hk0 \ldots hk4$ data were obtained on an integrating Weissenberg camera with Cu Kα (1.5418 A) radiation. Intensities of 623 reflections were determined on a densitometer comparator, and 867 reflections were estimated visually. The usual Lorentz and polarization corrections were applied, but no absorption corrections were made.

Determination and Refinement of the Structure

Two sets of approximate coordinates for zinc and chlorine atoms were determined from an analysis of the largest peaks in a three-dimensional Patterson function map. For each of these sets of coordinates, a Fourier synthesis was carried out based upon the observed magnitudes and calculated phases for structure factors which met the criterion that $|F_c| \geqq {}^1/_2 |F_o|$. One of these Fourier syntheses yielded approximate atomic coordinates for twelve carbon atoms and two nitrogen atoms while the other synthesis yielded nothing that appeared correct.

The structure obtained by the above analysis was refined by complete matrix least-squares methods using the coordinates of the 17 atoms, isotropic temperature factors, and individual level scale factors as variables. The quantity $\Sigma w(|F_o| - |F_c|)^2$ was minimized with the following weighting scheme: $w = 1$ for $|F_o| < 15$ and $w = 15/|F_o|$ for $|F_o| > 15$. Scattering factors employed were taken from the International Tables for X-ray Crystallography.[4] The agreement factor $R = \Sigma|\Delta F|/\Sigma|F_o|$ based upon observed data only decreased smoothly to 0.106.

Further refinement with anisotropic thermal variables was undertaken. The individual level scale factors were refined while holding the atom positions and temperature factors constant. The level scale factors were then held constant, and atomic positions and temperature factors were allowed to vary. The same form factors and weighting scheme as described above were used, and the R factor decreased to 0.066. A difference synthesis based upon the best atomic coordinates yielded no spurious peaks but indicated only that the form factor for the zinc atom had been slightly underweighted as the zinc(II) ion. In Table II the final positional parameters are given and the anisotropic thermal parameters are listed in Table III. Table IV lists the observed and calculated structure factors.

TABLE II

ATOMIC COORDINATES

Atom	X	Y	Z
Zn	0.54423 (12)[a]	0.27901 (6)	0.78268 (19)
Cl_1	0.50082 (27)	0.18598 (15)	0.57276 (42)
Cl_2	0.61011 (26)	0.22244 (14)	1.03912 (38)
N_1	0.6719 (7)	0.3726 (4)	0.7185 (11)
N_2	0.4218 (7)	0.3850 (4)	0.8051 (12)
C_1	0.7970 (9)	0.3638 (5)	0.6783 (15)
C_2	0.8713 (10)	0.4343 (6)	0.6303 (16)
C_3	0.8132 (9)	0.5136 (6)	0.6251 (15)
C_4	0.6802 (9)	0.5244 (5)	0.6691 (14)
C_5	0.6136 (11)	0.6049 (5)	0.6660 (15)
C_6	0.4879 (11)	0.6119 (5)	0.7143 (15)
C_7	0.4199 (9)	0.5383 (5)	0.7667 (14)
C_8	0.2909 (10)	0.5411 (6)	0.8247 (16)
C_9	0.2326 (10)	0.4687 (7)	0.8748 (16)
C_{10}	0.2985 (9)	0.3898 (6)	0.8620 (15)
C_{11}	0.4794 (9)	0.4583 (5)	0.7635 (14)
C_{12}	0.6163 (9)	0.4506 (5)	0.7168 (15)

[a] The numbers in parentheses are standard deviations in the last significant figures.

TABLE III

ANISOTROPIC THERMAL PARAMETERS[a]

