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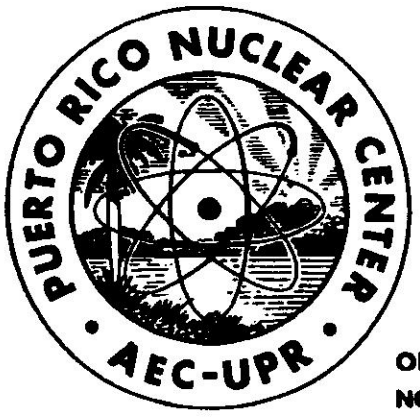
CRYSTAL STRUCTURE OF $CoBr_2 \cdot 6H_20$ AT ROOM TEMPERATURE BY NEUTRON DIFFRACTION



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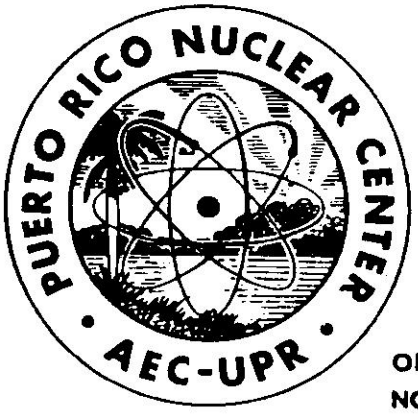
BY NEUTRON DIFFRACTION

By Robert Kleinberg



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Crystal Structure of $CoBr_2 \cdot 6H_2O$ at Room Temperature by Neutron Diffraction *

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Atomic parameters in paramagnetic $CoBr_2 \cdot 6H_2O$ have been determined at room temperature from a single-crystal neutron-diffraction study in which the intensities of 67 independent reflections of the $h0\ell$ zone were measured. Isotropic least-squares refinement of the structure gave a final value of 0.051 for the reliability factor R. A study of the atomic parameters shows that this salt is isomorphous to cobalt and nickel chloride hexahydrate. The Co-Br, and H···Br bond lengths were found to be 2.58, and 2.36 Å, respectively. Unit cell parameters were found to be $a = 10.93$, $c = 6.86$, and $\beta = 124°50'$.

* Work performed under the auspices of the U. S. Atomic Energy Commission.

INTRODUCTION

The magnetic structure and spin direction in antiferromagnetic $CoCl_2 \cdot 6H_2O$ has been discussed in a previous report.[1] In the present paper, the same properties are discussed for $CoBr_2 \cdot 6H_2O$. In a preliminary experiment on the latter salt, the magnetic structure was confirmed to be the same as in the chloride. An attempt to accurately determine the spin direction was not successful, since the crystal used in the experiment was not a single crystal, and neither of the individual crystallites could be aligned to give reflections exclusive of the other crystallite. It was decided, therefore, to repeat this experiment as soon as low-temperature facilities became available at the Puerto Rico Nuclear Center. Unfortunately the crystal to be used was again composed of two crystallites, but in this case it was noted that the splittings of the reflections were quite small and were constant. It was decided to make a room-temperature study on the $h0\ell$ zone, to determine just how good an R factor could be obtained with this crystal before proceding with the low-temperature work. Further it would be possible to confirm that the crystal structure of this salt is indeed isomorphous to that of the cobalt and nickel chlorides, and also to make a direct measurement of the Co-Br bond length.

EXPERIMENTAL

A large crystal of $CoBr_2 \cdot 6H_2O$ was grown from aqueous solution at about 27°C, and had a habit similar to that of the corresponding cobalt and nickel chlorides.[2] The crystal was ground into a cylinder with b as axis. Grinding was accomplished by slowly rubbing the crystal over a damp cotton cloth. The cylinder obtained by this process had the dimensions: diameter = 4.2 mm; length = 7 mm. The crystal was glued to an aluminum mount and protected from atmosphere by means of a thin-walled titanium-zirconium cap, sealed with silicone grease. Under this condition it remained stable during the course of the experiment.

