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$CuWO_4$, a Distorted Wolframite-Type Structure

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The crystal structure of $CuWO_4$, previously reported by the authors to be of a distorted wolframite type, has been refined from single-crystal X-ray diffractometer data. The least-squares procedure including anisotropic thermal parameters resulted in a conventional $R=0.029$. The structure is triclinic, space group $P\bar{1}$, with unit-cell dimensions $a=4.7026\ (\pm 6)$, $b=5.8389\ (\pm 7)$, $c=4.8784\ (\pm 6)$ Å, $\alpha=91.677\ (\pm 9)$, $\beta=92.469\ (\pm 7)$ and $\gamma=82.805\ (\pm 10)°$. The copper atom is surrounded by six oxygen atoms, four of these in an approximately square planar configuration and the remaining two at a longer distance completing an elongated octahedron. The tungsten atom is located within a slightly distorted octahedron but is considerably displaced from its centre. Interatomic distances and angles are given. The refinement gave no evidence for oxygen deficiency and new density measurements have given values which, although still somewhat low, are closer to that expected for stoichiometric composition than was the previously reported value.

Introduction

In a previous communication from this Institute we reported a preliminary investigation of the crystal structure of copper tungstate, $CuWO_4$, which we found to be a distorted version of the wolframite type (Gebert & Kihlborg, 1967). Density measurements led us to believe that our samples were strongly oxygen deficient; hence we preferred to give the formula as $CuWO_{4-x}$. The study was based on photographically recorded X-ray diffraction intensities obtained from a twinned crystal. The relatively poor quality of the data limited the degree of accuracy that could be achieved. The final R value was 0·20.

When the preliminary investigation had reached a final stage we found an untwinned single crystal of the phase. This paper reports a refinement of the structure based on diffractometer data obtained from this crystal.

Experimental

The crystal was selected from a sample prepared by heating an equimolar mixture of CuO and WO_3 (reagent grade) in an evacuated platinum tube for 4 days at 800°C. The preparation did not appear homogeneous under the microscope; it contained both light yellow, well-developed crystals and amber-coloured pieces with a glassy appearence. Its powder pattern, however, showed only the lines characteristic for $CuWO_{4-x}$ (Gebert & Kihlborg, 1967) and single-crystal photographs revealed that both types of crys-

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tal were structurally identical although all species of the clear yellow type that were examined exhibited polysynthetic twinning. The crystals were twinned across (010).

The unit-cell dimensions given in Table 1 were obtained from a powder pattern recorded in a Guinier–Hägg focusing camera using Cu $K\alpha_1$ radiation and KCl as internal standard (a = 6·2919 Å). The lattice parameters were refined using a least-squares program written by P.-E. Werner at this Institute. Powder patterns were recorded from several samples prepared but no significant variations in the cell dimensions were observed.

Table 1. *Crystallographic data for* $CuWO_4$

Symmetry: triclinic, space group $P\bar{1}$
Unit-cell dimensions:
a = 4·7026 (±6) Å α = 91·677 (±9)°
b = 5·8389 (±7) β = 92·469 (±7)
c = 4·8784 (±6) γ = 82·805 (±10)
V = 132·73 Å^3
Z = 2
Density: D_{meas} = 7·61 – 7·65 g.cm^{-3}
D_{calc} = 7·790 g.cm^{-3}

A chemical analysis of the phase gave 20·66% (by weight) copper *versus* the theoretical 20·40% copper content in $CuWO_4$.

The density of the phase was determined previously by pycnometric measurements and was reported to be D = 7·44 (±7) g.cm^{-3}. This value is rather low compared with that calculated for $CuWO_4$ (Table 1) and was the main reason for our believing that this phase normally exhibits a considerable oxygen deficiency. New measurements, using a slightly more refined pycnometric technique, have been made on another sample which gave values within the range 7·61–7·65 g.cm^{-3}. Although still low compared with the value calculated for $CuWO_4$, the difference is not necessarily significant since systematic errors of this sign and magnitude are sometimes encountered in density determinations on fine powders. Considering the light colour and transparency of the crystals as well as the result of the structure refinement, reported below, we do not believe that the specimen used in our investigation was significantly oxygen deficient. The stoichiometry of $CuWO_4$ under various conditions will be the subject of a separate study at this Institute.

