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The Crystal Structure of a Molybdenum(III) Hexaisothiocyanate: $K_3Mo(NCS)_6 \cdot H_2O \cdot CH_3COOH$[1]

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The crystal structure of $K_3Mo(NCS)_6 \cdot H_2O \cdot CH_3COOH$ has been determined. The substance crystallizes in the orthorhombic space group $Pm2_1n$ with $a = 13.547$ (2), $b = 8.568$ (2), and $c = 9.660$ (1) A. With $Z = 2$ the $D_x = 1.89$, while $D_M = 1.85$ g/cm^3. A total of 884 photographic, visually estimated intensities was collected. The data were refined by least-squares methods to a conventional R factor of 6.8%. The molybdenum coordination is sixfold with the thiocyanate groups bonded *via* nitrogen; the average Mo–N distance is 2.088 ± 0.019 A. Each potassium ion is surrounded by six sulfur atoms in a trigonal prism. In half of the prisms a disordered potassium ion is replaced half of the time by a water molecule; this causes the prism to expand, distorting the octahedron so that four MoNC angles deviate from linearity. Six sulfur prisms form a cavity in which the acetic acid molecule is located and bonded by a hydrogen bond to the water molecule.

Introduction

A knowledge of whether molybdenum(III) bonds to the ambidentate thiocyanate ligand through the nitrogen or sulfur end is a good criterion for placing this ion into one of the two acceptor classes proposed by Ahrland, Chatt, and Davies.[2] Similarly, the NCS^- ligand is an ideal species with which to measure the ion's "hard–soft" character defined by Pearson.[3] The nitrogen end is "harder" than the sulfur end and tends to bond to a "hard" metal ion. Borderline "hard–soft" character for Mo(III) might result in bridging through both ends of the thiocyanate ion (Mo–NCS–Mo).

The incomplete X-ray work of Zhdanov[4] indicated sulfur bonding in $K_3Cr(NCS)_6 \cdot 4H_2O$, a compound isomorphous with the Mo(III) tetrahydrate complex. However, the spectroscopic data of Lewis, Nyholm, and Smith[5] pointed to nitrogen bonding in the molybdenum complex. Because the tetrahydrate of Mo(III) forms twinned crystals that are unstable in air, we have studied a related compound, $K_3Mo(NCS)_6 \cdot H_2O \cdot CH_3COOH$, which is one in the series $(K,NH_4)_3Mo(NCS)_6 \cdot H_2O \cdot HA$ where HA = HCl, KHC_2O_4, C_2H_5OH, C_3H_7OH, or CH_3COOH. The presence in all of these Mo(III) complexes of the singlet water molecule led Lewis and co-workers to reinvestigate whether the complex ion in the hydrated salts is six- or seven-coordinated, $Mo(NCS)_6{}^{3-}$ or $Mo(NCS)_6H_2O^{3-}$, a question first inconclusively debated 60 years ago by Rosenheim and Maas.[6]

Experimental Section

Preparation of $K_3Mo(NCS)_6 \cdot HO_2 \cdot CH_3COOH$ Crystals.—The compound was prepared by adding a half-volume of 2 *N* acetic acid to one volume of a concentrated aqueous solution of $K_3Mo(NCS)_6 \cdot 4H_2O$; the tetrahydrate had been synthesized by the electrolytic procedure given by Maas and Sand,[7] using in the cathode compartment only half of the hydrochloric acid concentration suggested by the authors. After standing at 10° for 24 hr, the solution yielded yellow, transparent, rodlike crystals which were recrystallized twice from 2 *N* acetic acid. The crystals underwent no color change in air. *Anal.* Calcd for $K_3Mo(NCS)_6 \cdot H_2O \cdot CH_3COOH$: Mo, 15.00; N, 13.14; C, 15.02; H, 0.945. Found: Mo, 15.15; N, 12.98; C, 15.22; H, 1.12.

X-Ray Examination.—Weissenberg photographs with copper Kα radiation (λ 1.542 A) revealed that the lattice has Laue symmetry mmm; the systematic extinctions are $h + k = 2n + 1$ for $hk0$ reflections, showing the space group[8] is either $Pm2_1n$ (no. 31, alternatively $P2_1mn$) or Pmmn (no. 59). Approximate cell dimensions obtained from the photographs were refined[9] by least squares using 38 equally weighted powder diffraction maxima obtained with a Norelco powder diffractometer. The refined dimensions are $a = 13.547 \pm 0.002$ A, $b = 8.568 \pm 0.002$ A, and $c = 9.660 \pm 0.001$ A. Assuming two formula units per cell, the calculated density is 1.89 g/cm^3; the density measured by pycnometer is 1.85 g/cm^3.

Optical Examination.—The four crystal faces parallel to the rod axis b were found to be $\{101\}$; at the ends of the rods the faces are $\{110\}$. The crystals are biaxial negative, with n_α, n_β, and n_γ coincident with c, a, and b, respectively. There was no evidence of macroscopic twinning in the crystals used for data collection.

X-Ray Data Collection.—A single crystal was ground to a sphere of 0.229-mm diameter. With a precession camera and molybdenum Kα radiation (λ 0.7107 A) 887 nonunique intensity data for the hkL (L = 0–4) and hKl (K = 0–4) reflections were recorded on Ilford Industrial G film. A series of six exposures was made of each level, the maximum exposure being 60 hr. From another crystal measuring $0.120 \times 0.093 \times 0.095$ mm^3 an additional 431 Hkl (H = 0–4) reflections were collected with a Weissenberg camera and copper Kα radiation. By the two methods a total of 884 visually estimated independent reflections of measurable intensity were gathered at room temperature.

Following the method of Simpson[10] the standard deviation $\sigma(|F_o|^2)$ of each intensity reading was estimated from the precision of the film-scaling factors and then correlated with experimental parameters such as film number, $(\sin^2 \theta)/\lambda^2$, and raw

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(2) S. Ahrland, J. Chatt, and N. Davies, *Quart. Rev.* (London), **12**, 262 (1958).

(3) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

(4) G. S. Zhdanov, Z. V. Zvonkova, and V. P. Glushkova, *Zh. Fiz. Khim.*, **27**, 106 (1953).

(5) J. Lewis, R. Nyholm, and P. Smith, *J. Chem. Soc.*, 4590 (1961).

(6) A. Rosenheim, *Ber.*, **42**, 2295 (1909).

(7) J. Maas and J. Sand, *ibid.*, **41**, 1506 (1908).

(8) "International Tables for X-ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1965.

(9) C. B. Shoemaker, "LSCELP, Least-Squares Cell Parameters," Massachusetts Institute of Technology, 1963.

(10) P. G. Simpson, Ph.D. Thesis, Harvard University, 1963, Chapter 5.

intensity. Through the conversion $\sigma(|F_o|) = \sigma(|F_o|^2)/2|F_o|$ this error analysis of the intensity readings made possible the assignment of weights $1/\sigma^2(|F_o|)$ in the subsequent least-squares refinement of the structure.

Lorentz-polarization corrections were applied to all data. Absorption corrections for the precession data were neglected because μR (μ, absorption coefficient; R, crystal radius) is only 0.19 and therefore the absorption changes little with θ. The μR for the Weissenberg data is larger (0.93), the absorption changing 24% as θ goes from 0 to 90°; hence, absorption corrections were applied to the Weissenberg data.

Solution and Refinement of the Structure

A three-dimensional Patterson function[11] showed the Mo–Mo interaction near u, v, w coordinates $^1/_2$, $^1/_2$, $^1/_2$. Two other prominent Patterson peaks near 0, $^1/_2$, $^1/_5$ and $^1/_4$, $^1/_4$, $^1/_4$ were assumed to be overlapping Mo–S interactions; this allowed the thiocyanate groups to be arranged octahedrally around the molybdenum ion and linked to it through the nitrogen end. The only Mo–K interaction found was near $^1/_5$, $^1/_2$, 0. The second Mo–K peak, expected to fall on 0, v, w, was not seen. On the basis of this interpretation, the space group of the crystal is noncentrosymmetric, $Pm2_1n$.