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Zn	124 (1)[b]	29 (1)	164 (5)	−2 (1)	46 (2)	2 (1)
Cl_1	150 (3)	38 (1)	154 (10)	−3 (1)	31 (4)	−21 (2)
Cl_2	168 (3)	30 (1)	131 (10)	10 (1)	55 (4)	3 (2)
N_1	85 (8)	24 (2)	139 (26)	−2 (4)	34 (10)	−10 (6)
N_2	88 (8)	33 (3)	106 (27)	−11 (4)	20 (10)	−9 (6)
C_1	90 (10)	36 (4)	149 (35)	3 (5)	25 (13)	5 (8)
C_2	126 (12)	41 (4)	139 (35)	−4 (5)	39 (15)	14 (8)
C_3	105 (11)	38 (4)	115 (35)	−9 (5)	34 (14)	−10 (8)
C_4	119 (11)	26 (3)	131 (34)	−4 (5)	29 (14)	2 (6)
C_5	152 (13)	29 (3)	75 (36)	1 (5)	29 (15)	−7 (7)
C_6	170 (15)	25 (3)	96 (35)	0 (5)	29 (16)	−3 (7)
C_7	100 (11)	37 (4)	85 (34)	6 (5)	16 (13)	−12 (8)
C_8	112 (12)	44 (4)	152 (37)	11 (6)	30 (15)	−20 (9)
C_9	116 (12)	56 (5)	106 (37)	9 (6)	25 (15)	−25 (10)
C_{10}	100 (11)	46 (4)	93 (34)	7 (5)	26 (14)	0 (8)
C_{11}	93 (10)	28 (3)	133 (34)	4 (4)	21 (12)	−9 (7)
C_{12}	101 (10)	25 (3)	116 (34)	4 (4)	35 (13)	8 (7)

[a] The general anisotropic temperature factor has the form: $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. [b] The numbers in parentheses are standard deviations in the last significant figure.

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[2] G. F. Kokoszka, C. W. Reimann, and H. C. Allen, Jr., in preparation.

[3] The uncertainties quoted on the cell dimensions are estimates based on past experience with the camera and measuring device used. In the authors' opinion a conservative estimate of error will be obtained if these uncertainties are treated as standard deviations.

[4] "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 202–205.

TABLE IV

OBSERVED AND CALCULATED STRUCTURE FACTORS[a,b,c]

