tively small change in the enthalpy of formation because of strain energy could have a major effect on the equilibrium constants. Probably more important, however, is the greater loss in configuration entropy on formation of the six-membered ring. Ellison, *et al.*,[20] have measured thermodynamic parameters for the formation of diol complexes of the tellurate ion and found entropies of formation 4–11 eu more negative for the 1,3-diols than for the 1,2-diols but almost no difference in the enthalpies. Such a difference in the present case would decrease K_1 and K_2 sufficiently that virtually no complex would form under the conditions normally employed, *i.e.*, ligand-to-metal mole ratios ≤ 10.

The failure to observe complex formation in the case of α-amino or α-amido carboxylic acids is particularly interesting. Copper(II) has been shown to form stable complexes with peptides in which the amide proton is removed with the formation of a strong copper–nitrogen bond.[21] The absence of such complexes of vanadyl ion is further evidence for the importance of π bonding involving partial donation of a second unshared pair of electrons from oxygen or sulfur to vanadium. Such bonding is not possible with amino or amido groups.

The failure to observe stable complexes in solutions of vanadyl ion containing ethylene glycol or acetoin suggests the importance of an anionic ligand for the initial formation of a complex with vanadyl ion.

The failure to observe a stable complex of vanadyl ion with methoxyacetic acid above pH 4 is not surprising in light of the interpretation given for the equilibria involving α-hydroxy carboxylic acids. This result does, however, supply further evidence for the conclusions drawn, particularly since there is evidence in the esr spectra for the formation of a 1:1 and possibly a 1:2 complex. The equilibrium constant for the formation of the 1:1 complex with this ligand is apparently smaller than those for the α-hydroxy acids however. A combination of the steric effect introduced by the methyl group and the electronic effect involved in replacement of a proton by a methyl group probably accounts for the reduction in this equilibrium constant.

Esr Line Widths.—The esr line widths observed in spectra IV and IVa, $VO(A)_2^{2-}$, were substantially less than were observed in the spectra of the other species. There are two factors which are responsible for this effect. In the first place, the line widths in the spectrum of the aquovanadyl ion contain a contribution from an unresolved proton hyperfine interaction with the equatorial water molecules;[22] this splitting is approximately 1.1 G,[15] giving a 4–5-G contribution to the esr line widths. A similar splitting would no doubt arise from the hydroxyl protons in the various complexes and from remaining equatorial water molecules. Only in the cases of $VO(A)_2^{2-}$ are such protons missing from the complexes, so that this contribution is absent in the spectra of these species. The second factor which is important in accounting for the narrower observed lines is that the anisotropies of the a and g tensors are probably somewhat smaller. These factors are harder to assess since the tensor components are not known. In any case, accurate line width measurements are extremely difficult to make for these spectra because of the partial resolution of spectra IV and IVa, so that a detailed accounting of the line widths is not presently possible.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF WASHINGTON, SEATTLE, WASHINGTON 98105

Redetermination of the Crystal Structure of Potassium Lead Hexanitrocuprate(II), $K_2PbCu(NO_2)_6$

BY DAVID L. CULLEN AND E. C. LINGAFELTER*

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The structure of potassium lead hexanitrocuprate(II), $K_2PbCu(NO_2)_6$, has been redetermined using three-dimensional X-ray data and anisotropic thermal parameters. The space group is $Fm3$, with a_0 = 10.672 (1) Å. The calculated density for four formula units in the unit cell is 3.42 g/cm^3; 1366 reflections, of which 464 are independent, were collected with an automated four-circle diffractometer. The structure was refined by full-matrix least-squares techniques to a conventional R factor of 0.028. The hexanitrocuprate ion has T_h symmetry in apparent violation of the Jahn–Teller theorem, but the thermal parameters of the nitrogen atom are in accord with the assumption of a dynamic Jahn–Teller effect. The Cu–N bond length is 2.111 (4) Å, the N–O bond length is 1.260 (4) Å, and the O–N–O angle is 117.9 (4)°. $K_2SrCu(NO_2)_6$ has also been prepared and it is not isomorphous with $K_2PbCu(NO_2)_6$ but with $K_2BaCu(NO_2)_6$.