For the partial structure $K_2Mo(NCS)_6^-$ thus found, structure factor calculations in space group Pmnn gave a reliability factor $R = \Sigma||F_o| - k|F_c||/\Sigma|F_o|$ equal to 42%. Several three-dimensional Fourier syntheses, first in Pmnn, later in $Pm2_1n$, failed to show in the twofold positions (0, y, z of the mirror section) the water oxygen atom, the remaining potassium ion, or a complete acetic acid skeleton. For this reason and because two unidentified peaks appeared above the mirror section in fourfold positions, static disorder was suspected; therefore, the stronger peak was assigned as half of a potassium ion. Following least-squares refinement[12] of the parameters of the $K_3Mo(NCS)_6$ unit, normal and difference Fourier syntheses now revealed the remaining atoms and showed that only the carbon atoms of the acid molecule were lying in the mirror section, the two oxygen atoms being on opposite sides of this section. Thus the acetic acid molecule has an imposed mirror symmetry which makes the two C–O bonds equivalent. No attempt was made to locate the hydrogen atoms.

In the full-matrix refinement the quantity minimized was $\Sigma w||F_o| - |F_c||^2$, where w is a weighting term equal to the reciprocal of the variance of each $|F_o|$ as estimated from the precision of film-scaling factors. Scattering curves were taken from the "International Tables for X-ray Crystallography," the curve for singly ionized molybdenum being used. Potassium K(2) and the water oxygen O(2) were refined as half-atoms. With isotropic temperature factor coefficients the refinement proceeded smoothly through four cycles, giving final parameter shifts which were less than $0.6\sigma_i$, where σ_i is the standard error estimated from the least-squares inverse matrix. The reliability factors R and wR stood at 9.8 and 12.3% for all 884 individually weighted reflections. The weighted factor $wR = (\Sigma w||F_o| - k|F_c||^2/\Sigma w|F_o|^2)^{1/2}$.

Anisotropic temperature factor coefficients were assigned to all atoms and the refinement was continued. Each cycle had to be divided into two parts so that the positional and thermal parameters were varied separately. For the last two cycles the scattering curve of the molybdenum ion was corrected for the real part of the dispersion effect. From the anisotropic refinement with all observed reflections the reliability factors R and wR were 6.8 and 8.2%, and the errors in an observation of unit weight were 1.43 and 1.48 for the two parts of the last cycle. A final difference electron density map did not show any abnormalities. Observed and calculated structure factors are listed in Table I. The 400 unobserved reflections were not used in the refinement and are not listed. There were no significant discrepancies between calculated values for these reflections and their threshold values. Positional and thermal parameters are shown in Table II together with the standard errors resulting from the least-squares procedure. The thermal parameters were not used for any further analysis of thermal motion in the crystal. Important interatomic distances and angles are given in Table III.

Description and Discussion of the Structure

In this hydrated isothiocyanate complex the water molecule is not coordinated to the molybdenum ion. The ion bonds octahedrally to the nitrogen end of the thiocyanate group rather than to the sulfur end (Figure 1). These findings agree with the spectroscopic and magnetic data of Lewis, Nyholm, and Smith.[5] In the terminology of Pearson,[3] the preference of Mo(III) for the "hard" nitrogen end classifies this ion as a "hard" acid. The ion falls into the group of class a acceptor ions defined by Ahrland, Chatt, and Davies.[2]

The weighted average of the Mo–N distances and the standard deviation of the mean are 2.088 and 0.019 A, respectively. This Mo–N distance is within experimental error of the 2.10-A value obtained from the atomic radii of Slater.[13] We assume that for this system d_π–p_π bonding is unlikely and that the thiocyanate nitrogen atom is sp hybridized (see below). While comparable Mo–N (sp) distances are not known to us, the Mo–N(sp^3) distances in $(dien)MoO_3$[14] and *cis*-Mo(dien)$(CO)_3$[15] are 2.32 ± 0.01 A. A comparison with these distances may be made through the fact that in $MCr(NH_3)(NCS)_4$[16] (M = NH_4^+, pyH^+, choline) the Cr–N(NH_3) distances are longer than the Cr–N(NCS) distances by about 0.18 A, giving $2.09 + 0.18 = 2.27$ A as the expected Mo–N(sp^3) distance. The further lengthening of the Mo–N(dien) bonds

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(11) W. G. Sly, D. P. Shoemaker, and J. H. van den Hende, "A Two- and Three-Dimensional Crystallographic Fourier Summation Program for the IBM 709/7090 Computer," Massachusetts Institute of Technology, Esso Research and Engineering Co., 1962.

(12) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least-Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, 1962.

(13) J. C. Slater, *J. Chem. Phys.*, **41**, 3199 (1964).

(14) F. A. Cotton and R. C. Elder, *Inorg. Chem.*, **3**, 397 (1964).

(15) F. A. Cotton and R. M. Wing, *ibid.*, **4**, 314 (1965).

(16) Y. Takeuchi and Y. Saito, *Bull. Chem. Soc. Japan*, **30**, 319 (1957).

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS (×10) FOR $K_3Mo(NCS)_6 \cdot H_2O \cdot CH_3COOH$[a]