k	sF_o	F_c
	0,K,0	
2	451	-449
4	852	820
6	412	-386
8	96	138
10	321	264
12	812	-739
14	97*	80
16	281	-273
18	327	305
	1,K,0	
1	946	861
2	117	-107
3	242	273
4	46*	-16
5	446	-390
6	36*	28
7	254	-253
8	98	-135
9	674	637
10	96	107
11	711	-617
12	290	263
13	95*	13
14	195	195
15	217	-217
16	93*	-16
17	86*	-18
18	76*	14
19	188	155
	2,K,0	
0	1225	1142
1	943	-886
2	1544	-1499
3	1175	1073
4	542	470
5	881	-740
6	359	-285
7	115	-101
8	451	-367
9	135	-139
10	344	308
11	88	-134
12	246	-216
13	361	321
14	81*	82
15	250	-236
16	129	-132
17	252	228
18	232	209
19	132	-140
	3,K,0	
1	50*	-27
2	52*	10
3	165	109
4	58	-82
5	325	290
6	719	-596
7	565	-466
8	76*	36
9	607	531
10	150	-132
11	586	-512
12	112	114
13	457	415
14	87*	-70
15	84*	-106
16	89*	-6
17	80*	-8
	4,K,0	
0	317	294
1	862	-745
2	308	-261
3	817	718
4	59*	68
5	453	-415
6	390	346
7	78	119
8	142	-180
9	61*	68
10	128	136
11	94	-129
12	97*	-38
13	239	213
14	96	-109
15	303	-277
16	84*	44
17	258	208
	5,K,0	
1	70*	-58
2	71	-58
3	72	58
4	526	477
5	78*	-8
6	569	-516
7	281	-251
8	553	489
9	345	300
10	425	-383
11	363	-323
12	258	218
13	136	182
14	206	-250
	6,K,0	
0	137	134
1	329	-287
2	80*	11
3	307	233
4	145	-135
5	286	-238
6	267	243
7	91*	35
8	66*	-79
9	68*	86
10	53*	65
11	53*	-87
12	95*	53
13	92*	60
	7,K,0	
1	89	-119
2	297	-231
3	181	192
4	478	414
5	229	-191
6	134	-153
7	236	214
8	552	480
9	69*	-56
10	374	-343
11	94*	-10
12	238	227
	8,K,0	
0	95*	-64
1	214	-227
2	96	-3
3	136	117
4	97*	-30
5	131	126
6	97*	28
7	238	247
8	254	-214
9	94*	47
10	90*	-1
11	85*	-64
12	56*	70
	9,K,0	
1	97*	-74
2	97*	-68
3	291	246
4	52*	80
5	302	-250
6	54*	-54
7	205	178
8	198	184
9	146	-163
10	55*	-82
11	101	125
	10,K,0	
0	64*	80
1	91	-79
2	110	109
3	80*	88
4	107	-105
	0,K,1	
2	838	-766
3	351	333
4	471	433
5	207	-170
6	446	-421
7	65	-45
8	843	760
9	332	299
10	751	-706
11	326	-284
12	759	674
13	315	282
14	45*	-65
15	100*	-35
16	68*	67
17	89*	-12
18	35*	28
19	45*	53
	1,K,1	
0	806	-724
1	904	-832
2	338	296
3	317	268
4	483	-425
5	24*	1
6	523	457
7	67*	15
8	465	-446
9	112	101
10	85	91
11	111	-90
12	215	180
13	316	251
14	487	-437
16	192	213
17	62*	71
18	134	-168
19	63	-65
	2,K,1	
1	45	-85
2	152	110
3	824	803
4	444	466
5	926	-841
6	1051	-961
7	451	449
8	693	644
9	379	-326
10	734	-652
11	148	128
12	537	453
13	100	-103
14	287	-289
15	99*	27
16	66*	75
17	85*	-41
18	52*	63
19	41*	54
	3,K,1	
0	146	152
1	201	-197
2	91	103
3	147	129
4	462	-429
5	370	-313
6	488	432
7	480	-398
8	57*	-63
9	87	69
10	65*	65
11	96*	40
12	100	119
13	101*	6
14	174	-198
15	97*	-31
16	257	231
17	81*	-0
18	118	-136
	4,K,1	
1	372	-343
2	106	83
3	686	640
4	72*	10
5	993	-890
6	238	-193
7	927	848
8	39*	38
9	531	-470
10	272	-235
11	330	286
12	101	106
13	304	-282
14	98	-105
15	93	101
16	85*	-36
17	52*	-60
18	72	87
	5,K,1	
0	378	299
1	240	-211
2	456	416
3	147	134
4	281	-243
5	37*	-36
6	276	236
7	64*	-35
8	188	-161
9	69*	51
10	100*	-27
11	71*	-71
12	101*	-18
13	70*	-64
14	230	-238
15	86*	-18
16	188	174
	6,K,1	
1	227	172
2	123	108
3	450	429
4	312	-277
5	570	-516
6	355	306
7	506	490
8	222	-172
9	226	-222
10	176	168
11	100	70
12	69*	-61