Introduction

In their well-known theorem, Jahn and Teller[1] have predicted that a molecule possessing a symmetry-induced electronic degeneracy of either orbital or spin nature must distort in order to remove as much degeneracy as possible. The classic example of an ion which exhibits this effect is Cu(II), a d^9 system. In virtually all six-coordinate complexes of this ion, the coordination octahedron is distorted, usually with two bonds longer than the other four. However three X-ray determina-

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[1] H. A. Jahn and E. Teller, *Proc. Roy. Soc., Ser. A*, **161**, 220 (1937); H. A. Jahn, *ibid., Ser. A*, **164**, 117 (1938).

tions of copper(II) complexes have been reported in which all six copper–donor atom bonds are the same length. Only one of these, tris(octamethylpyrophosphoramide)copper(II) perchlorate, $Cu(OMPA)_3(ClO_4)_2$,[2] employed three-dimensional data and anisotropic temperature factors. The original reports on the other two complexes, potassium lead hexanitrocuprate(II), $K_2PbCu(NO_2)_6$[3] and tris(ethylenediamine)copper(II) sulfate, $Cu(en)_3SO_4$,[4] were based on results using two-dimensional data and overall temperature factors.

The usual explanations for these apparent violations of the Jahn–Teller theorem invoke the dynamic Jahn–Teller effect or equivalent tetragonal distortions, both of which result in an average structure which appears to be regular. Either of these two possibilities should affect the shape of the thermal ellipsoids representing the apparent thermal motion of the atoms in the complex. Since the earlier data for $K_2PbCu(NO_2)_6$ were neither accurate enough nor complete enough to permit such a detailed examination of the structure, the crystal structure has been redetermined using three-dimensional data and anisotropic thermal parameters. It also provides interesting comparisons with the recently reported neutron diffraction study.[5]

Experimental Section

Crystals were prepared by the method of Ferrari and Colla[6] as brownish black cubes, {100}, on which most of the edges and corners are truncated by small faces of the forms {110} and {111}. The crystal used for intensity measurements had the dimensions 0.190 × 0.174 × 0.194 mm in the directions of *a*, *b*, and *c*, respectively, and was mounted along *b*.

Oscillation and Weissenberg photographs taken about {100}, {110}, and {111} using Cu Kα radiation showed cubic symmetry and only those reflections for which *h*, *k*, and *l* were all odd or all even, indicating a face-centered lattice. The cell dimension, $a_0 = 10.672$ (1) Å, was obtained by the least-squares refinement of the differences between observed and calculated 2θ values for 20 reflections, measured on a Picker manual diffractometer equipped with a General Electric goniostat. The radiation was niobium-filtered Mo Kα (λ 0.71069 Å). Room temperature was 23°. Refinement assuming an orthorhombic lattice gave values for a_0, b_0, and c_0 which were all equal within two standard deviations.

Since crystals of $K_2PbCu(NO_2)_6$ sank in tetrabromoethane, the density is greater than 2.96 g/cm³. The most reasonable density is 3.42 g/cm³, which corresponds to four formula units in the unit cell, in agreement with all earlier work.

Intensities were collected by the θ–2θ scan method on a Picker automated four-circle diffractometer equipped with a pulse height analyzer. The takeoff angle was 3.5°. Even though the photographs had indicated a cubic space group, the intensities of all the reflections in one octant of the reciprocal sphere, out to a 2θ value of 90°, were collected. This would be the unique set for orthorhombic space groups. Molybdenum Kα radiation, filtered by a 0.001-in. thickness of niobium foil, was used. The scan range for each reflection was calculated by the formula of Alexander and Smith[7]

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

The constant *A*, which is in part a function of the mosaicity of the crystal, was estimated to be 0.9° by observing the width of several intense reflections. *B* was set at the recommended value of 1.0°. The scan speed was 2°/min. Background counts were collected for 18 sec at each end of the scan range.

Group scale factors, calculated from the weighted average of the intensities of four standard reflections (060, 006, 600, 444) collected every 2–3 hr, increased about 2% over the course of data collection, indicating a drop in intensities. Since the appearance of the crystal also changed, the intensity drop was attributed to crystal decomposition and the group scale factors were applied.

The standard deviations of the intensities, σ_I, were estimated from the formula

$$\sigma_I = \{[S + (T_s/2T_b)^2(B_1 + B_2)] + K^2[S + (T_s/2T_b)(B_1 + B_2)]^2\}^{1/2} \qquad (2)$$

where *S* is the counts collected during scan time T_s, and B_1 and B_2 are background intensities, each collected during the background time T_b.