H	K	L	F_o	kF_c
2	0	0	479	394
4	0	0	2031	2139
6	0	0	550	495
8	0	0	1713	1685
10	0	0	946	914
12	0	0	801	828
14	0	0	368	324
16	0	0	464	466
18	0	0	368	362
1	1	0	466	460
3	1	0	793	730
5	1	0	712	615
7	1	0	674	605
9	1	0	299	298
11	1	0	515	511
13	1	0	341	357
15	1	0	159	188
17	1	0	279	260
0	2	0	976	973
2	2	0	1667	1820
4	2	0	210	175
6	2	0	1277	1287
8	2	0	429	424
10	2	0	1225	1189
14	2	0	572	550
16	2	0	182	154
18	2	0	302	258
1	3	0	645	544
3	3	0	961	962
5	3	0	365	331
7	3	0	487	449
9	3	0	251	218
11	3	0	243	251
13	3	0	274	262
15	3	0	284	275
17	3	0	218	216
0	4	0	1466	1610
2	4	0	438	398
4	4	0	1633	1747
6	4	0	320	314
8	4	0	991	973
10	4	0	280	286
12	4	0	454	452
14	4	0	339	322
16	4	0	376	324
3	5	0	475	488
5	5	0	675	705
7	5	0	554	589
9	5	0	253	220
11	5	0	275	231
13	5	0	315	340
15	5	0	150	155
17	5	0	169	157
0	6	0	433	413
2	6	0	899	1019
4	6	0	410	386
6	6	0	1019	1065
8	6	0	237	236
10	6	0	540	559
12	6	0	353	374
14	6	0	401	393
16	6	0	210	183
1	7	0	168	180
3	7	0	150	117
5	7	0	221	251
7	7	0	223	153
11	7	0	203	189
15	7	0	140	139
0	8	0	617	596
2	8	0	313	290
4	8	0	583	602
6	8	0	161	130
8	8	0	475	461
10	8	0	160	171
12	8	0	313	292
14	8	0	151	143
1	9	0	300	313
3	9	0	275	268
5	9	0	293	282
7	9	0	226	180
9	9	0	423	388
0	10	0	162	160
2	10	0	482	492
4	10	0	158	160
6	10	0	354	291
8	10	0	258	248
10	10	0	334	288
1	11	0	241	250
5	11	0	190	169
7	11	0	157	158
2	0	1	112	101
3	0	1	613	594
5	0	1	1667	1704
7	0	1	513	522
9	0	1	678	737
11	0	1	494	522
13	0	1	270	279
15	0	1	336	354
17	0	1	222	208
0	1	1	545	534
1	1	1	87	88
2	1	1	1026	1011
3	1	1	539	479
4	1	1	576	514
5	1	1	365	377
6	1	1	406	396
7	1	1	155	165
8	1	1	786	828
9	1	1	309	312
10	1	1	271	271
11	1	1	176	179
12	1	1	320	325
13	1	1	224	215
16	1	1	255	237
0	2	1	460	419
1	2	1	629	644
3	2	1	563	576
4	2	1	587	541
5	2	1	1189	1157
6	2	1	152	156
8	2	1	140	135
9	2	1	589	616
10	2	1	173	200
11	2	1	297	292
13	2	1	363	352
15	2	1	279	258
0	3	1	939	956
1	3	1	515	495
2	3	1	1082	1119
4	3	1	221	175
5	3	1	176	189
6	3	1	334	305
8	3	1	561	562
9	3	1	405	394
10	3	1	292	276
12	3	1	347	369
14	3	1	215	211
16	3	1	269	228
1	4	1	708	742
2	4	1	250	240
3	4	1	857	908
4	4	1	136	126
5	4	1	892	949
6	4	1	481	448
7	4	1	373	393
8	4	1	187	198
9	4	1	456	456
10	4	1	136	141
11	4	1	421	420
12	4	1	169	143
13	4	1	360	358
15	4	1	321	357
0	5	1	596	561
1	5	1	160	127
2	5	1	634	634
3	5	1	418	425
4	5	1	511	516
6	5	1	495	532
7	5	1	283	276
8	5	1	394	379
10	5	1	321	315
11	5	1	168	194
12	5	1	390	389
14	5	1	282	255
16	5	1	217	197
0	6	1	508	526
1	6	1	505	518
2	6	1	156	100
3	6	1	572	601
4	6	1	317	341
5	6	1	660	721
7	6	1	431	467
8	6	1	297	335
9	6	1	361	352
11	6	1	343	309
12	6	1	205	211
13	6	1	322	335
15	6	1	204	218
0	7	1	480	456
1	7	1	132	131
2	7	1	316	303
4	7	1	323	333
5	7	1	285	313
6	7	1	332	323
8	7	1	233	216
10	7	1	230	202
12	7	1	191	204
0	8	1	171	97
1	8	1	311	325
2	8	1	295	316
3	8	1	379	384
5	8	1	254	239
7	8	1	331	340
9	8	1	268	245
10	8	1	221	214
11	8	1	222	217
0	9	1	386	383
1	9	1	149	129
2	9	1	298	278
3	9	1	196	204
4	9	1	323	310
5	9	1	188	128
6	9	1	268	212
7	9	1	174	195
8	9	1	283	250
10	9	1	304	279
0	10	1	301	296
1	10	1	290	304
3	10	1	268	276
4	10	1	204	197
7	10	1	177	254
0	11	1	300	206
0	0	2	678	657
1	0	2	86	74
2	0	2	1194	1254
3	0	2	135	115
4	0	2	516	474
6	0	2	610	632
8	0	2	125	112
10	0	2	909	949
12	0	2	221	713
14	0	2	483	484
16	0	2	183	164
0	1	2	120	101
1	1	2	1050	1055
2	1	2	308	294
3	1	2	2050	2094
4	1	2	768	727
5	1	2	772	753
7	1	2	1055	1055
8	1	2	294	261
9	1	2	464	452
11	1	2	654	680
12	1	2	176	173
13	1	2	535	534
15	1	2	363	372
17	1	2	329	306
0	2	2	2003	2359
1	2	2	387	346
2	2	2	992	1006
3	2	2	447	445
4	2	2	1038	1019
5	2	2	239	246
6	2	2	281	242
8	2	2	744	736
10	2	2	183	162
12	2	2	297	284
16	2	2	242	225
0	3	2	736	695
1	3	2	587	588
2	3	2	179	186
3	3	2	1054	1077
4	3	2	145	78
5	3	2	1019	994
6	3	2	153	132
7	3	2	987	1011
8	3	2	355	342
9	3	2	360	356
10	3	2	173	136
11	3	2	528	530
13	3	2	451	444
15	3	2	219	200
17	3	2	271	285
2	4	2	618	653
4	4	2	386	315
5	4	2	306	294
6	4	2	792	804
8	4	2	256	238
10	4	2	580	569
12	4	2	198	150
14	4	2	304	299
1	5	2	526	569
2	5	2	373	308
3	5	2	808	843
4	5	2	155	128
5	5	2	590	565
7	5	2	623	624
9	5	2	405	426
10	5	2	196	183
11	5	2	400	412
13	5	2	344	301
15	5	2	303	288
0	6	2	637	615
1	6	2	293	277
2	6	2	377	345
3	6	2	192	179
4	6	2	611	629
6	6	2	192	150
7	6	2	182	201
8	6	2	465	428
12	6	2	232	219
16	6	2	219	154
1	7	2	491	511
2	7	2	186	128
3	7	2	500	529
4	7	2	185	175
5	7	2	492	514
6	7	2	186	138
7	7	2	431	427
9	7	2	419	434
10	7	2	207	120
11	7	2	268	268
13	7	2	239	265
1	8	2	133	105
2	8	2	450	467
6	8	2	363	376
8	8	2	205	173
10	8	2	301	239
1	9	2	406	390
2	9	2	177	163
3	9	2	249	248
4	9	2	163	143
5	9	2	347	359
6	9	2	207	162
7	9	2	300	289
9	9	2	216	220
11	9	2	240	240
0	10	2	247	261
1	10	2	149	127
2	10	2	168	190
4	10	2	276	262
6	10	2	236	173
8	10	2	219	215
1	11	2	219	226
3	11	2	219	182
1	0	3	928	866
2	0	3	105	88
4	0	3	241	221
5	0	3	1036	998
7	0	3	474	463
9	0	3	258	267
11	0	3	213	197
13	0	3	214	212
15	0	3	158	140
0	1	3	926	937
1	1	3	156	153
2	1	3	1494	1564
3	1	3	374	377
4	1	3	669	693
5	1	3	196	213
6	1	3	040	881
7	1	3	347	327
8	1	3	897	938
9	1	3	222	218
10	1	3	330	344
11	1	3	247	236
12	1	3	448	490
14	1	3	299	279
16	1	3	332	329
18	1	3	249	176
0	2	3	301	301
1	2	3	315	297
2	2	3	193	183
3	2	3	406	380
4	2	3	91	96
5	2	3	852	896
6	2	3	262	257
8	2	3	200	194
9	2	3	212	198
11	2	3	357	379
13	2	3	204	179
15	2	3	280	300
0	3	3	1149	1229
1	3	3	227	200
2	3	3	958	1122
3	3	3	118	104
4	3	3	438	445
5	3	3	281	273
6	3	3	655	684
7	3	3	232	248
8	3	3	660	690
10	3	3	466	468
11	3	3	212	217
12	3	3	525	565
14	3	3	221	212
16	3	3	233	243
0	4	3	260	233
1	4	3	570	608
2	4	3	279	274
3	4	3	349	363
4	4	3	176	163
5	4	3	494	539
6	4	3	239	253
7	4	3	233	232
9	4	3	418	422
10	4	3	228	206
11	4	3	192	200
13	4	3	307	295
0	5	3	869	946
1	5	3	144	105
2	5	3	857	949
3	5	3	220	219
4	5	3	465	455
6	5	3	439	450
7	5	3	165	137
8	5	3	593	653
10	5	3	439	438
12	5	3	349	325
14	5	3	231	215
0	6	3	143	133
1	6	3	239	229
2	6	3	195	184
3	6	3	395	409
4	6	3	207	206
7	6	3	294	290
9	6	3	294	269
11	6	3	203	169
0	7	3	545	532
1	7	3	191	209
2	7	3	495	502
4	7	3	511	535
6	7	3	411	404
8	7	3	459	446
9	7	3	233	186
10	7	3	367	407
12	7	3	312	268
14	7	3	222	234
0	8	3	136	125
1	8	3	263	276
2	8	3	251	238
3	8	3	271	277
5	8	3	268	295
6	8	3	208	210
7	8	3	231	251
4	9	3	294	305
6	9	3	324	336
10	9	3	216	171
0	9	3	374	378
2	9	3	280	248
0	10	3	139	151
1	10	3	144	172
3	10	3	214	226
5	10	3	209	158
7	10	3	214	246
4	11	3	217	242
0	0	4	1631	1855
2	0	4	337	319
3	0	4	192	182
