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The Structure of $K_2BaCo(NO_2)_6$ at 233°K.: A Static Jahn-Teller Distortion

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The structure of $K_2BaCo(NO_2)_6$ has been determined at 233°K; the crystals, which are cubic at room temperature, are orthorhombic, space group Fmmm, at 233°K with $a = 10.51(3)$ *Å,* $b = 10.68(3)$ *Å, and* $c = 10.51(3)$ *Å. The hexanitrocobaltate(II) ion, which appears to be octahedral with a cobalt-nitrogen distance of 1.98(2) Å at room temperature, is elongated along one axis to give cobalt-nitrogen distances of 1.90(2) Å, 1.94(6) Å, and 2.10(2) Å. The results are indicative of a dynamic Jahn-Teller distortion at room temperature and a static Jahn-Teller distortion at 233°K; the elongation along one axis is the type of distortion observed for most complexes of copper(II).*

Introduction

In a recent paper,[1] we reported the structure of $K_2BaCo(NO_2)_6$; although a Jahn-Teller distortion[2] was expected for the low-spin d^7 complex, $Co(NO_2)_6^{4-}$, the structure study gave no evidence of such a distortion. The nitrite groups along the x, y, and z axes of the complex were related by a three-fold axis of the cubic space group (Fm3) and, thus, no static distortion was possible. Although a dynamic Jahn-Teller effect could not be ruled out, the temperature parameters did not seem unusual when compared to values from other structure; however, an adequate comparison could not be made since values were not available for similar compounds which would not be subject to a Jahn-Teller distortion. Similar results from a neutron diffraction study[3] have been reported for $K_2PbCu(NO_2)_6$, which should also show a Jahn-Teller distortion.

ESR and X-ray diffraction studies[4] of powdered samples of $K_2PbCu(NO_2)_6$ have provided evidence for a static Jahn-Teller effect at 235°K. The ESR spectrum changed from isotropic at room temperature to anisotropic at the lower temperature; the x-ray data indicated a transition from cubic to tetragonal. ESR data[5] have indicated a similar change in $K_2BaCo(NO_2)_6$.

In order to obtain more information about the Jahn-Teller distortion in $K_2BaCo(NO_2)_6$, we have determined the crystal structure at 233°K.

Experimental Section

An octahedral-shaped crystal of $K_2BaCo(NO_2)_6$, *ca.* 0.1 mm from apex-to-apex, was mounted on a precession camera equipped with a Cryo-Tip refrigeration system.[6] An x-ray diffraction photograph of the *hk0* zone was obtained at room temperature; the crystal was then cooled and additional photographs were obtained at 10° intervals. At 263°K, a teransition occurred; the *hk0* zone still showed mm symmetry and the same systematic absences ($h+k=2n+1$ absent) but the two axes were no longer equal ($a=10.51(3)$ Å, $b=10.86(3)$ Å). The *0kl* zone at 263°K also showed mm symmetry with $c=10.51(3)$ Å. Although two axes were found to be of equal length and the powder diffraction pattern of the crystal could thus be indexed as tetragonal, the intensities of reflections in the two zones were not consistent with the four-fold symmetry necessary for a tetragonal cell. The diffraction symmetry and the systematic extinction of $hk\ell$ reflections with odd values of $(h+k)$, $(k+\ell)$, or $(h+\ell)$ indicated a face-centered orthorhombic lattice. Since removal of the three-fold axis of the cubic space group, Fm3, found at room temperature would give orthorhombic space group Fmmm, that space group was assumed; the successful refinement of the structure confirms that choice.

Photographs taken below the transition temperature always showed a second lattice of lower intensity; the second lattice was identical to the first but was elongated along *a* rather than along *b* and was rotated *ca* 5° with respect to the first. On warming the crystal to room temperature, the diffraction photographs again showed only one cubic lattice; the same result was obtained repeatedly with several different crystals.

Intensity data were collected with the precession camera, using Zr-filtered Mo Kα radiation, and estimated visually; although there were two lattices, the reflections of the two were sufficiently separated to allow estimation of the intensities of the more intense lattice. A total of 244 independent, non-zero reflections from the $hk\ell$ (ℓ=0-3) and $hk\ell$ (h=0-3) levels were collected; the intensities were corrected for Lorentz and polarization effects but no absorption corrections were made

Computations were carried out on a Burroughs B-5500 computer and on a Univac 1108 computer; programs employed included modified versions of the

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(1) J. A. Bertrand and D. A. Carpenter, *Inorg. Chem.*, 5, 415 (1966).

(2) H. A. Jahn and E. Teller, *Proc. Roy. Soc.* (London) *A161*, 220 (1937).

(3) N. W. Isaacs and C. H. L. Kennard, *J. Chem. Soc.* (A), 386 (1969).

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

(5) B. J. Hathaway, Private Communication.