13	161	-186
14	86	109
	7,K,1	
0	212	-164
1	95*	-6
2	253	225
3	96*	-24
4	353	-320
5	54*	43
6	100	109
7	175	-160
8	203	-191
9	101*	-36
10	99*	6
11	95*	33
12	64*	65
13	83*	15
14	197	-207
	8,K,1	
1	110	-104
2	175	184
3	175	150
4	337	-315
5	176	-179
6	78*	-37
7	100*	-15
8	355	-324
9	95	-75
10	129	138
	9,K,1	
0	123	-88
1	265	219
2	122	97
3	133	-107
4	98	-66
5	97*	8
6	164	166
7	260	-208
8	88*	-32
9	83*	29
10	77*	8
11	69	68
12	41*	65
	10,K,1	
1	91*	-10
2	90	74
3	62*	32
4	67*	-60
5	84*	-21
6	114	121
7	76*	35
8	50*	-63
9	35*	17
10	54	66
	11,K,1	
1	73	89
2	71	-49
3	121	-133
4	67*	11
5	89	102
	-1,K,1	
2	35*	22
3	1417	1383
4	535	-502
5	689	-637
6	642	541
7	36*	-15
8	205	-172
9	78	67
10	120	108
11	314	-276
12	95	95
13	331	277
14	124	-126
15	318	-279
16	236	236
17	218	245
18	124	-147
19	169	-191
	-2,K,1	
1	260	-251
2	290	268
3	144	114
4	248	-184
5	78	-35
6	847	-752
7	360	-337
8	184	177
9	436	415
10	274	-245
11	462	-412
12	274	253
13	266	221
14	176	-162
15	158	-143
16	95*	-18
17	39*	-35
18	76	94
19	90	96
	-3,K,1	
0	1288	1223
1	1362	-1319
2	786	-724
3	1088	990
4	515	492
5	781	-733
6	207	-161
7	165	-101
8	364	-315
9	60*	58
10	201	178
11	233	-213
12	70*	-62
13	268	237
14	101	106
15	341	-321
16	65*	-55
17	290	268
18	113	133
19	86	-127
	-4,K,1	
1	533	-472
2	177	151
3	64	9
4	96	101
5	32*	27
6	131	-114
7	179	-145
8	208	190
9	348	276
10	231	-229
11	219	-186
12	100	73
13	287	302
14	158	-165
15	95*	-3
16	88*	-21
17	42*	-51
18	45*	59
19	65	106
	-5,K,1	
0	448	487
1	285	-277
2	1384	-1307
3	268	249
4	713	643
5	113	-79
6	204	-185
7	87*	-24
8	204	-187
9	190	191
10	241	228
11	100*	-17
12	101	-75
13	71*	75
14	290	282
15	49*	-52
16	178	-197
17	69*	28
18	148	153
	-6,K,1	
1	140	-125
2	82*	33
3	84	74
4	72*	72
5	217	205
6	158	-162
7	211	-180
8	61*	31
9	359	303
10	226	-176
11	227	-213
12	200	228
13	272	254
	-7,K,1	
0	786	688
1	203	195
2	520	-480
3	161	-181
4	267	227
5	96*	-37
6	98	74
7	447	-401
8	124	108
9	101	-92
10	225	188
11	69*	54
12	177	-162
13	68*	-60
14	122	118
15	70	67
16	88	-88
	-8,K,1	
1	108	76
2	140	136
3	173	-176
4	174	-173
5	55*	21
6	249	-200
7	268	-230
8	142	-120
9	356	318
10	60*	37
11	288	-287
12	84*	23
13	136	135
14	41*	-35
15	50	-68
	-9,K,1	
0	227	184
1	227	188
2	176	-134
3	101	-80
4	101*	35
5	173	113
6	62*	-41
7	68*	-69
8	94	-101
9	89*	47
10	84	81
11	77	76
12	69*	-35
13	73	-76
	-10,K,1	
1	96*	15
2	96*	27
3	95*	6
4	162	-128
5	91	85
6	234	187
7	103	-97
8	126	-113
9	128	146
10	94	103
11	94	-99
	-11,K,1	
0	82	71
3	80	-83
	0,K,2	
0	1328	-1532
1	163	-155
2	575	-529
3	278	241
4	44	5
5	235	192
6	396	377
7	453	-423
8	446	-359
9	263	211
10	111	120
11	334	303
12	505	419
13	91	91
14	91*	-36
15	169	153
17	123	-123
18	152	-152
19	53	64
16	171	172
	1,K,2	
1	2211	-2106
2	1356	1220
3	432	369
4	824	-744
5	601	-558
6	765	699
7	587	530
8	681	-603
9	646	-601
10	581	469
11	611	491
12	343	-272
13	170	154
14	91*	35
15	179	182
16	146	-140
17	34*	-62
18	29*	49
19	22*	-30
	2,K,2	
0	686	-710
1	20*	32
2	240	199
3	50*	-23
4	235	-224
5	247	221
6	592	535
7	310	-249
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4	88	-92