4	0	4	992	1090
5	0	4	124	139
8	0	4	501	539
10	0	4	269	243
12	0	4	300	312
14	0	4	269	288
16	0	4	192	190
1	1	4	148	168
2	1	4	197	200
3	1	4	1153	1203
4	1	4	291	268
5	1	4	579	598
6	1	4	337	330
7	1	4	595	604
8	1	4	237	225
10	1	4	167	171
11	1	4	369	401
13	1	4	409	442
15	1	4	187	220
0	2	4	962	993
1	2	4	189	185
2	2	4	965	956
3	2	4	236	211
4	2	4	466	435
5	2	4	208	210
6	2	4	1054	1024
8	2	4	351	331
10	2	4	795	828
14	2	4	450	478
0	3	4	298	296
1	3	4	253	248
2	3	4	119	121
3	3	4	706	713
4	3	4	260	253
5	3	4	402	404
7	3	4	566	570
8	3	4	269	245
11	3	4	349	336
0	4	4	1296	1264
1	4	4	282	306
2	4	4	365	357
4	4	4	707	735
5	4	4	259	264
6	4	4	168	155
7	4	4	178	192
8	4	4	631	664
10	4	4	339	331
12	4	4	208	251
1	5	4	316	319
2	5	4	395	379
3	5	4	305	314
4	5	4	163	129
5	5	4	301	313
6	5	4	189	206
7	5	4	423	411
9	5	4	351	338
10	5	4	268	269
0	6	4	337	341
1	6	4	188	193
2	6	4	547	599
3	6	4	189	167
4	6	4	166	160
6	6	4	425	430
8	6	4	270	262
10	6	4	427	407
0	7	4	331	298
1	7	4	365	387
3	7	4	313	313
4	7	4	185	198
5	7	4	345	300
7	7	4	338	298
9	7	4	265	254
0	8	4	440	456
1	8	4	110	132
2	8	4	315	328
3	8	4	187	194
4	8	4	456	479
6	8	4	238	281
8	8	4	356	334
1	9	4	196	168
2	9	4	197	181
3	9	4	148	143
4	9	4	125	57
5	9	4	281	291
1	10	4	127	124
2	10	4	304	282
4	10	4	219	198
6	10	4	226	249
0	0	5	217	112
1	0	5	364	373
2	0	5	247	271
3	0	5	481	518
4	0	5	124	62
5	0	5	1223	1214
6	0	5	317	328
7	0	5	373	404
9	0	5	201	218
10	0	5	167	139
11	0	5	430	435
13	0	5	235	246
15	0	5	304	333
0	1	5	259	195
1	1	5	102	152
2	1	5	496	503
3	1	5	327	353
4	1	5	497	452
6	1	5	345	331
7	1	5	287	267
8	1	5	392	386
9	1	5	164	124
10	1	5	215	181
12	1	5	279	257
0	2	5	461	409
1	2	5	757	767
3	2	5	753	744
4	2	5	368	295
5	2	5	1235	1219
7	2	5	220	237
8	2	5	203	213
9	2	5	700	706
11	2	5	303	296
13	2	5	469	473
15	3	5	237	270
0	3	5	807	804
1	3	5	167	195
2	3	5	769	786
3	3	5	179	222
4	3	5	292	273
5	3	5	223	187
6	3	5	263	282
7	3	5	158	194
8	3	5	410	456
10	3	5	187	194
0	4	5	143	128
1	4	5	591	674
2	4	5	305	250
3	4	5	568	665
4	4	5	176	173
5	4	5	541	540
6	4	5	165	121
7	4	5	401	412
9	4	5	411	424
10	4	5	152	130
11	4	5	395	428
15	4	5	300	296
0	5	5	331	323
1	5	5	195	187
2	5	5	312	269
3	5	5	137	160
4	5	5	181	162
0	6	5	262	239
1	6	5	545	593
2	6	5	224	160
3	6	5	357	378
4	6	5	187	154
0	7	5	464	512
1	7	5	132	118
2	7	5	329	305
4	7	5	275	254
1	8	5	336	339
2	8	5	183	124
3	8	5	400	426
0	9	5	154	120
1	9	5	96	47
2	9	5	149	145
3	9	5	115	113
4	9	5	237	227
0	0	6	1182	1236
1	0	6	239	217
2	0	6	524	549
4	0	6	321	348
5	0	6	253	268
6	0	6	613	636
8	0	6	237	276
10	0	6	620	653
12	0	6	146	170
13	0	6	145	149
14	0	6	302	342
16	0	6	151	163
0	1	6	167	201
1	1	6	221	209
2	1	6	248	242
3	1	6	621	631
4	1	6	149	143
5	1	6	146	180
6	1	6	341	352
7	1	6	400	420
8	1	6	163	158
11	1	6	329	304
13	1	6	261	241
0	2	6	1069	1129
1	2	6	180	196
2	2	6	256	250
3	2	6	200	228
4	2	6	674	672
6	2	6	270	278
7	2	6	171	188
8	2	6	516	538
10	2	6	373	384
12	2	6	205	196
14	2	6	235	243
1	3	6	158	167
2	3	6	241	261
3	3	6	638	659
4	3	6	261	247
5	3	6	355	372
7	3	6	478	451
9	3	6	274	245
11	3	6	201	215
13	3	6	215	259
0	4	6	377	390
1	4	6	213	228
2	4	6	388	373
4	4	6	300	291
5	4	6	113	160
6	4	6	368	404
8	4	6	271	258
9	4	6	151	197
10	4	6	357	358
14	4	6	202	231
0	5	6	188	208
1	5	6	191	183
2	5	6	178	210
3	5	6	318	296
4	5	6	163	160
0	6	6	536	557
1	6	6	134	150
2	6	6	338	324
4	6	6	421	429
0	7	6	271	275
1	7	6	288	276
3	7	6	231	203
0	8	6	177	143
1	8	6	94	114
2	8	6	275	306
3	8	6	191	177
4	8	6	154	178
0	9	6	80	103
1	9	6	215	210
2	9	6	98	93
0	0	7	407	368
1	0	7	240	251
2	0	7	126	83
4	0	7	285	293
5	0	7	559	607
8	0	7	266	280
9	0	7	396	407
0	1	7	566	537
1	1	7	189	202
2	1	7	698	742
3	1	7	157	193
4	1	7	282	266
5	1	7	207	237
6	1	7	462	463
8	1	7	545	561
10	1	7	238	251
12	1	7	233	272
0	2	7	120	105
1	2	7	182	146
2	2	7	294	302
3	2	7	199	200
4	2	7	167	90
5	2	7	356	355
6	2	7	278	263
0	3	7	453	481
1	3	7	211	200
2	3	7	635	673
3	3	7	166	193
4	3	7	404	367
6	3	7	438	435
8	3	7	473	466
10	3	7	368	326
12	3	7	343	362
14	3	7	223	206
0	4	7	357	387
1	4	7	199	185
2	4	7	165	100
3	4	7	192	200
4	4	7	281	259
5	4	7	347	399
7	4	7	161	130
8	4	7	154	199
9	4	7	161	211
0	5	7	558	530
2	5	7	585	556
3	5	7	181	191
4	5	7	408	386
1	6	7	193	180
2	6	7	189	218
3	6	7	346	324
0	7	7	291	281
1	7	7	162	142
2	7	7	312	281
3	7	7	147	125
4	7	7	307	314
0	8	7	134	135
1	8	7	160	128
2	8	7	101	83
3	8	7	177	170
4	8	7	155	192
0	0	8	687	711
1	0	8	128	142
2	0	8	163	135
3	0	8	253	242
4	0	8	212	199
7	0	8	144	176
8	0	8	269	271
10	0	8	306	345
14	0	8	137	167
15	0	8	136	131
0	1	8	125	182
1	1	8	404	411
2	1	8	193	229
3	1	8	660	672
5	1	8	253	272
7	1	8	480	470
9	1	8	282	264
11	1	8	318	314
13	1	8	275	245
0	2	8	468	457
1	2	8	150	180
3	2	8	117	92
10	2	8	257	220
0	3	8	197	246
1	3	8	316	255
3	3	8	449	468
4	3	8	182	177
5	3	8	352	353
7	3	8	403	418
9	3	8	199	117
11	3	8	250	263
0	4	8	331	288
2	4	8	213	193
4	4	8	272	262
6	4	8	167	209
0	5	8	120	93
1	5	8	274	241
2	5	8	172	181
3	5	8	421	414
0	6	8	151	128
2	6	8	197	180
4	6	8	220	200
0	7	8	93	114
1	7	8	233	208
3	7	8	266	242
4	7	8	153	165
1	8	8	77	82
1	0	9	214	234
2	0	9	261	291
3	0	9	210	216
5	0	9	361	303
6	0	9	174	205
9	0	9	264	233
10	0	9	196	222
14	0	9	136	113
0	1	9	240	181
1	1	9	150	195
2	1	9	415	410
3	1	9	176	203
4	1	9	179	132
6	1	9	256	232
8	1	9	330	339
0	2	9	310	298
1	2	9	229	236
2	2	9	178	90
3	2	9	197	152
4	2	9	243	214
5	2	9	419	401
9	2	9	242	241
0	3	9	357	316
1	3	9	130	155
2	3	9	322	297
3	3	9	111	148
4	3	9	191	131
0	4	9	123	138
1	4	9	305	278
2	4	9	220	228
3	4	9	307	317
5	4	9	319	351
6	4	9	220	236
0	5	9	195	179
1	5	9	98	121
2	5	9	308	273
3	5	9	165	156
4	5	9	205	202
0	6	9	140	134
1	6	9	166	181
3	6	9	241	235
4	6	9	174	187
0	7	9	284	257
0	0	10	610	559
1	0	10	157	168
2	0	10	168	152
3	0	10	162	98
4	0	10	314	295
5	0	10	189	183
6	0	10	267	218
8	0	10	228	224
9	0	10	145	136
10	0	10	288	230
0	1	10	186	190
2	1	10	150	146
3	1	10	277	278
7	1	10	183	206
0	2	10	479	433
1	2	10	104	130
2	2	10	236	226
3	2	10	225	170
4	2	10	294	256
6	2	10	297	267
8	2	10	245	197
10	2	10	317	268
2	3	10	150	146
3	3	10	156	158
0	4	10	383	384
1	4	10	172	163
2	4	10	212	193
4	4	10	290	272
6	4	10	205	206
8	4	10	179	236
10	4	10	184	197
0	5	10	140	118
2	5	10	117	109
3	5	10	170	162
1	6	10	76	104
0	0	11	260	256
1	0	11	168	136
3	0	11	142	119
4	0	11	213	177
5	0	11	344	317
11	0	11	152	95
1	1	11	103	134
2	1	11	211	207
1	2	11	194	174
2	2	11	196	213
3	2	11	195	186
5	2	11	277	273
9	2	11	215	160
1	3	11	100	111
2	3	11	202	197
3	3	11	120	162
0	4	11	161	165
1	4	11	218	184
0	0	12	198	188
5	0	12	264	118
3	1	12	253	229