The first term in eq 2 is the error due to normal counting statistics, while the second is an empirical term used to account for other random errors in data collection. *K* was estimated by collecting 8 reflections, varying in intensity from weak to very strong, 24 times each, during the course of the data collection. A *K* value of 0.01 caused the best fit of the calculated standard deviations to the empirical standard deviations. Of the 1366 intensities collected, 74 had $I \leq 2\sigma_I$ and were coded as unobserved, being given "intensities" equal to $I + 2\sigma_I$.

Since the most intense peaks had a scan count of only 10,000 dekacounts, no correction for coincidence loss was made. The large linear absorption coefficient (μ = 162.5 cm^{-1}) made correction for absorption necessary. The correction factors, which were calculated using a Fortran IV version of the analytical integration method of de Meulenaer and Tompa,[8] ranged from 5.9 to 14.7 with most of the factors in the range 6–8.

Structure Determination and Refinement

Further calculations were performed using the "X-Ray 63" crystallographic computing system of Stewart.[9] Scattering factors of K$^+$, Pb^{2+}, Cu, N, and O were those tabulated by Cromer and Waber.[10] In the original work[3] the space group was assumed to be the cubic space group, *Fm*3, which for four formula units in the unit cell allows only one independent nitrogen atom and one independent oxygen atom. Since enough data for a unique set assuming an orthorhombic space group had been collected, initial refinement in the present study was carried out in the space group *Fmmm*, which allows three independent nitrogen atoms and three independent oxygen atoms. The positions of the lead, potassium, and copper ions, as well as the initial overall temperature factor of 1.2 Å², were taken from the original work.[3a] The metal ions are all in special positions. A structure factor calculation using only these ions gave a conventional *R* factor of 0.175. The conventional *R* is defined as $\Sigma|F_o - F_c|/\Sigma|F_o|$. A Fourier synthesis phased on these atoms gave the nitrogen and oxygen positions. Least-squares refinement of the structure, using the "X-Ray 63" version of the ORFLS program with isotropic temperature factors, lowered *R* to 0.096, and further refinement with anisotropic temperature factors lowered it only slightly further to 0.094. In all refinements the function minimized was $\Sigma w|F_o - F_c|^2$. If the structure factor of a reflection coded as unobserved was calculated to be less than the observed structure factor in any cycle, *w* for that re-

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TABLE I: OBSERVED AND CALCULATED STRUCTURE AMPLITUDES[a]