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[a] All tabulated structure factors have been multiplied by 10. [b] Asterisks indicate that the observed intensities for these reflections were less than the threshold for measurement. The F_o values for these reflections were determined by assuming an intensity equal to this threshold value. [c] The scale factors for the five observed levels are as follows: *hk*0, $s = 2.4793$; *hk*1, $s = 2.48987$; *hk*2, $s = 2.74754$; *hk*3, $s = 2.39455$; *hk*4, $s = 2.21731$.

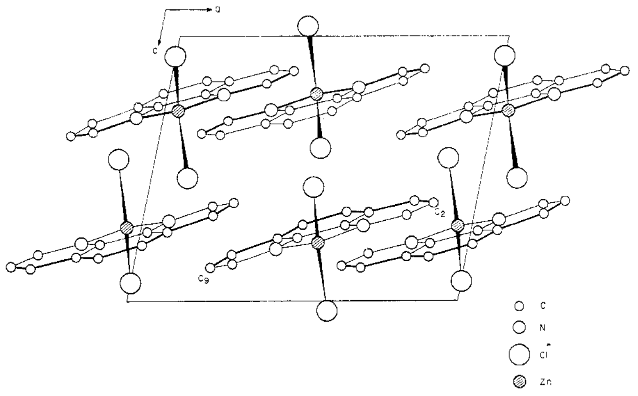

Figure 1.—The structure projected along the *b* axis. Atoms C_2 and C_9 are numbered according to the scheme shown in Figure 2.

All computer computations on this structure were carried out using the X-ray 63 system of programs developed at the University of Maryland and at the University of Washington.

Description of the Structure

There are no crystallographic restrictions on the symmetry of the $ZnCl_2$·phen molecule since all atoms lie in general positions. The $ZnCl_2$·phen structure consists of discrete $ZnCl_2$·phen molecules packed into the unit cell as shown in the projection along the *b* axis in Figure 1. The long axis (C_9–C_2) of the phenanthroline ring system makes an angle of 4.5° with the *ac* plane. The phenanthroline molecule itself was found to be very nearly planar. The least-squares plane and individual atom deviations from this plane are given in Table V. The plane of the phenanthroline molecule is inclined 8.1° to the *b* axis. This projection along the *b* axis shows that $ZnCl_2$ is chelated by the bidentate phenanthroline molecule and that the coordination of the nitrogen and chlorine atoms about the zinc atom is essentially tetrahedral. The highest symmetry possible for such an atomic arrangement is C_{2v} and the actual molecular geometry will be described in terms of the degree of departure from the elements of C_{2v} symmetry. If C_{2v} symmetry obtained, the zinc atom would lie on a twofold axis which would be the line of intersection of the plane of the phenanthroline molecule and a plane perpendicular to it which would be defined by the zinc and chlorine atoms. Figure 2 shows the detailed geometry of the $ZnCl_2$·phen molecule and demonstrates that none of the requirements of C_{2v} is strictly met. The zinc atom departs from the plane of the phenanthroline molecule by 0.13 A, which is about three times as large as the mean deviation of the carbon and nitrogen atoms from the plane.

Table V

Deviations of the Ring Atoms from the Least-Squares Plane of the Phenanthroline Ring[a]

Atom	Dev, A	Atom	Dev, A
N_1	0.019	C_6	0.024
N_2	0.070	C_7	0.009
C_1	−0.018	C_8	−0.047
C_2	−0.048	C_9	−0.077
C_3	−0.033	C_{10}	−0.000
C_4	0.006	C_{11}	0.048
C_5	0.037	C_{12}	0.008

[a] The mean standard deviation of the atoms defining the plane from the plane is 0.041. Equation of plane in direct space: $PX + QY + RZ = S$, where $P = 2.7452$, $Q = 2.2160$, $R = 6.9921$, $S = 7.7141$.

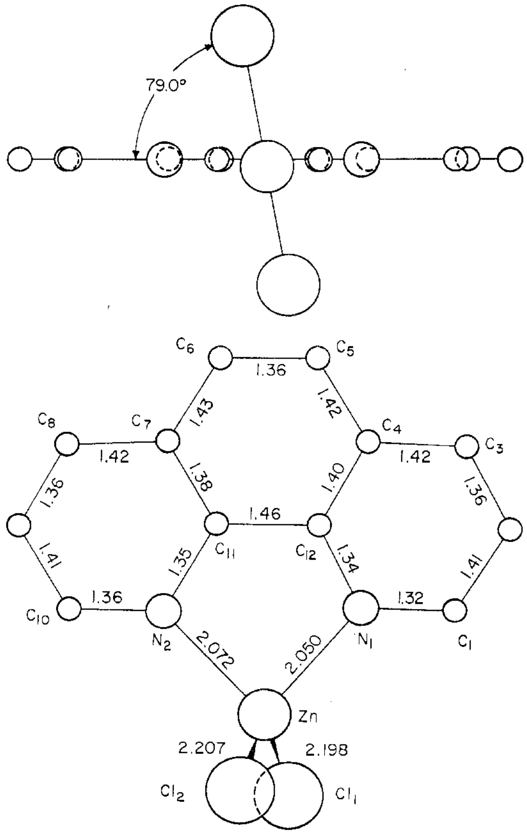

Figure 2.—Molecular structure with the plane of the 1,10-phenanthroline molecule perpendicular to page (top) and with the 1,10-phenanthroline molecule parallel to page (bottom). Average standard deviations are as follows: Zn–Cl, ±0.003; Zn–N, ±0.007; C–C, ±0.01; C–N, ±0.01.