[a] Absolute values are equal to the tabulated values divided by 1.128.

TABLE II

FRACTIONAL ATOMIC COORDINATES (×10^4)[a] AND ANISOTROPIC TEMPERATURE FACTOR COEFFICIENTS (×10^5)[b]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	0000	0000	2603 (1)	221 (7)	512 (16)	548 (17)	000	000	−044 (21)
N(1)	0000	2041 (19)	1387 (18)	157 (96)	588 (266)	929 (205)	000	000	510 (204)
C(1)	0000	3414 (29)	1020 (19)	240 (141)	1260 (401)	533 (216)	000	000	−150 (261)
S(1)	0000	5165 (9)	0538 (6)	503 (56)	961 (106)	1280 (79)	000	000	315 (81)
N(2)	5000	2958 (22)	6323 (18)	497 (160)	769 (324)	860 (226)	000	000	−191 (231)
C(2)	5000	1708 (32)	5926 (20)	148 (125)	1825 (513)	781 (248)	000	000	1173 (339)
S(2)	5000	−0231 (7)	5521 (6)	497 (56)	559 (94)	1164 (74)	000	000	−258 (67)
N(3)	1080 (11)	1009 (16)	3818 (13)	309 (84)	862 (214)	1055 (167)	36 (126)	2 (119)	−113 (162)
C(3)	1638 (10)	1617 (18)	4505 (16)	184 (72)	639 (199)	1200 (213)	−3 (111)	−39 (121)	−254 (193)
S(3)	2474 (3)	2552 (6)	5396 (4)	350 (23)	1252 (68)	1488 (72)	−194 (40)	−294 (46)	66 (62)
N(4)	3888 (10)	4050 (16)	8690 (15)	235 (79)	789 (207)	1657 (210)	−145 (114)	20 (125)	−251 (184)
C(4)	3232 (12)	3315 (20)	9169 (16)	396 (101)	754 (254)	1103 (213)	252 (135)	−93 (141)	−73 (195)
S(4)	2334 (3)	2313 (5)	9845 (6)	338 (25)	1265 (77)	1888 (79)	−336 (42)	264 (45)	−342 (74)
K(1)	2088 (3)	4609 (5)	2503 (3)	548 (22)	1564 (85)	922 (44)	−26 (35)	−49 (33)	99 (45)
K(2)	3875 (8)	0309 (18)	2489 (16)	703 (62)	1857 (309)	1414 (185)	−125 (108)	126 (132)	−366 (185)
C(5)	0000	−0738 (51)	7434 (26)	241 (127)	3787 (968)	1228 (425)	000	000	−1472 (530)
C(6)	0000	1122 (53)	7426 (32)	817 (305)	2648 (809)	1754 (672)	000	000	−814 (472)
O(1)	0802 (10)	−1434 (23)	7514 (14)	473 (80)	2812 (405)	1922 (273)	63 (164)	−108 (121)	−121 (200)
O(2)	3699 (22)	0445 (46)	2576 (30)	679 (152)	2016 (738)	365 (253)	630 (360)	41 (246)	602 (354)

[a] $10^4\sigma$ is given in parentheses. [b] Coefficients have the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. $10^5\sigma$ is given in parentheses.