Unit cell parameters were determined by measuring the coordinates of 11 reciprocal lattice points, ten of which were below 36° in two-theta, and then finding the parameters which gave the best least-squares fit between the measured and calculated coordinates. The quantities minimized were $\left[\sum\theta_o(2\theta_o-2\theta_c)^2/\sum\theta_o\right]^{1/2}$, and $\left[\sum(\phi_o-\phi_c)^2\right]^{1/2}$. Parameters determined by this procedure are as follows: a = 10.93, c = 6.86 Å, and β = 124° 50'. The wavelength used was 1.064 Å.

Intensity measurements yielded 67 observed independent h0ℓ reflections. A reflection was defined to be unobserved, when from counting statistics the intensity was less than three times its standard deviation. Measurements were made for theta less than 45.5°. Since the incoherent scattering from hydrogen is large, cylindrical absorption corrections were applied to each intensity measurement ($\Sigma R = 0.956$). Absorption-correction factors were determined from Table 5.35B in the International Tables for X-Ray Crystallography.[3]

REFINEMENT OF THE STRUCTURE

The data were refined by full-matrix least squares based on F, using the Los Alamos Crystal Structure Least Squares Program, GENLES.[4] Twenty-five parameters, including 2 scale factors, 14 atomic parameters, 8 isotropic thermal parameters, and 1 extinction parameter, were determined from the 67 reflections. Scattering lengths for Co, Br, O, and H were assumed to be 0.250, 0.670, 0.577, and -0.374 $\times 10^{-12}$ cm. respectively, and were held constant during the least-squares calculation. The quantity minimized was $\sum w \left||F_o| - |F_c^*|\right|^2$, where

$$F_c^* = KF_c\left[1 + g\frac{F_c^2}{\sin 2\theta}\right]^{-1/4},$$

in which g is proportional to the secondary extinction parameter.[5] The weights w are given by $\left[\sigma(F_o) + 0.025F_o\right]^{-2}$, where $\sigma(F_o)$ is the standard deviation of the structure factor as determined from counting statistics. Unobserved reflections were given zero weight, and were not included in the reliability factor calculations. Refinement was continued until $\Delta\xi_i / \sigma(\xi_i) < 7.4 \times 10^{-4}$ for all least-squares parameters ξ_i. At the termination of the computation, the reliability factor $R = \sum\left||F_o| - |F_c^*|\right| / \sum |F_o|$, was 0.051. The root-mean-square reliability factor $\left[\sum w|\Delta F|^2 / \sum wF_o^2\right]^{1/2}$ was 0.0666. Final positional and isotropic-thermal parameters with their calculated standard deviations are given in Table I, while the observed and calculated structure factors are listed in Table II. Structure factors calculated from unobserved intensities are enclosed in parenthesis.

DISCUSSION

As expected, the bromine atomic parameters are different from the chlorine parameters in cobalt chloride hexahydrate,[6] giving a longer metal-halogen bond of 2.58 as compared to 2.43 Å, for Co-Cl. The remaining parameters agree reasonably well with the corresponding parameters in the cobalt and nickel chlorides.

Bond lengths and angles calculated from the parameters of Table I, are listed in Table III. On comparing these results with the corresponding bond lengths in cobalt and nickel chloride hexahydrate, it is observed that: bond lengths involving bromine are longer than the equivalent lengths in the chlorides, and fall within the expected range of values; bond lengths involving hydrogen and no bromine atoms agree within experimental error with the corresponding lengths in the nickel chloride; and bond lengths and angles not involving hydrogen or bromine agree within experimental error with the lengths and angles in $CoCl_2 \cdot 6H_2O$.

The object of the experiment reported here was to determine the hydrogen-atom positions, and to determine the feasibility of using the crystal for precise low-temperature work. It has resulted in an R factor which indicates that the crystal should give accurate values for the magnetic properties at low temperatures. It has also given the atom positions, as well as the Co-Br bond distance.

