PRNC145

PRNC ~ 145

PUERTO RICO NUCLEAR CENTER

?A LEAST-SQUARE REFINEMENT OF THE X-RAY DATA

ON AZURITE, Cu (01, (CO,),

OPERATED BY UNIVERSITY OF PUERTO RICO UNDER CONTRACT

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

---Page Break---

PRNC ~ 145

PUERTO RICO NUCLEAR CENTER

?A LEAST-SQUARE REFINEMENT OF THE X-RAY DATA

AZURITE, Cu (OH

oN az 1 {OH),{CO.),

?OPERATED BY UNIVERSITY OF PUERTO RICO UNDER CONTRACT

NO, AT (40-11-1839 FOR U. §, ATOMIC ENERGY COMMISSION

---Page Break---

A Least-squares Refinement of the X-Ray Data on Azurite, Cus(Ot) (C03) *

by

ROBERT KLEINBERG

Puerto Rico Nuclear Center, and Physics Department

University of Puerto Rico at Mayaguez, Mayaguez, Puerto Rico 00708

quares refinevent of reported x-ray

Gata on azurive, Cus(OH)(C0,)2, gives a set of positional

Peraneters which is statistically equivalent to the eet origin~

?ally determined from tvo-dinensional Patterson and Pourier work.

The largest difference between any to corresponding positional

Parameters is equivalent to a distance of 0.062 &.

* Work performed under the auspices of the U, 5. Atomic Energy Comission.

---Page Break---

?ereopuctrox

Im conjunction with our seutron-diffraction determination of the cryetal

structure of azurite,! we have refined the x-ray data taken from the Literature,?

?This was done because there were sone rather large differences between some of

che positional

raneters obtained from che neutron and x-ray determinations,

land because the original analysis vas performed by means of tvo.

mensional

Patterson and Fourier work. The heavy-atom structure of azurite deduced by

Gattow and Zenann,? has monoclinic symmetry, P2/e, with two molecules in a

unit cetl, The unit cell dimensions ace

a= 5.00 t 0.02, b= 5.85 $0.02, © = 10.35 t 0,02k,

@ = 92°20" + 20"

?The general position is four fold with equivalent sites at

xaysti KE: Ky1/2ey,1/2-25 xpl/2-y,1/24e, One set of copper atoms is located

ina

mneral position set, while the other is located in the special position

set 0,0,0;0,1/2,1/2. ALL other atoms are located in general positions. The

paraneters given by Gattow and Zenann were determined from two-dimensional

Patterson and Fourier work and are reproduced here in Table I. Using isotropic

zonal temperature factors, the reliability factors over observed reflections

for the Okf hOL and hkO zones are 0.088, 0.072, and 0.066 respectively.

---Page Break---

REFINEMENT OF THE STRUCTURE

Tne data were refined by full-matrix isotropic least squares based on F,

a

sing the Los Alenos Crystal Structure Least-Square

Fotal of 149 independent nonzero, and 15 duplicate reflections from the three

Principal zones were used to obtain three scale, @ isotropic-thermal, and

18 positional paraneters, The quantity minimized was Swing ~ Irtil?,

where FE 4s equal to the calculated structure factor F_, and the weights ¥

?are given by the expression (1.0 + 0.018,)"1, Refinement was continued until

4 &/o(E)< 1.06 x 10°F for alt Least

quares parameters fj. At the end of

Fetinewent the reliedslity factor R= S1ari/Srgl, for ehe onl, nol, and

KO zones, and for all observed reflections, vas 0.062, 0.077, 0.064, and

0.069 respectively. The weight

[be nyo]! wares. tint postin ant tone

Since the thermal

rameters were quite low, and since the structure

factors appeared to be affected by extinction, a second least-squares analysis,

with an extinction correction, was performed, Unfortunately, « preci

son

type extinction-correction program vas not readily available. Therefore, the

terorlevel Veissenberg extinction correction which was avatlable was adapted

by using @ wavelength of 1.6%. The quantity minimized vas

Liv liegt - ifi?, with ehe onty difference being that here

ne Me

rte. [teats]

a,

---Page Break---

where @ 18 proportional to the

secondary extinction paraneter.* At the end of

refimenent AE/o(§) < 4.5 x 10°?, and the reliability factors tn the order

siven above are 0.074, 0.061, 0.052, 0.064, and 0.085. Pinal positional and

Asotropic-thermal. pa

meters are given in Table 11,

---Page Break---

Discusstow

Coaparing che 18 positional peraneters given by Gatto and Zemann, to

tho:

Getermined by che Least-squares refinenent we find chat all differences

?re less than or equal fo three tines the extinated acandard deviations given

?im the former work, and less than six tines the standard deviations given in

?he present work, The Largest paraneter shift corresponds to a distance of

0.062 4. thus the evo sets of paraneters are statistically equivelent,

Sone interatomic distances and bond angles in azurite, calcula

from

the refined set of data, are given in Table 111,

---Page Break---

ACKNOWLEDGEMENTS

This work vas perforaed while the author vas a Visieing Research Associate at the Los Alamos Scientific Laboratory of the University of California, The author wishes to express his thanke to the Laboratory for making available its facilities and computers, and his appreciation to Drs. A.C. Larson and Don T, Cromer of LASL, for the use of their prograns

and for thetr many hel

ful suggestions.

---Page Break---

REFERENCES

1. R, Kleinberg, to be publishe

2 G. Gattow and J, Zemann, Acts Cryst. 11, 866 (1958).

3A. G. Larson, (private communication) Operators Manual for the

Los Alanos Crystal Structure Least-Squares Program, CENLES.

4. AC. Larson, Acta Cryst. 23,

664 (1967).

---Page Break---

TABLE T. Positional parameters (x 10%) in azurite determined from Patterson

and Pourter work.

atom x y *

uy ° ° °

oy 252(2)* 4950) 085(2)

4, 0924) a2 4464)

¢ 329(4) 298¢6) n19¢4

%, o9a(uy 380(4) 338¢4)

on wa7¢ay 224¢4 aan)

Oy ann 303(4) 2124)

??

oY

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

st

Parenthesis folloving the function, and ite value corresponds to the least

significant digits in the function value.

---Page Break---

TABLE I1. Positional and thermal paraneters of azurite determined from

isotropic Least-squares refinement of x-ray data,

eS

SEO

atom x y 2 2

eee

cuy ° ° ° 0.4607)

° ° ° 02580)

copy 9.282004)" 0.4958(5) ??_0,0839(2) 0.27¢6)

0.251706) 01436205) ???B0Bao(2) 0.408)

% 9.080 (3) 0,808 (3) 42 «ay 0.1 (2)

8.080 (2) 0.809 G3) saa 0:2 (2)

© 0.339 (3) 9,287 (@) 0,320 a) 0.1 Gy

0.3393) 0.2983) 318 0:3 @

7 2.102 (30,3933) 0,332 ay 0.5 2)

0.1033) 01396. G) 0.332) 0.6 2)

on 9.467 (3) 0.222 (3) oa? ay 0.3 @)

0.447 (2) 0.222 GG) onate (Ly 04 @)

Ont 0.439 (2) 0,308 (3) 0, 207809) 0.1 @

0.436 Gy 0.308. (3) z07et3) 0.3 @)

oe

eS

?In each atom set of unbere, the upper and lover subsets were deter

frow isotropic 1

Ist squares, without, and with extinction cor-

rection, respectively,

---Page Break---

TABLE 21,

Sone iuteratonie distances and bond angles in azuritc.

ee

5

1.3e(e) neq)

eae) LT (2)

Lette) ur (2)

2.19(e)

2.23(2) 87.55)

eveu(e) 9.9 (5)

1.95(2) £00(2)

2.9302) #,02(2)

2.92(4) 2.9u(e)

2.01(a)

+362)

5.90(2)

-7(2)

£.85(2)

oy 01, = 35(2)

Oy *.93e)

---Page Break---