TABLE III

DISTANCES (A) AND ANGLES (DEG) WITH STANDARD DEVIATIONS IN PARENTHESES

Distances and Angles in the Mo(NCS)$_6^{3-}$ ION

Atoms	Value	Multiplicity	Atoms	Value	Multiplicity
Mo–N(1)	2.107 (15)	1	N(2)^{b}–Mo–N(3)	94.0 (0.5)	2
Mo–N(2)	2.034 (18)	1	N(2)–Mo^{a}–N(4)	88.3 (0.5)	2
Mo–N(3)	2.065 (14)	2	N(3)–Mo–N(3)^{c}	90.2 (0.8)	1
Mo–N(4)	2.119 (14)	2	N(3)–Mo–N(4)^{b}	89.6 (0.4)	2
N(1)–C(1)	1.228 (29)	1	N(4)–Mo–N(4)^{c}	90.6 (0.8)	1
N(2)–C(2)	1.138 (31)	1	N(1)–Mo–N(2)^{b}	176.8 (0.8)	1
N(3)–C(3)	1.133 (17)	2	N(3)–Mo–N(4)^{c,b}	177.7 (0.6)	2
N(4)–C(4)	1.184 (21)	2	Mo–N(1)–C(1)	162.9 (1.7)	1
C(1)–S(1)	1.571 (25)	1	Mo^{a}–N(2)–C(2)	169.0 (1.8)	1
C(2)–S(2)	1.706 (29)	1	Mo–N(3)–C(3)	176.4 (1.3)	2
C(3)–S(3)	1.633 (15)	2	Mo^{a}–N(4)–C(4)	165.6 (1.4)	2
C(4)–S(4)	1.626 (18)	2	N(1)–C(1)–S(1)	179.5 (1.9)	1
			N(2)–C(2)–S(2)	173.5 (1.9)	1
N(1)–Mo–N(3)	88.2 (0.5)	2	N(3)–C(3)–S(3)	175.9 (1.6)	2
N(1)–Mo–N(4)^{b}	89.4 (0.5)	2	N(4)–C(4)–S(4)	179.3 (1.6)	2

Contacts Involving Sulfur Atoms

Atoms	Value	Atoms	Value
K(1)–S(1)	3.439 (5)	O(2)–S(1)^{d}	3.494 (27)
K(1)–S(2)^{a}	3.415 (5)	O(2)–S(2)	3.396 (30)
K(1)–S(3)	3.346 (6)	O(2)–S(3)	3.665 (30)
K(1)–S(3)^{a}	3.291 (6)	O(2)–S(3)^{b}	3.536 (35)
K(1)–S(4)	3.252 (6)	O(2)–S(4)^{b}	3.825 (40)
K(1)–S(4)^{a}	3.335 (6)	O(2)–S(4)^{e}	3.598 (30)
K(2)–S(1)^{d}	3.300 (14)	O(1)^{a}–S(3)	3.756 (15)
K(2)–S(2)	3.334 (16)	O(1)^{a}–S(4)^{e}	3.746 (15)
K(2)–S(3)^{b}	3.618 (16)	N(2)–S(3)	3.554 (6)
K(2)–S(3)	3.896 (13)	C(2)–S(3)	3.535 (7)
K(2)–S(4)^{b}	3.789 (16)	N(1)–S(4)^{e}	3.503 (8)
K(2)–S(4)^{e}	3.719 (17)	C(1)–S(4)^{e}	3.489 (10)

Other Important Distances and Angles

Atoms	Value	Atoms	Value
C(5)–C(6)	1.593 (52)	C(6)–C(3)	3.614 (29)
C(5)–O(1)	1.242 (26)	O(2)–N(3)	3.78 (3)^{f}
O(1)^{a}–O(2)	2.76 (5)^{f}	O(2)–N(4)^{b}	3.90 (4)^{f}
K(1)–O(1)^{a}	2.995 (15)	O(1)–N(1)	4.904 (25)
K(2)–O(1)^{a}	2.83 (3)^{f}	O(1)–N(2)^{b}	3.897 (22)
K(2)–O(2)^{c}	3.29 (3)^{f}	O(1)–N(3)	4.156 (20)
K(1)–N(1)	3.742 (13)	O(1)–N(4)^{b}	3.714 (22)
K(1)–N(3)	3.605 (14)	Mo–O (2)	5.026 (30)
K(2)–N(3)	4.04 (2)^{f}		
K(2)–N(4)^{b}	4.06 (2)^{f}	O(1)–C(5)–O(1)^{c}	122.1 (4.1)
O(1)^{a}–C(4)^{e}	3.468 (21)	C(5)–C(6)–O(1)	118.7 (2.0)

[a–e] Symmetry transformations: $^{a}M = M(^1/_2 - x, {}^1/_2 + y, 1 - z)$, $^{b}M = M(^1/_2 - x, y - {}^1/_2, 1 - z)$, $^{c}M = M(-x, y, z)$, $^{d}M = M(^1/_2 - x, y - {}^1/_2, -z)$, $^{e}M = M(x, y, z - 1)$. [f] Positions of K(2) and O(2) are only approximate, as a result of the disorder. Distances involving these two atoms are given in two decimal places only.

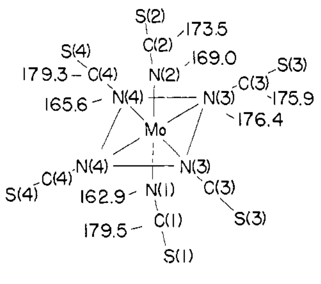

Figure 1.—Angles NCS and MoNC in Mo(NCS)$_6^{3-}$.

to 2.32 A has been attributed to Mo═O and Mo═C multiple bonding *trans* to the Mo—N(dien) bonds.[15]

Six of the twelve octahedral N–Mo–N angles vary from 90° by more than 3σ, so the molybdenum-nitrogen arrangement appears to have only the C$_s$ symmetry required by the space-group mirror plane. The angle NCS(2) is 3.4σ from 180°, indicating a possible nonlinearity in that NCS group.[17] The weighted averages of the N–C and C–S distances are 1.159 ± 0.027 and 1.630 ± 0.024 A, respectively. In no case does an individual bond distance deviate significantly from its average value.

Given the two resonance forms

A B

one would expect that in N-bonded thiocyanate complexes the distances N–C and C–S and the angle MNC

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[17] A. Ferrari, *et al.*, *Acta Cryst.*, **18**, 367 (1965).

are mutually dependent. To detect correlation between the distances and the angle MNC, Hazell[18] suggested plotting these distances against angle. From crystallographic data for twelve thiocyanates he showed that the N–C distances generally decrease with the increasing angle MNC, while the C–S distances increase. Adding the more recent data[17,19] to this plot and using our average distances with either the averaged or (more realistically) the unaveraged angles, it is found that our $Mo(NCS)_6^{3-}$ data points fall well within the ranges defined by the other data points. In $Mo(NCS)_6^{3-}$ the variation in the unaveraged N–C distances correlates with angle while the C–S variation does not. The insignificant variation of the unaveraged distances from their mean value does not allow a full discussion of this point.

To find out which of the two resonance forms is dominant in this structure, we note that Pauling[20] gives the following distances: $S{-}C = 1.81$, $S{=}C = 1.61$, $N{=}C = 1.29$, and $N{\equiv}C = 1.15$ A. A comparison of the average N—C distance with Pauling's values indicates a major contribution from resonance form A. However, the B form is favored by the average C—S distance, a contradiction often seen in the thiocyanate data.[21]

The angles MoNC are all nearer 180 than 120°; in fact, within experimental error two of the six are linear, suggesting the dominance of resonance form A. Following a description of the crystal structure, we shall show that the nonlinearity observed in four of the MoNC angles is likely to be due to packing conditions in the crystal.