(6) Air Products and Chemicals, Inc., Advanced Products Dept., Allentown, Penn

Busing-Martin-Levy ORFLS and ORFFE least-squares and function and error programs and various locally written programs. In structure factor calculations, the scattering factors tabulated by Ibers[7] were employed for all atoms.

All atoms were assigned coordinates from the room temperature cubic structure; because of the lower symmetry the nitrogen and oxygen atoms along each crystallographic axis were no longer equivalent and could be varied independently. Least-squares refinement using isotropic temperature factors and with all reflections weighted at unity converged to a conventional R value ($R=\Sigma\,||F_o|-|F_c||\;/\;\Sigma|F_o|$) of 0.09. Final coordinates and thermal parameters are listed in Table I; final F_o and F_c values are listed in Table II.

Table I. Final positional and thermal parameters for $K_2BaCo(NO_2)_6$

Atom	x	y	z	B(Å²)
K	¼	¼	¼	2.4(1)
Ba	½	0	0	1.1(1)
Co	0	0	0	0.8(1)
N1	0	0	0.184(6)	2.2(5)
N2	0	0.193(2)	0	1.1(4)
N3	0.181(2)	0	0	0.3(4)
01	0.099(1)	0	0.249(3)	2.5(3)
02	0	0.255(2)	0.107(3)	2.1(3)
03	0.246(2)	0.098(1)	0	1.8(3)

Table II. Observed and calculated structure factors (electrons) for $K_2BaCo(NO_2)_6$

H	K	L	FO	FC
4	0	0	1003	1071
6	0	0	300	331
8	0	0	653	654
10	0	0	243	288
0	2	0	541	514
2	2	0	552	572
4	2	0	87	84
6	2	0	308	310
8	2	0	178	181
10	2	0	326	342
0	4	0	1170	1110
2	4	0	707	678
4	4	0	509	480
6	4	0	683	676
8	4	0	606	635
10	4	0	314	341
0	6	0	361	312
2	6	0	435	434
4	6	0	73	74
6	6	0	690	655
8	6	0	144	132
0	8	0	689	680
2	8	0	316	298
4	8	0	453	439
6	8	0	222	233
8	8	0	333	336
0	10	0	321	347
2	10	0	286	301
4	10	0	217	207
6	10	0	224	235
0	12	0	387	409
2	12	0	189	189
4	12	0	338	293
3	1	1	244	233
5	1	1	43	62
7	1	1	116	134
9	1	1	83	110
1	3	1	214	188
3	3	1	256	267
5	3	1	126	133
7	3	1	133	149
9	3	1	134	150
1	5	1	81	81
3	5	1	156	167
5	5	1	75	74
7	5	1	82	82
9	5	1	107	111
1	7	1	111	110
3	7	1	188	140
5	7	1	102	96
7	7	1	106	109
9	7	1	109	117
1	9	1	122	111
3	9	1	163	158
5	9	1	88	82
7	9	1	109	109
1	11	1	89	94
1	13	1	103	94
3	13	1	115	123
4	0	2	625	647
6	0	2	670	622
8	0	2	297	292
10	0	2	271	280
12	0	2	180	271
4	2	2	609	590
6	2	2	255	277
8	2	2	322	347
10	2	2	118	113
12	2	2	233	249
0	4	2	97	99
2	4	2	572	699
4	4	2	332	278
6	4	2	726	666
8	4	2	129	130
10	4	2	343	320
12	4	2	168	138
0	6	2	414	389
2	6	2	291	279
4	6	2	458	459
6	6	2	367	352
8	6	2	238	250
10	6	2	163	181
12	6	2	180	205
0	8	2	223	194
2	8	2	301	349
4	8	2	248	251
6	8	2	396	385
8	8	2	125	134
10	8	2	181	219
12	8	2	120	126
0	10	2	452	402
2	10	2	124	127
4	10	2	440	403
6	10	2	180	190
8	10	2	246	257
10	10	2	123	108
0	12	2	183	179
2	12	2	236	226
4	12	2	182	187
6	12	2	220	243
8	12	2	98	116
0	14	2	176	191
2	14	2	124	125
4	14	2	168	184
5	1	3	117	122
7	1	3	149	167
9	1	3	115	135
1	1	3	75	83
3	1	3	81	86
5	3	3	103	103
7	3	3	190	180
9	3	3	160	178
11	3	3	109	95
13	3	3	116	125
1	5	3	123	126
3	5	3	168	175
5	5	3	100	99
7	5	3	114	101
9	5	3	106	123
1	7	3	108	183
3	7	3	218	221
5	7	3	137	141
7	7	3	146	144
9	7	3	133	143
11	7	3	81	78
1	9	3	144	118
3	9	3	156	141
5	9	3	76	87
7	9	3	112	112
9	9	3	115	100
1	11	3	113	91
3	11	3	139	127
7	11	3	82	88
9	11	3	82	70
1	13	3	83	83
3	13	3	118	121
7	13	3	81	86
0	14	3	147	156
0	0	2	657	589
0	2	2	609	604
0	0	4	998	1061
0	2	4	679	677
0	4	4	657	586
0	6	4	435	418
0	8	4	416	442
0	10	4	325	376
0	12	4	299	307
0	14	4	192	175
0	0	6	317	358
0	2	6	670	612
0	4	6	122	125
0	6	6	459	470
0	8	6	170	164
0	10	6	416	390
0	12	6	148	155
0	14	6	181	195
0	0	8	701	701
0	2	8	279	276
0	4	8	471	472
0	6	8	216	204
0	8	8	383	370
0	10	8	235	233
0	12	8	271	262
0	0	10	390	328
0	2	10	273	303
0	4	10	222	199
0	6	10	290	242
0	8	10	183	181
0	10	10	295	247
0	0	12	444	387
0	2	12	210	280
0	4	12	318	241
0	6	12	214	188
0	8	12	295	289
0	0	14	157	154
0	2	14	242	225
0	4	14	115	96
1	1	3	187	202
1	3	3	237	282
1	1	5	42	63
1	3	5	131	148
1	7	5	134	120
1	1	7	140	117
1	3	7	172	160
1	5	7	59	88
1	7	7	120	120
1	9	7	93	90
1	11	7	85	81
1	1	9	117	106
1	3	9	136	130
1	5	9	78	87
1	7	9	107	97
1	9	9	110	88
1	11	9	48	44
1	1	11	93	63
1	3	11	116	86
1	5	11	59	49
1	7	11	70	67
1	9	11	66	55
1	1	13	96	69
1	3	13	117	90
1	5	13	44	40
2	14	0	165	218
2	0	4	108	74
2	2	4	741	697
2	4	4	238	279
2	6	4	597	664
2	8	4	101	126
2	10	4	252	334
2	12	4	91	106
2	14	4	195	228
2	0	6	407	407
2	2	6	301	238
2	4	6	491	487
2	6	6	277	330
2	8	6	226	275
2	10	6	142	164
2	12	6	178	188
2	14	6	174	197
2	0	8	276	214
2	2	8	346	313
2	4	8	246	287
2	6	8	323	358
2	8	8	140	155
2	10	8	203	202
2	12	8	126	116
2	14	8	117	152
2	0	10	403	343
2	2	10	130	102
2	4	10	404	374
2	6	10	166	170
2	8	10	249	235
2	10	10	90	96
2	12	10	215	152
2	0	12	141	141
2	2	12	305	244
2	4	12	290	176
2	6	12	291	263
2	8	12	143	105
2	10	12	221	163
2	0	14	238	150
2	2	14	147	110
2	4	14	225	170
2	6	14	196	141