ACKNOWLEDGMENTS

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TABLE I. Positional and thermal parameters in $CoBr_2 \cdot 6H_2O$ determined from isotropic least-squares refinement of room-temperature neutron-diffraction data.

atom	x	z	B
Co	0	0	2.2 (4)
Br	0.281 (1)[a]	0.179 (1)	2.5 (2)
O_I	0.0370(7)	0.2454(9)	3.4 (2)
O_{II}	0.285 (1)	0.696 (2)	3.4 (3)
H1	0.104 (1)	0.276 (2)	4.7 (3)
H2	0.452 (1)	0.226 (1)	4.7 (3)
H3	0.196 (2)	0.558 (3)	5.7 (6)
H4	0.265 (3)	0.821 (3)	4.3 (4)

[a] Throughout this paper the standard deviation of a function is given in the parenthesis following the function, and its value corresponds to the least significant digits in the function value.

TABLE II. Observed and calculated structure factors for $CoBr_2 \cdot 6H_2O$, determined from room-temperature neutron-diffraction data.

h	k	l	F_o	F_c	h	k	l	F_o	F_c
0	0	1	160	165	6	0	-2	453	-456
0	0	1	158	165	6	0	-2	454	-456
0	0	2	200	-195	6	0	-1	565	550
0	0	3	86	92	6	0	-1	551	550
0	0	4	89	71	6	0	0	184	182
0	0	5	(0)	19	6	0	1	373	-370
0	0	6	70	77	6	0	1	386	-370
0	0	7	(21)	26	6	0	2	117	119
2	0	-8	120	111	6	0	3	343	305
2	0	-7	72	-90	6	0	4	(41)	-50
2	0	-6	188	-174	8	0	-9	191	177
2	0	-5	255	243	8	0	-8	(0)	17
2	0	-4	97	86	8	0	-7	167	-174
2	0	-3	92	-72	8	0	-6	229	216
2	0	-2	147	162	8	0	-5	367	349
2	0	-1	50	51	8	0	-4	336	-323
2	0	0	55	-53	8	0	-3	488	-465
2	0	1	122	-123	8	0	-2	437	424
2	0	1	119	-123	8	0	-1	515	465
2	0	2	238	237	8	0	0	(13)	23
2	0	3	52	55	8	0	1	399	-358
2	0	4	192	176	8	0	2	(16)	-76
2	0	5	(33)	-69	8	0	3	186	171
2	0	6	170	-179	10	0	-9	103	116
4	0	-8	(39)	-47	10	0	-8	185	-196
4	0	-7	(0)	12	10	0	-7	292	-277
4	0	-6	272	287	10	0	-6	153	175
4	0	-5	(50)	0	10	0	-5	358	366
4	0	-4	100	-91	10	0	-4	125	120
4	0	-3	223	-235	10	0	-3	242	-228
4	0	-2	(60)	2	10	0	-2	126	-131
4	0	-1	378	381	10	0	-1	150	143
4	0	-1	379	381	10	0	0	(45)	4
4	0	0	448	450	10	0	1	(67)	35
4	0	0	439	450	12	0	-8	(44)	24
4	0	1	314	-336	12	0	-7	(51)	54
4	0	1	316	-336	12	0	-6	90	118
4	0	2	561	-552	12	0	-5	80	-29
4	0	3	330	350	12	0	-4	261	-275
4	0	4	374	380	12	0	-3	103	89
4	0	5	77	-82	12	0	-2	304	321
6	0	-9	106	130	12	0	-1	(52)	33
6	0	-8	(56)	30	12	0	0	146	-150
6	0	-7	270	-284	14	0	-7	(55)	67
6	0	-6	245	-238	14	0	-6	130	159
6	0	-5	524	542	14	0	-5	(44)	-23
6	0	-4	415	421	14	0	-4	(53)	41
6	0	-3	446	-456	14	0	-3	(62)	47

TABLE III. Interatomic distances and bond angles in $CoBr_2 \cdot 6H_2O$ at room temperature.

Co-Br	2.58 (1) Å
Co-O_{II}	3.94 (2)
O_I-O_I	2.98 (1)
O_{II}-H3	0.89 (3)
O_{II}-H4	0.99 (2)
H3-H4	1.51 (3)
O_{II}-Br"	3.33 (2)
Br"-H4	2.36 (2)
H3-O_{II}-H4	107 (2)°
O_{II}-H4-Br"	168 (1)°