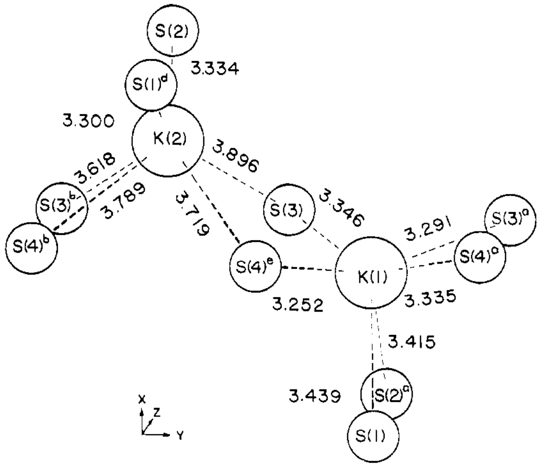


Figure 2.—Trigonal-prismatic coordination of potassium by sulfur in $K_3Mo(NCS)_6 \cdot H_2O \cdot CH_3COOH$.

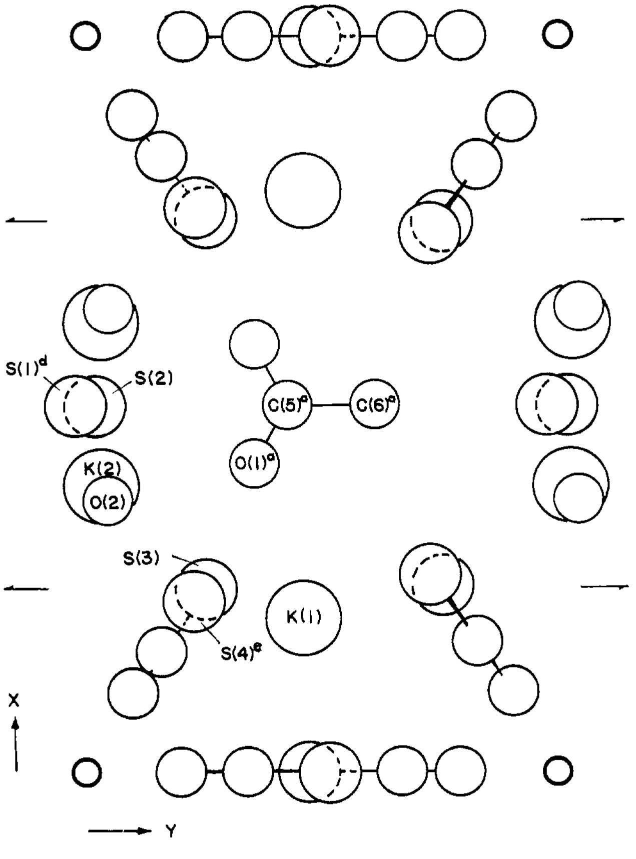
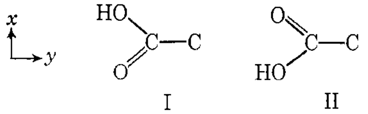


Figure 3.—Cavity enclosing acetic acid molecule.

The closest approach between $Mo(NCS)_6^{3-}$ ions is the S(1)···S(2)^a distance of 3.82 A, very near the 3.80-A S···S contact in $[Zn(N_2H_4)_2(NCS)_2]$.[17] Each potassium ion is surrounded by six sulfur atoms, which form a distorted trigonal prism (Figure 2). K(2) is replaced half of the time by a water molecule. Six prisms share edges to form a cylindrical cavity in which the acetic acid is contained (Figure 3), leading one to suspect the presence of similar cavities in the related compounds $M_3Mo(NCS)_6 \cdot H_2O \cdot HA$, where HA = HCl, C_2H_5OH, C_3H_7OH, KHC_2O_4, or CH_3COOH.[5] Stabilization of HA in the cavity would result from hydrogen bonding between it and either the water molecule or a thiocyanate group. Indeed, a hydrogen bond between the acetic acid and water was found, the O(1)···O(2) distance being 2.76 A (Figure 4). The O(2)···N distances show that the water is not hydrogen bonded to a thiocyanate nitrogen atom, consistent with the assumption that the resonance in the molybdenum complex is primarily form A, for hydrogen bonding to the formally positive nitrogen atom is unlikely. A hydrated thiocyanate complex with the B resonance form is more likely to have a water–nitrogen bond, as found, for example, in $K_2Co(NCS)_4 \cdot 4H_2O$,[22] which has a CoNC angle equal to 111°.

There seem to be reasonable chemical explanations for the structural disorder of O(1), O(2), and K(2). (a) In its crystal environment (see Figure 3) the acid molecule may have orientation I or II



I II

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[18] A. C. Hazell, *J. Chem. Soc.*, 5745 (1963). For $Cd(etu)_2(NCS)_2$ the MNC angle should read 143°.

[19] (a) "Abstracts of Papers Presented before the 7th Congress of the International Union of Crystallography," Moscow, July 1966, No. 9-61; (b) M. Nardelli, *et al.*, *Acta Cryst.*, **20**, 349 (1966).

[20] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 224, 228, 274.

[21] See ref 19a, Abstract No. 9-38. See tables in ref 17 and 18.

[22] G. S. Zhdanov and Z. V. Zvonkova, *Zh. Fiz. Khim.*, **24**, 1339 (1950).

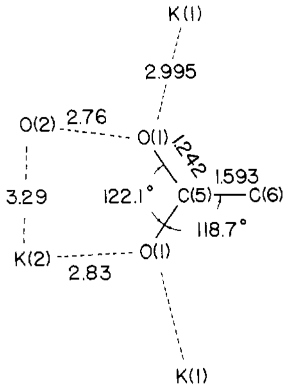
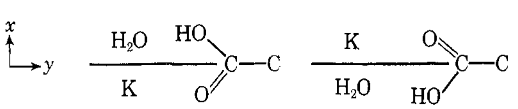


Figure 4.—Acetic acid coordination.

If the water molecule is to form a hydrogen bond with the carboxyl oxygen atom and if K(2) is to coordinate to the carbonyl oxygen atom, orientation I′ exists in 50% of the cells and orientation II′ exists in the other 50%



I′ II′

Thus the disorder of the acetic acid molecule correlates with that of K(2) and O(2). (b) Alternatively, one may say that because the water molecule and potassium ion are equally able to fit into the sulfur atom prisms, the orientation of the acid in each cell is determined by whichever arrangement of H_2O and K(2) is present

In the acid the observed CCO angle is the average of the CC=O and CC—OH angles in solid acetic acid.[23] The methyl carbon C(6) is 7° from the plane of O(1)–C(5)–O(1)^c.

To see what effect, if any, the crystal structure (Figure 5) has on the MoNC angles, one argues that, in view of the formal charges in resonance forms A and B, the amount of nonlinearity in the angles should be proportional to the K···N distances and inversely proportional to the K···S distances.[16] From Table IV a comparison of the two compounds reveals an electrostatic correlation between the angle MNC and the distance of the positive ion from the thiocyanate ligand. However, within the molybdenum complex itself, the correlation breaks down. That is, the largest angles are not associated with the shortest K···S distances and longest K···N distances. This fact suggests that steric or packing effects within the crystal may have upset the expected relationship.

