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PUERTO RICO NUCLEAR CENTER

CRYSTAL STRUCTURE OF Colley 6H,0 AT ROOM TEMPERATURE

BY NEUTRON DIFFRACTION

OPERATED BY UNIVERSITY OF PUERTO RICO UNDER CONTRACT

NO. AT 40-11-1833 FOR U. 5. ATOMIC ENERGY COMMISSION

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PUERTO RICO NUCLEAR CENTER

CRYSTAL STRUCTURE OF CoBr2.6H20 AT ROOM TEMPERATURE

BY NEUTRON DIFFRACTION

By Robert Kleinberg

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Crystal Structure of CoBr,"6ii0 at Room Temperature by Neutron Diffraction *

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Atomic parameters in

Fanagnetic CoBry: 64,0 have been deternined

?At room teaperature from a single-crystal neutron-di fraction

eudy im

which the intensities of 67 independent reflections of the hOL zone

were measured. Isotropic least-squares refinesent of the structure

@ Final velue of 0.051 for the reliability factor R, A study of the atonie Parameters shovs that thie salt is isomorphous to cobalt and nickel chloride hexahydrate, The ComBr, and H+--Br bond Lengths were found to be 2.58,

and 2.362, respectively. Unit cell parane

8 were found to be 4 = 10.93,

© = 6.86, and §= 124°50",

Work performed under the auspices of the U, S, Atonle Energy Comal

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INTRODUCTION

?The magnetic structure and spin direction in anti ferromagnetic

(Cochz"61ig0 has been discussed in a previous report.! In rhe present

Paper, the same properties are discussed for CoBr,"6i0. In a prelim

Amary experiment on the Latter salt, the magnetic structure was confirmed

co be the sane

in the chloride. An attempt to accurately determine

the spin direction vas not successful, since the crystal used in the

riment vas not a single crystal, and neither of the individual

cryatallites could be aligned to give reflections exclusive of the other

crystallite, It was decided, therefore, to repeat thie experiment as

low-temperature facilities becane available at the Puerto Rico

Nuclear c

er. Unfortunately the crystal to be used vas again composed

of two crystallites, but in this case <t was noted that the

Aiteings

Of the reflections were quite small and vere constant. It was decided

to make @ room-temperature study on the nOL zone, to determine just how

food an R factor could be obtained with this crystal before proceding

with the low-temperature work. Further it vould be possible to confira

that the crystal structure of this salt 18 indeed taomorphous to the

of the cobalt and nickel chlorides, and algo to make a direct measurement

of the Co-Br bond Length.

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EXPERIMENTAL

?A Large crystal of Conrg'6i20 was grovn from aqueous solution at about

27°C, and had « habit similar to that of the corresponding cobalt

nickel chlorides.?

The crystal was ground into a cylinder with b

Grinding was accomplished by slovly rubbing the crystal over a

cloth. The cylinder obtained by thie proct

had the dimensions:

daneter = 4,2 um; length = 7 mm, The crystal vas glued to an alusinun

vount and protects

from atmosphere by means of a thin-walled eitantua-

sirconium cap, sealed vith silicone grease, Under this condition i¢

Fenained stable during the course of the experiment.

Unde cell paranetere were deterutned by measuring the coordinates of

AL reciprocal lattice potm

ten of which were below 36° in two-cheta,

and then finding the paranete

which gave the best least-squares f1¢

between the ses

ured and calculated coordinates, The quantities aininized

wre [Leegew7yy of, ane [Zee-497]2, rarenecers

determined by this procedure are as follows: «= 10.93, ¢ = 6.86%, and

9 = 1249 50". The wavelength used was 1.066 A.

?Intensity measurements yielded 67 observed independent nOL reflections.

A reflection vas defined to be unobservi

when from counting statistics

Antensity vas less than thre

times ice standard deviation, Measure:

ments vere mac

for theta less than 45.5° Since the incoherent scattering

from hydrogen i# large, cylindrical absorption corrections were appli

to each tn

naity measurement (IR = 0.956). Absorption-correction factors

were deternined from Table 5.358 in the International Tables for X-Ray

Cryatallography.?