0,0,L		
2	2302E	3793
4	3442E	6345
6	2066	2379
8	3007E	3785
10	1578	2116
12	1885	1937
14	533	962
16	545	926
18	583	591
20	518	499
2,0,L		
2	2648E	3898
4	3064E	4335
6	3028E	3783
8	1582	2051
10	1818	1858
12	1240	1283
14	1210	1235
16	836	821
18	553	555
20	350	367
4,0,L		
2	1522	1563
4	3029E	3814
6	1236	1380
8	2494	2749
10	1588	1621
12	1568	1570
14	811	809
16	806	802
18	500	524
20	450	445
6,0,L		
2	2296E	2676
4	2389	2765
6	2459	2699
8	1576	1586
10	1530	1544
12	1077	1093
14	1083	1051
16	727	715
18	497	493
20	327	334
8,0,L		
2	1674	1789
4	2403	2687
6	1347	1425
8	1876	1572
10	1246	1279
12	1189	1163
14	675	661
16	610	621
18	417	416
10,0,L		
2	2101	2286
4	1941	2086
6	1514	2030
8	1300	1315
10	1237	1241
12	873	879
14	774	795
16	557	547
18	356	380
12,0,L		
2	1164	1199
4	1512	1533
6	965	1021
8	1134	1179
10	836	857
12	757	743
14	464	481
16	408	428
14,0,L		
2	1038	1040
4	945	951
6	991	975
8	654	683
10	657	683
12	471	509
14	446	460
16,0,L		
2	653	674
4	763	785
6	601	611
8	621	627
10	493	504
12	401	422
18,0,L		
2	581	598
4	529	554
6	518	539
8	407	409
10	390	390
20,0,L		
2	429	420
4	436	438
6	352	372
1,1,L		
1	1641E	1669
3	1727	1831
5	1318	1294
7	1227	1228
9	1099	1114
11	735	732
13	738	730
15	414	419
17	375	380
19	302*	237
21	293*	173
3,1,L		
3	1939	2084
5	1606	1614
7	1393	1401
9	1145	1141
11	764	751
13	761	756
15	473	469
17	397	407
19	257	245
5,1,L		
3	1260	1270
5	889	869
7	917	929
9	912	908
11	649	641
13	604	604
15	316	336
17	319	309
19	235	205
7,1,L		
3	1419	1452
5	1228	1229
7	1082	1100
9	861	854
11	589	592
13	605	597
15	394	398
17	365	334
19	280*	198
9,1,L		
3	1031	1049
5	736	757
7	754	786
9	721	733
11	538	557
13	473	479
15	279	277
17	234	243
19	207*	170
11,1,L		
3	858	863
5	736	745
7	665	696
9	497	524
11	353	382
13	355	380
15	251	267
17	251	217
13,1,L		
3	685	699
5	519	527
7	521	546
9	486	491
11	391	391
13	334	322
15	210	196
15,1,L		
3	468	484
5	404	415
7	398	399
9	267	298
11	307*	228
13	215	220
17,1,L		
3	365	371
5	283	285
7	318	297
9	260	260
11	200	211
19,1,L		
3	257	263
5	219	223
7	197	215
9	294*	164
2,2,L		
2	1045	956
4	3312E	4415
8	2192	2230
6	2002	2099
10	1151	1141
12	1341	1368
14	899	931
16	830	830
18	436	448
20	362	358
4,2,L		
4	2251	2386
6	2638	2917
8	1846	1916
10	2127	2177
12	1177	1161
14	985	978
16	635	633
18	562	549
20	385	384
6,2,L		
4	3198E	3763
6	2110	2179
8	2074	2082
10	1233	1212
12	1266	1259
14	867	870
16	761	742
18	415	420
20	320	329
8,2,L		
4	1383	1334
6	1720	1739
8	1189	1193
10	1423	1419
12	819	805
14	715	706
16	470	483
18	395	415
10,2,L		
4	1840	1886
6	1228	1235
8	1228	1235
10	826	836
12	841	845
14	609	622
16	540	525
18	288	319
12,2,L		
4	964	986
6	1110	1140
8	784	826
10	873	905
12	560	565
14	478	490
16	304	355
14,2,L		
4	1146	1168
6	855	868
8	788	798
10	586	602
12	524	543
14	404	409
16,2,L		
4	687	689
6	702	713
8	535	549
10	523	544
12	388	373
18,2,L		
4	524	521
6	462	425
8	373	385
0	318	323
20,2,L		
4	271	324
6	323	326
3,3,L		
3	2192	2377
5	1643	1642
7	1611	1632
9	1106	1118
11	880	888
13	743	737
15	521	530
17	394	399
19	251	269
5,3,L		
5	1037	1030
7	1200	1181
9	912	926
11	788	767
13	584	602
15	387	397
17	286	309
19	214	227
7,3,L		
5	1274	1277
7	1238	1242
9	841	867
11	679	686
13	605	595
15	421	440
17	301	332
19	171	216
9,3,L		
5	747	778
7	843	863
9	716	725
11	588	607
13	456	476
15	296	310
17	287*	244
11,3,L		
5	730	738
7	726	730
9	493	524
11	404	419
13	356	380
15	245	286
17	329*	218
13,3,L		
5	541	552
7	569	583
9	479	498
11	432	414
13	357	325
15	212	212
15,3,L		
5	438	446
7	405	434
9	304	319
11	266	253
13	250	228
17,3,L		
5	279	309
7	334	319
9	253	272
11	230	224
19,3,L		
5	355*	229
7	238	222
4,4,L		
4	2333	2391
6	1749	1803
8	1933	1993
10	1608	1625
12	1259	1255
14	797	801
14	663	683
18	478	490
20	387	391
6,4,L		
6	2523	2671
8	1152	1147
10	1521	1530
12	846	879
14	990	986
16	612	612
18	455	460
8,4,L		
6	1442	1497
8	1499	1546
10	1230	1232
12	966	963
14	636	635
16	541	537
18	363	386
10,4,L		
6	1877	1900
8	1065	1064
10	1172	1171
12	728	744
14	747	734
16	497	478
18	362	351
12,4,L		
6	963	985
8	948	984
10	794	802
12	619	639
14	439	451
16	342	379
14,4,L		
6	897	906
8	581	586
10	609	635
12	412	446
14	415	422
16,4,L		
6	536	572
8	505	549
10	472	466
12	380	375
18,4,L		
6	483	494
8	353	365
10	358	358
5,5,L		
5	534	532
7	842	862
9	576	601
11	601	605
13	409	433
15	297	324
17	229	232
19	266*	189
7,5,L		
7	970	971
9	589	620
11	564	559
13	451	452
15	370	365
17	286	260
19	213*	181
9,5,L		
7	712	729
9	548	564
11	508	511
13	364	375
15	244	260
17	207	193
11,5,L		
7	624	630
9	383	423
11	351	357
13	310	306
15	216	240
17	270*	175
13,5,L		
7	483	482
9	368	396
11	291	343
13	273	262
15	257*	176
15,5,L		
7	322	335
9	216	238
11	272*	198
13	193	178
17,5,L		
7	225	251
9	206	212
11	235*	179
19,5,L		
7	173	186
6,6,L		
6	1956	2012
8	1642	1651
10	1201	1193
12	1064	1056
14	788	797
16	637	641
18	409	392
8,6,L		
8	987	1007
10	1256	1270
12	703	710
14	643	658
16	399	440
18	361	375
10,6,L		
8	1043	1055
10	807	819
12	702	736
14	566	572
16	470	462
12,6,L		
8	693	729
10	790	815
12	503	510
14	431	453
16	317	324
14,6,L		
8	679	695
10	517	561
12	464	478
14	360	372
16,6,L		
8	471	488
10	479	486
12	322	336
18,6,L		
8	329	346
7,7,L		
7	897	983
9	662	693
11	581	574
13	497	476
15	323	358
17	233	265
9,7,L		
9	548	562
11	474	485
13	347	378
15	228	258
17	169	198
11,7,L		
9	386	416
11	312	345
13	266	303
15	222	229
13,7,L		
9	387	396
11	305	333
13	235	262
15	192	176
15,7,L		
9	281	265
11	185	213
13	211	186
17,7,L		
9	250	221
8,8,L		
8	1112	1177
10	830	849
12	731	748
14	468	474
16	389	428
10,8,L		
10	826	836
12	557	592
14	519	533
16	385	378
12,8,L		
10	585	584
12	476	496
14	333	346
14,8,L		
10	451	477
12	321	356
16,8,L		
10	349	358
9,9,L		
9	505	490
11	377	378
13	278	327
15	319*	201
11,9,L		
11	253	284
13	258	263
15	300*	181
13,9,L		
11	240	260
13	246	218
15,9,L		
11	232*	159
10,10,L		
10	598	604
12	561	573
14	425	419
12,10,L		
12	423	411
14	333	339
14,10,L		
12	376	366
11,11,L		
11	283*	213
13	343*	206
12,12,L		
12	344	340