Discussion

The only change in the hexanitrocobaltate(II) ion in going from room temperature to 233°K is in the lengths of the cobalt-nitrogen bonds. At room temperature, all of the cobalt-nitrogen bonds are equivalent and 1.98(2) Å in length; below the transition point the three independent cobalt-nitrogen bond lengths are 1.94(6) Å, 2.10(2) Å, and 1.90(2) Å along the x, y, and z axes, respectively. Although the standard deviation of the bond along x is extremely high, the complex appears to be elongated along one axis in the same way as most copper(II) complexes. The magnitude of the distortion agrees well with theoretical predictions.[8]

Table III.

Atoms	This Work	Reference 1
Co-N1	1.93(6)Å	
Co-N2	2.10(2)	
Co-N3	1.91(2)	
Co-N(Avg)	1.98(8)	1.98(2)Å
N1-01	1.25(4)	
N2-02	1.31(3)	
N3-03	1.26(2)	
N-0(Avg)	1.27(3)	1.23(2)
Ba-01	2.84(2)	
Ba-02	2.89(2)	
Ba-03	2.87(2)	
Ba-0(Avg)	2.87(2)	2.87(2)
01-N1-01′	113(5)°	
02-N2-02′	118(3)	
03-N3-03′	115(2)	
0-N-0′(Avg)	115(3)	114(2)°

Three possible explanations[4] for the lack of distortion in the hexanitrocobaltate(II) ion at room temperature have been given: (1) the environment of each ion is tetragonal with the unique axis in one of three mutually perpendicular directions, the distribution of these directions throughout the lattice being random; (2) the ion environments are undergoing a dynamic tetragonal distortion in three perpendicular directions in the lattice; (3) the statically distorted hexanitrocobaltate(II) anions are undergoing free rotation in the lattice. The third possibility is not consistent with the observation of discrete nitrogen and oxygen positions at room temperature and the first possibility is not consistent with a transition to an ordered structure as the temperature is lowered; thus, only the second possibility — a dynamic tetragonal distortion — is consistent with all of the observations.

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