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REPINEMEYE OF THE STRUCTURE

y full-matrix least squares based on F, using

che Loe Alamos Crystal Structure Least Squares Program, cEwuzs.* twenty-five

tncluding 2 scale factors, 14 atomte parameters, 8 Seotropic

thermal parameters, and 1 extinces:

Paraneter, vere determined from the 67

reflections, Scattering lengths for Co, Br, 0, and H vere assumed to be

0-250, 0.670, 0.577, and -0.376 x10"? em, respectively, and vere held con

stant during the 1 calculation. The quantity minimized vas

y?

im which g {8 proportional to the secondary extinction paramater.> The

Delle = lei ?, where

ft se tel

stab woe ates tg) + ase}? sare

deviation of the structure factor as determined from counting stattetice observed reflections vere given sero weight, and vere not incl Jed in the reliability factor calculations, Refinement vas continued unt!

SEL CE) < 7.6 x 10" for all Least-aquares parameters §:. At the Kermination of the computation, the reliability factor R= Silo - wey ZX igl wee 0.051. the root-mean

ware reliability factor

[Eviari?/De,7] was 0086s, rinat postion snd intzope-thecet

Peraneters with their calculated standard deviations are given in Table 1,

wile the observed and calculated structure factors are Listed in Table IT.

Structure factors calculated from unobserved intensities are enclo

parenthesis,

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prscussow

As expected, the bromine atoaic parameters are different from the

chlorine parameters in cobalt chloride hexahyérate,® giving a longer setal-

halogen bond of 2.58 as compared to 2.43 2, 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 parauaters of 1

1, are

Listed in Table 111. On comparing these results with the corresponding

bond Lengths in cobalt and nickel chloride hexahydrate, it 1s observed chat.

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 atons agree within experimental error

with the corresponding lengths in the nickel chloride; and bond Lengths and

ee within experimental error

sgles not involving hydrogen or bromine

with the Lengths and angles tn CoCl,*6i1,0.

?The object of the experiment reported hare vas to determine the

hhydrogen-atom positions, and to deternine the feasibility of using the

eryatal for precise lov-cemperature work. sm an R factor

which indicate

that che crystal should give accurate values for the

Te has a

magnetic properties at low teaperaturt

Elven the aton poritions,

?a5 well as the Co-Br bond distance.

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TABLE I. Positional and thermal paraneters in CoBry"6itz0 determined

fom isotropic Le

squares refinement of room-tenperature neutron

4iteraction data,

atom x : 8

eo

co ° ° 2.2 (4)

ar 0.281 @)* 0.179 ay 2.5 (2)

° 9.0370(7) 0, 2454¢9) 3.4 (2)

Oy 0.285 (1) 0,696 (2) 3.4 3)

m1 106 (1) 0,276 (2) 4.7 (3)

Ww 0.452 1) 0.226 (ay 4.7)

ry 0.196 (2) 0,558 (3) 76)

Ha 0.265 (3) 0.821 (3 43

eee eee

? Throughout this paper the standard deviation of a function is given

4 che parenthesis folloving the function, and ite value corresponds

lease significant digits in the function value.

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TABLE II. Observed and calculated structure factors for CoBrp* 611.0,

Getencned roa room-temperature neutron-diffraction data.

2

a

6

5

4

23

+2

a

1601s 453-450

188 168 ae 7456

260-195 S65 589,

ee 32 ss1 550

87 18682

(19 373-370

777 356-370,

(2) 26 nn? 1s

qo ait 343,305,

2-99 Gp -s0

128-178 1B?

285 243 Cod i

37 ?Be 1er = 174,

92 =72 229216

1st 162 36739

fo 31 336 -323

$553 see i665,

122-123 ?3780

ns 123 S15 465,

238 237 a ?33

52 ?55 395-358

182176 (Qe) =76

Ga 269 ies an

179-175 tes 16

(35) 47 18s -196

to ?a2 252-277

are 287 153 "175

(50) 3 356 04,

too -91 qe 180

223-235 23-205

(s0 2 126-131

37838) 150143

375361 es) e

See 450 (en) 35

439459 (28

31e -336 (ey 53

316 ?336 30118

Ber -552 £0 -29

330 350 261-275

374360 103 ?99

77 = 82 306 321

108 130 i32) ?33

(Se 30 146-150

270-264 (ss) 67

245-238, 130159

520 S42 (4) 223

41s 62) ($3) 4)

she 858, «ao

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TABLE IIT, Interatomic distances and bond angles in CoBr"6i1,0 at

room temperature.

SS

OOO

co-nr

co-0y,

2.58 ay)

3.94 (2)

2.98 (1)

0.89 (3)

0.99 (2)

151 (3)

3.33 @)

2.36 (2)

107 (2)?

tes (1)

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