[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 F's obtained from $I + 2\sigma_I$). Reflections suspected of suffering secondary extinction are indicated by an E.

TABLE II
Positional Parameters ($\times 10^4$) and Thermal Parameters ($\times 10^2$)[a]

Species	x/a	y/b	z/c	B_{11} or B	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
K^+	1/4	1/4	1/4	371 (4)					
Pb^{2+}	0	0	1/2	163 (1)					
Cu	0	0	0	136 (1)					
N	0	0	1978 (4)	217 (13)	218 (12)	300 (16)	0	0	0
O	0	1011 (2)	2586 (3)	498 (19)	223 (9)	336 (13)	0	0	−55 (7)

Root Mean Square Displacements (Å) for Principal Axes of Thermal Ellipsoids[b]

Species	Axis 1	Axis 2	Axis 3
K^+	0.217 (1)	0.217 (1)	0.217 (1)
Pb^{2+}	0.143 (1)	0.143 (1)	0.143 (1)
Cu	0.131 (1)	0.131 (1)	0.131 (1)
N	0.166 (5)	0.166 (5)	0.198 (5)
O	0.159 (3)	0.213 (4)	0.251 (5)

[a] Parameters for which no standard deviations are given are fixed by symmetry considerations. The anisotropic temperature factor is defined as $\exp(-{}^1/_4\Sigma_{i=1}{}^3\Sigma_{j=1}{}^3 B_{ij}h_ih_ja_i{}^*a_j{}^*)$. [b] Orientation of thermal ellipsoids may be seen by reference to Figure 1.