The zinc atom also lies 0.02 ± 0.01 A closer to N_1 than to N_2 as well as 0.010 ± 0.004 A closer to Cl_1 than to Cl_2. Moreover, the plane defined by the zinc and chlorine atoms makes an angle of 11.0° with the normal to the phenanthroline ring. This angle corresponds very nearly to an 11.0° rotation of the $ZnCl_1Cl_2$ plane around the would-be twofold axis of the molecule. Remaining details of the structure can be visualized with the aid of Figure 2 and with Table VI, which lists principal bond angles and standard deviations.

Discussion

The $ZnCl_2$·phen molecule is rather distorted compared with the $ZnCl_2 \cdot 2NH_3$[5] molecule. The latter molecule has also been shown to consist of zinc atoms with a tetrahedral array of chlorine and nitrogen atoms. The bond angles in $ZnCl_2 \cdot 2NH_3$, however, were found to correspond to tetrahedral angles which stand in contrast to those observed for $ZnCl_2$·phen, in which only N_1–Zn–Cl_1 and N_2–Zn–Cl_2 are approximately tetrahedral. The major difference between the bond angles in these two structures is undoubtedly a consequence

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(5) C. H. MacGillavry and J. M. Bijvoet, *Z. Krist.*, **94**, 249 (1936).

TABLE VI

BOND ANGLES

Bonded atoms	Bond angle, deg	Bonded atoms	Bond angle, deg
Cl_1–Zn–Cl_2	114.7 ± 0.1	C_5–C_4–C_{12}	121.0 ± 0.9
N_1–Zn–Cl_1	108.7 ± 0.3	C_4–C_5–C_6	120.1 ± 0.9
N_1–Zn–Cl_2	115.9 ± 0.2	C_5–C_6–C_7	120.7 ± 0.8
N_2–Zn–Cl_1	124.6 ± 0.2	C_6–C_7–C_{11}	120.4 ± 0.9
N_2–Zn–Cl_2	108.2 ± 0.3	C_8–C_7–C_{11}	115.7 ± 0.8
N_1–Zn–N_2	80.4 ± 0.3	C_7–C_8–C_9	120.9 ± 0.9
C_{12}–N_1–Zn	113.2 ± 0.6	C_8–C_9–C_{10}	119.3 ± 1.0
C_{11}–N_2–Zn	112.9 ± 0.6	C_9–C_{10}–N_2	121.0 ± 0.9
C_{12}–N_1–C_1	118.8 ± 0.7	C_{10}–N_2–C_{11}	118.0 ± 0.7
N_1–C_1–C_2	121.8 ± 0.8	N_2–C_{11}–C_7	124.9 ± 0.9
C_1–C_2–C_3	119.4 ± 1.0	C_7–C_{11}–C_{12}	119.1 ± 0.8
C_2–C_3–C_4	119.7 ± 0.9	C_{11}–C_{12}–C_4	118.5 ± 0.7
C_3–C_4–C_{12}	116.4 ± 0.8	N_1–C_{12}–C_4	124.0 ± 0.9

of the fact that in $ZnCl_2 \cdot$phen the N_1 and N_2 atoms are separated by 2.67 A and fixed in a relatively rigid ring system. Thus an N_1–Zn–N_2 tetrahedral angle would require Zn–N bond distances of 1.64 A, which would represent a drastic reduction from the Zn–N bond distance of 2.04 A observed in $ZnCl_2 \cdot 2NH_3$, in which the N–N distance is not fixed.