The source of this disruption is most likely the water molecule, which half the time replaces the potassium ion K(2) in half of the sulfur atom prisms. Because the water molecule is larger (R = 1.7 A) and less electrophilic than the potassium ion (R = 1.3 A) which it replaces, the sulfur prism is forced to expand. Atoms S(1) and S(2) are forced apart, each moving to within

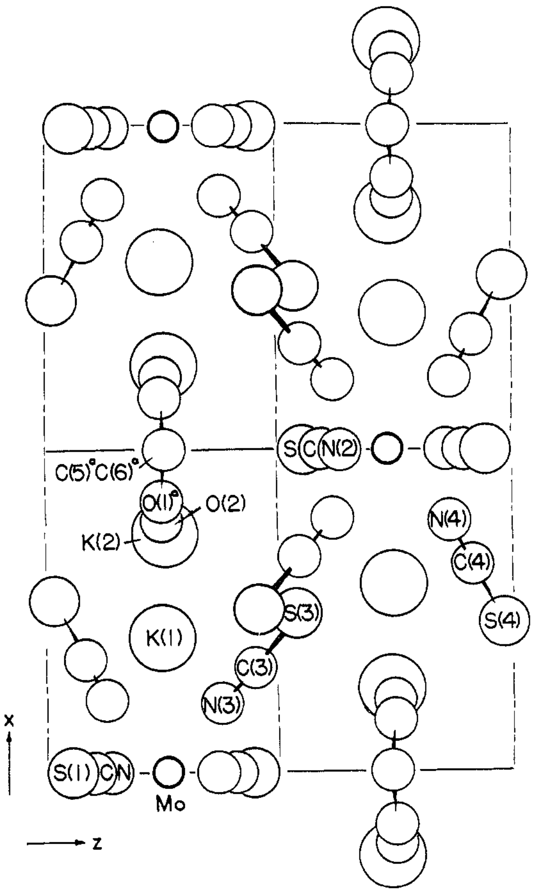


Figure 5.—(010) projection of $K_3Mo(NCS)_6\cdot H_2O\cdot CH_3COOH$.

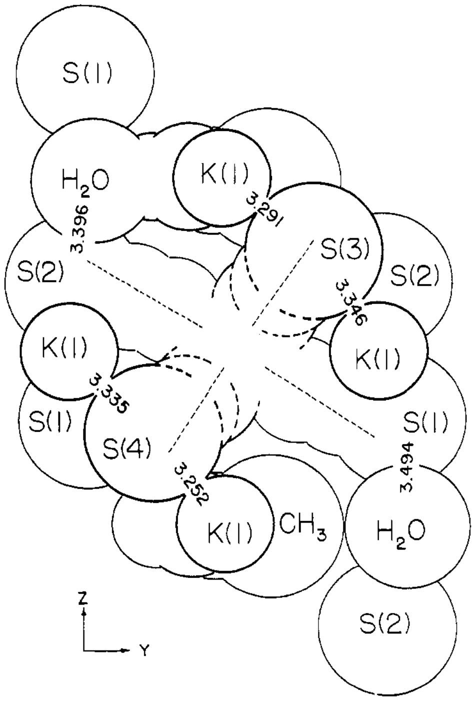


Figure 6.—Packing diagram showing crystal environment of $Mo(NCS)_6{}^{3-}$ octahedron in $K_3Mo(NCS)_6\cdot H_2O\cdot CH_3COOH$. Dashed lines drawn along the Mo–N bonds show the amount and direction of bending of the Mo–NCS linkages.

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(23) R. E. Jones and D. H. Templeton, *Acta Cryst.*, **11**, 484 (1958).

Table IV

Relationship of MNC Angles (deg) to K···S and K···N Distances (A) in Two Thiocyanates

Compound	Angle MNC	K···S distance		K···N distance	
		Average	Shortest	Average	Shortest
$K_2Co(NCS)_4 \cdot H_2O$	111	3.66	3.59	3.24	2.62
$K_3Mo(NCS)_6 \cdot H_2O \cdot CH_3COOH$	163	3.39	3.30	>4	3.74
	169	3.39	3.33	>4	4.19
	176 (two)	3.46	3.29	>4	3.60
	166 (two)	3.45	3.25	>4	4.06

the van der Waals limit of the neighboring sulfur atom (Figure 6). The water molecule is rather close to the S(1) and S(2) atoms, the two contacts being 3.40 and 3.49 A. Consequently, a torque is applied to the ends of two ligands, NCS(1) and NCS(2). This torque would force the octahedron to rotate (counterclockwise in the figure) were it not for the other potassium ion K(1), which prevents any movement of the sulfur atom ends of the remaining four ligands, NCS(3) (two) and NCS(4) (two).

From this argument it should follow, and indeed does, that the four K(1)···S distances in the direction of the forced rotation are significantly shorter than the four distances in the reverse direction. The two MoNC(4) angles are more bent (166°) than the two MoNC(3) angles (176°), agreeing with the fact that the ends of the NCS(4) groups approach K(1) ions and neighboring NCS(1) groups more closely than the NCS(3) groups approach K(1) ions and NCS(2) groups. The bending occurs in the expected direction (see Figure 6).

Thus, the effect of the crowding of the water molecules against the S(1) and S(2) atoms is not to initiate rigid-body rotation but to cause four of the six Mo–NCS linkages to bend at the nitrogen atom. The remaining two linkages, being relatively free from steric effects, have MoNC angles which are nearest the 180° value expected for form A resonance.

Acknowledgments.—We wish to thank Dr. Robert Thomas for helpful discussions during the early part of this research. Calculations were done at the Computation Centers of Boston University and the Massachusetts Institute of Technology.

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Organometallic Chemistry of the Transition Metals. XXII. The Synthesis of Unusual Cyclopentadienylmolybdenum Nitrosyl Derivatives Using Thallium Cyclopentadienide[1,2]

By R. B. King[3]

Received July 18, 1967

Thallium cyclopentadienide reacts with $[C_5H_5Mo(NO)I_2]_2$ in tetrahydrofuran solution to give green-black $(C_5H_5)_2Mo(NO)I$ apparently containing a novel type of allylic π-cyclopentadienyl ring. Reaction of this iodide derivative with methylmagnesium bromide gives the brown volatile σ-methyl derivative $(C_5H_5)_2Mo(NO)CH_3$. Reaction of the molybdenum nitrosyl chloride $[Mo(NO)_2Cl_2]_n$ with thallium cyclopentadienide in tetrahydrofuran solution gives yellow-green unstable $C_5H_5Mo(NO)_2Cl$. The reactivity of metal halide derivatives toward thallium cyclopentadienide is discussed.

Introduction

A common method for the synthesis of π-cyclopentadienyl derivatives is the reaction of sodium cyclopentadienide with various transition metal halides.[4] However, in some cases sodium cyclopentadienide does not give π-cyclopentadienyl derivatives with metal halides owing to destruction of the metal complex arising from the strongly reducing and basic properties of sodium cyclopentadienide. More recently thallium cyclopentadienide has been shown to be a suitable reagent for the preparation of many π-cyclopentadienyl derivatives.[5] Since thallium cyclopentadienide is a weaker reducing agent and base than sodium cyclopentadienide, certain reactions of halide derivatives which failed to give isolable π-cyclopentadienyl derivatives with sodium cyclopentadienide were reinvestigated using thallium cyclopentadienide.

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[1] For Part XXI of this series see R. B. King and M. B. Bisnette, *J. Organometal. Chem.* (Amsterdam), **8**, 287 (1967).

[2] Portions of this work were presented at the Third International Symposium on Organometallic Chemistry, Munich, Germany, Aug 1967.

[3] Fellow of the Alfred P. Sloan Foundation, 1967–1969.

[4] For a review on the synthesis of cyclopentadienylmetal derivatives see J. Birmingham, *Advan. Organometal. Chem.*, **2**, 365 (1964).

[5] A. N. Nesmeyanov, R. B. Materikova, and N. S. Kochetkova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1334 (1963); *Chem. Abstr.*, **59**, 12841*d* (1963); A. N. Nesmeyanov, K. N. Anisimov, and N. E. Kolobova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2220 (1964); *Chem. Abstr.*, **62**, 7788*b* (1965); C. C. Hunt and J. R. Doyle, *Inorg. Nucl. Chem. Letters*, **2**, 283 (1966); T. J. Katz and J. J. Mrowca, *J. Am. Chem. Soc.*, **89**, 1105 (1967).