TABLE III

INTERATOMIC DISTANCES AND ANGLES

	This work	Neutron[5]	Ref 3a	Ref 3b	$K_2BaCo(NO_2)_6$[a]	$NaNO_2$[b]
Cu–N, Å	2.111 (4)	2.114 (5)	2.24	2.03		
N–O, Å	1.260 (4)	1.224 (5)	1.15	1.38	1.23 (2)	1.240 (3)
Pb–O, Å	2.793 (3)	2.794 (5)	2.87	2.72	2.87 (2) (Ba–O)	
K–O, Å	3.106 (1)	3.116 (5)	3.10	3.13	3.13 (1)	
O–O, Å	2.159 (5)	2.098 (8)	2.13	2.23	2.04 (2)	2.090 (5)
O–N–O, deg	117.9 (4)	118.2 (1)	136	108	114 (2)	114.9 (5)

[a] Reference 12. [b] M. I. Kay and R. C. Fraser, *Acta Crystallogr.*, **14,** 56 (1961).

flection was set equal to zero. At this stage of refinement all other reflections were given unit weight.

A careful study of the list of structure factors showed several reflections with F_c very much larger than F_o. Since these reflections were all very intense, it appeared they were suffering from secondary extinction, a conclusion confirmed when the data were investigated by the method of Housty and Clastre.[11] The 31 most intense reflections were therefore not considered in further refinements. Further refinement with anisotropic temperature factors lowered R to 0.040.

The parameters at this point showed no significant deviations from those required by the cubic space group $Fm3$ and refinement was therefore continued in $Fm3$. Intensities of reflections related by threefold rotation were averaged. The standard deviations of the averaged intensities were taken as the higher of the two possible values, the empirical range deviation or the root-mean-square average of the three individual standard deviations. Of the 464 independent averaged intensities, 20 had $I_{av} \leq 2\sigma_{I,av}$ and were treated as "unobserved." Eleven reflections were considered to suffer from secondary extinction and were omitted from least-squares calculations.

Three cycles of refinement on the averaged data were performed, again assuming a unit weight scheme, lowering the conventional R to 0.029, while the weighted R, defined as $(\Sigma w|F_o - F_c|^2/\Sigma w|F_o|^2)^{1/2}$, was 0.035. Further refinement using a scheme in which w was inversely proportional to the variance of the F's decreased the conventional R to 0.028 and the weighted R to 0.027. The error in an observation of unit weight was 1.2, in good agreement with the ideal value of 1.0. All shifts in the last cycle were less than one standard deviation.

A list of F_o and F_c values is given in Table I. Positional and thermal parameters are given in Table II, along with the root-mean-square displacements of the atoms.

Description and Discussion of the Structure

The overall structure of $K_2PbCu(NO_2)_6$ confirms that obtained by earlier X-ray determinations,[3] as well as the recent neutron diffraction study.[5] It is isostructural with $K_2BaCo(NO_2)_6$.[12] In the $Cu(NO_2)_6^{4-}$ anion the NO_2^- groups trans to each other are coplanar and parallel to the axial planes. Figure 1 shows this anion.

If the unit cell is viewed down one of the crystallographic axes, the structure may be seen to consist of alternating layers of two types. At $z = 0$ there is a layer of lead ions and hexanitrocuprate anions alternating parallel to the crystallographic axes. The next layer, at $z = 1/4$, consists of potassium ions. The layer at $z = 1/2$ is the same as the first with the positions of the lead cations and hexanitrocuprate anions interchanged.

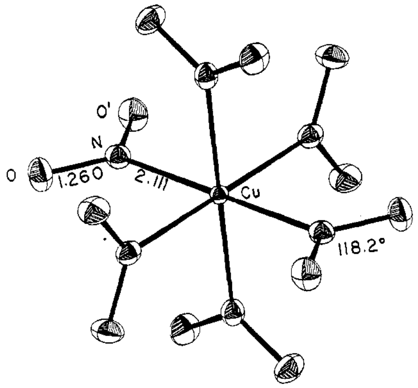

Figure 1.—Structure of the hexanitrocuprate anion.