The geometry of the phenanthroline molecule is similar to the geometry of the phenanthrene molecule determined by Trotter.[6] The latter molecule differs from the former by the replacement of nitrogen atoms by carbon atoms. In the phenanthroline molecule, it was observed that bond C_{11}–C_{12} is longer than bond C_5–C_6 while bonds C_7–C_8 and C_3–C_4 are longer than bonds C_{10}–N_2 and C_1–N_1, respectively. The corresponding bonds in phenanthrene were observed to be in the same order.

The interpretation of the paramagnetic resonance and electronic spectral data on copper(II)-doped dichloro-(1,10-phenanthroline)zinc is in progress. The hyperfine structure in the paramagnetic resonance spectrum has been shown to arise from a coupling to both the nitrogen and the chlorine nuclei. The extent of 4p admixture into the primarily 3d copper(II) orbitals, the bonding parameters, and all supporting spectroscopic data will be reported elsewhere.[2]

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(6) J. Trotter, *Acta Cryst.*, **16**, 605 (1963).

CONTRIBUTION FROM THE LAWRENCE RADIATION LABORATORY AND DEPARTMENT OF CHEMISTRY,
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The Crystal Structure of $(B_9C_2H_{11})Re(CO)_3Cs$[1]

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The crystal structure of the cesium salt of π-(1)-2,3-dicarbollylrhenium tricarbonyl, $(B_9C_2H_{11})Re(CO)_3Cs$, has been determined from an X-ray diffraction study of a single crystal specimen. The monoclinic cell, space group $P2_1/c$, with a = 11.435 A, b = 9.516 A, c = 12.730 A, and β = 92.87°, contains four formula units. The structure was determined by straightforward crystallographic techniques, and the atomic parameters of all but the hydrogen atoms were refined by a full-matrix least-squares procedure. The rhenium atom occupies an apex position of an icosahedron containing boron and carbon, and on the other side occupies the apex of a trigonal pyramid whose base is three carbonyls. In the icosahedron the two carbon atoms are adjacent to each other and to the rhenium.

Introduction

π-(1)-2,3-Dicarbollylrhenium tricarbonyl was synthesized by Hawthorne and Andrews.[2] The structure work was undertaken to reaffirm the results of our previous study on the dicarbollyliron structure[3] in $C_5H_5FeB_9C_2H_{11}$. In that study there was considerable thermal motion of the cyclopentadienyl ring, and to a lesser extent of the dicarbollyl portion, $B_9C_2H_{11}$. This thermal motion, evidenced by large thermal parameters, does not permit the calculation of accurate bond distances. The $B_9C_2H_{11}Re(CO)_3Cs$ crystal does not suffer these thermal effects as badly, and the resulting structure is we believe a more accurate description of the dicarbollyl geometry.

The present work confirms the geometry of this compound postulated by Hawthorne and Andrews.[2]

Experimental Section

The crystals were sent to us by Dr. M. F. Hawthorne of the Riverside campus of the University of California. A small white crystal, ~0.25 mm long and ~0.08 × ~0.08 mm in cross section, was glued to the end of a Pyrex glass fiber. The long direction of the crystal was parallel to the fiber and is the direction of the b axis. A General Electric XRD-5 X-ray diffraction setup equipped with a Molybdenum X-ray tube (Mo $K\alpha_1$, λ 0.70926 A), a scintillation counter, a pulse height discriminator, and a quarter-circle Eulerian-cradle type goniostat was used. The X-ray tube was operated at 50 kv and 20 ma, and a Zr filter was used on the receiving slit. The crystal was oriented such that the b axis was parallel to the ϕ axis. The cell dimensions were obtained from carefully measured 2θ (θ is the Bragg angle) values of the $0k0$, $h00$, and $00l$ reflections whose $\alpha1$ and $\alpha2$ components were resolved. The β angle was measured directly from the angle between the $h00$ and $00l$ sets of reflections.

A total of 2452 independent intensities were measured, of which 138 were recorded as zero. A stationary crystal, station-

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(1) Work done under the auspices of the U. S. Atomic Energy Commission.

(2) M. F. Hawthorne and T. D. Andrews, *J. Am. Chem. Soc.*, **87**, 2496 (1965).

(3) A. Zalkin, D. H. Templeton, and T. E. Hopkins, *ibid.*, **87**, 3988 (1965).