Table III lists the bond lengths and angles found in this determination and compares them with earlier work. The values agree quite well with the neutron diffraction data,[5] except for the N–O distance. The large discrepancies in the earlier X-ray studies are probably due to inaccuracies in two-dimensional structure determinations.

The Cu–N bond of 2.111 (4) Å is significantly longer than the equatorial Cu–N bonds in planar or distorted octahedral complexes, but it is shorter than the Cu–N distance of 2.150 (2) Å in $Cu(en)_3SO_4$,[13] which also has six donor atoms equidistant from the metal ion. Such a lengthening is also found in $Cu(OMPA)_3(ClO_4)_2$,[2] in which the Cu–O bond of 2.065 (2) Å is longer than those reported in more usual tetragonally distorted complexes.

The symmetry of the anion is T_h, which should be unstable according to the Jahn–Teller theorem.[1] Several explanations have been proposed for the apparent violation of this theorem. (1) The statically distorted hexanitrocuprate ions are undergoing hindered rotation in the lattice.[14] (2) The crystal is composed of blocks with tetragonal symmetry but with equal numbers of blocks in all three orthogonal orientations (microscopic twinning). (3) Each anion is trapped in one of three mutually perpendicular tetragonal distortions. Anions in each of these distortions are distributed at random throughout the crystal, so that, on a space average, the structure appears regular.[13,14] (4) The complex is oscillating among the three tetragonal distortions, so that, on a time average, the structure appears regular. This is generally referred to as the dynamic Jahn–Teller effect.[14,15] (5) There is something "special" about the lead ion.[14,16]

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

[12] J. A. Bertrand and D. A. Carpenter, *Inorg. Chem.*, **5,** 514 (1966).

[13] D. L. Cullen and E. C. Lingafelter, *ibid.*, **9,** 1858 (1970).

[14] H. Elliott, B. J. Hathaway, and R. C. Slade, *ibid.*, **5,** 669 (1966).

[15] N. S. Ham, *Spectrochim. Acta*, **18,** 775 (1962).

[16] B. J. Hathaway and R. C. Slade, *J. Chem. Soc. A*, 85 (1968).

The first explanation is incorrect since no evidence of disorder was found in the X-ray determination. The second explanation is unlikely, since it would be expected to give split or broadened spots in the diffraction photographs, and no such effect was observed. If either explanation 3 or 4 were correct, the apparent thermal motion of the atoms, particularly that of the nitrogen atom, should be affected. Dunitz and Orgel[17] have predicted that the temperature factors of atoms in a complex with a dynamic Jahn–Teller effect should be unusually large and explanation 3 would give the same effect. In fact, the thermal parameters of all the atoms in this complex are of normal magnitude. The root-mean-square displacements for the nitrogen atom in the direction of the principal axes of the thermal ellipsoid are 0.166 (5), 0.166 (5), and 0.198 (5) Å. However, the longest axis, which on the basis of the estimated standard deviations is significantly longer, is in the direction of the Cu–N bond. Since bond-bending amplitudes are normally greater than bond-stretching amplitudes, this orientation of the thermal ellipsoid is clearly abnormal and suggests the presence of either the dynamic Jahn–Teller effect (explanation 4, above) or a static Jahn–Teller distortion and random orientation (explanation 3, above). In order to assess the possible significance of the anisotropy of the nitrogen atom thermal parameters we have carried out the following model calculation. Structure factors, $h00$, were calculated for hypothetical one-dimensional crystals containing a Cu^{2+} ion at $x = 0$, nitrogen at $x = \pm 2.00$ Å with an occupancy factor of $^2/_3$, and nitrogen at $x = \pm d$ with an occupancy factor of $^1/_3$, all atoms having $B = 2.0$ Å^2. Calculations were made for $d = 2.1, 2.2, 2.3, 2.4$, and 2.5 Å. Each of these sets of structure factors was then used as "observed" structure factors and a least-squares refinement was carried out, starting with Cu^{2+} at $x = 0$ and N at $x = 2.00$ Å. In each case the nitrogen atom refined to a position with x very slightly less than the weighted mean position and to a temperature factor, B, which increased markedly with the assumed separation. Comparison of the results of these calculations indicates that the anisotropy observed in $K_2PbCu(NO_2)_6$ corresponds to a separation of 0.22 Å, which is quite comparable with the difference of 0.25 Å between the longest and shortest Cu–O bonds in the distorted $Cu(H_2O)_6^{2+}$ octahedron in $Cu(NH_4)_2(SO_4)_2 \cdot 6H_2O$.[18] Thus, the results are in good agreement with either explanation 3 or 4.

In the neutron diffraction determination,[5] the nitrogen atom thermal ellipsoids are isotropic within the estimated standard deviations. The thermal parameters for all the atoms in this neutron study are of about the same magnitude as those in the present work. The published report on $K_2BaCo(NO_2)_6$ gave only isotropic thermal parameters.[12] Using the published list of structure factors, we have carried out an anisotropic refinement of $K_2BaCo(NO_2)_6$. However, due to the relative inaccuracy of the visually estimated photographic data, as well as the small number of reflections, the standard deviations are quite large, so that little significant information could be obtained. In $Cu(OMPA)_2(ClO_4)_2$[2] the nitrogen atom thermal ellipsoid is reported as essentially isotropic and of the same magnitude as in the Mg and Co complexes. In $Cu(en)_3SO_4$ we have found[13] the nitrogen atom thermal ellipsoid to be slightly larger than that in the isostructural complex, $Ni(en)_3SO_4$,[19] and elongated along the Cu–N bond direction. The rms displacements for the donor atoms in all these complexes are summarized in Table IV.

TABLE IV
ROOT-MEAN-SQUARE DISPLACEMENTS FOR DONOR ATOMS IN COMPLEXES WHICH ARE APPARENT VIOLATIONS OF THE JAHN–TELLER THEOREM

	Axis 1	Axis 2	Axis 3	Donor atom
$K_2PbCu(NO_2)_6$[a]	0.166 (5)[b]	0.166 (5)	0.198 (5)[c]	N
$K_2PbCu(NO_2)_6$[d]	0.163 (4)	0.175 (10)[c]	0.176 (10)	N
$K_2BaCo(NO_2)_6$[e]	0.18 (2)	0.18 (2)	0.18 (2)	N
$K_2BaCo(NO_2)_6$[a]	0.18 (1)	0.18 (1)[c]	0.22 (1)	N
$Cu(en)_3SO_4$[f]	0.191 (3)	0.211 (4)	0.232 (3)[c]	N
$Ni(en)_3SO_4$[g]	0.105 (10)[c]	0.158 (9)	0.186 (8)	N
$Cu(OMPA)_3(ClO_4)_2$[h]	0.215	0.248	0.263	O

[a] Work done in the present study. [b] The figures in parentheses are the standard deviations in the least significant digit. [c] Axis closest to the metal–donor atom bond. [d] Reference 5. [e] Reference 12. [f] Reference 13. [g] Reference 19. [h] Reference 2. $Ni(en)_3SO_4$ is included for comparison.

More positive evidence for the existence of a dynamic Jahn–Teller effect comes from other techniques. The X-ray powder pattern of $K_2PbCu(NO_2)_6$ is tetragonal at −38°, and the esr spectrum is temperature dependent, being isotropic at room temperature and anisotropic at liquid nitrogen temperatures.[14] These data are consistent with the theory of the structure "freezing" into a single tetragonal distortion at low temperatures.

The possibility of the lead ion being "special" is based on the observation that $K_2PbCu(NO_2)_6$ is cubic at room temperature, but $K_2BaCu(NO_2)_6$ and $K_2CaCu(NO_2)_6$ have tetragonal unit cells, presumably allowing the anion to be tetragonally distorted.[14] The hitherto unreported complex $K_2SrCu(NO_2)_6$ has now been prepared by a method analogous to that used to prepare $K_2PbCu(NO_2)_6$.[6] Its X-ray powder pattern shows that it is isomorphous with the barium–copper complex and not with the lead–copper complex. This would tend to discount packing arguments as an explanation for the cubic nature of the lead–copper complex, since the radius of strontium (1.14 Å) is about the same as lead (1.21 Å). It has been postulated[16] that because of the polarizability of the lead ion as compared with the alkaline earths, there is a lead–oxygen interaction which tends to stabilize the cubic structure. However, the mechanism for stabilizing this structure has not been discussed.

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[19] Mazar-Ul-Haque, C. N. Caughlan, and K. Emerson, *Inorg. Chem.*, **9**, 2421 (1970). for publication.