The single-crystal studied was amber-coloured, transparent and roughly prismatic with a length (along **a**) of 0·22 mm and a maximum cross section of 0·085 mm. It was mounted on a manual diffractometer (General Electric Single Crystal Orienter) and angle settings were made for the 1111 reciprocal lattice points for which $l \geq 0$ and $\sin^2\theta \leq 0{\cdot}30$ ($d > 0{\cdot}649$ Å). The intensities were recorded according to the θ–2θ scan technique using Nb-filtered Mo K radiation.

All intensities for which $I/\sigma(I) < 1{\cdot}25$ (I = net intensity, σ = standard deviation based on counting statistics) were rejected which left a set of 998 values for use in the refinement.

Refinement

The data were corrected for Lorentz and polarization factors and also for the effect of absorption using a local version of the program of Coppens, Leiserowitz & Rabinovich (1965) modified by O. Olofsson and M. Elfström, University of Uppsala. The total linear absorption coefficient was assumed to be μ = 539·4 cm^{-1}.

Starting from the parameters reported previously (Gebert & Kihlborg, 1967) the initial least-squares cycles were carried out with use of a block-diagonal matrix program (*SFLS*, written by S. Åsbrink, Univ. of Stockholm and C.-I. Brändén, University of Uppsala, modified for IBM 1800 by B. Brandt, University of Stockholm). A full-matrix program (*LALS*, a local version of the program *UCLALS* by Gantzel, Sparks & Trueblood modified by R. Liminga, J.-O. Lundgren and C.-I. Brändén, University of Uppsala) was used in the final stage.

The HFS atomic scattering factors given by Hanson, Herman, Lea & Skillman (1964) were used and the complex anomalous dispersion correction calculated by Cromer (1965) was applied to the copper and tungsten values in the last cycles of refinement. The least-squares programs used minimize the function $\sum w(|F_o| - |F_c|)^2$ and the weights were calculated according to the expression suggested by Cruickshank,

$$w = (A + |F_o| + C|F_o|^2 + D|F_o|^3)^{-1}.$$

By inspection of the weight analysis the following values of the constants in this formula were chosen for the last cycles of refinement, $A = 113$, $C = -0{\cdot}130$ and $D = 0{\cdot}0030$. The weight analysis obtained in the final cycle is given in Table 2.

Table 2. *Weight analysis*

$\Delta = ||F_{obs}| - |F_{calc}||$, w = weighting factor, N = number of independent reflexions. The $w\Delta^2$ values have been normalized.

F_{obs}	N	$w\Delta^2$
0·0– 18·7	99	1·74
18·7– 27·1	100	0·94
27·1– 35·4	100	0·61
35·4– 42·6	100	0·73
42·6– 47·9	100	0·99
47·9– 53·6	99	1·02
53·6– 61·3	100	0·95
61·3– 70·8	100	0·53
70·8– 86·8	100	0·64
86·8–151·2	100	1·86

$\sin\theta$ (×10^4)	N	$\overline{w\Delta^2}$
0–2553	121	1·94
2553–3216	111	1·37
3216–3682	98	0·47
3682–4052	110	0·71
4052–4365	91	0·86
4365–4639	104	0·78
4639–4883	104	0·85
4883–5106	88	0·63
5106–5310	87	1·04
5310–5500	84	1·10

In the course of the refinement it became evident that the strongest reflexions suffered seriously from extinction since $|F_{\text{obs}}|$ was consistently smaller than $|F_{\text{calc}}|$. All data were then corrected for this effect by applying the formula of Zachariasen (Zachariasen, 1963; Zachariasen & Plettinger, 1965) modified as described by Åsbrink & Norrby (1970). The necessary functions were calculated by the absorption correction program (Åsbrink & Werner, 1966) and the empirical constant entering into the calculations was obtained in the usual way from the discrepancies between F_{obs} and F_{calc} (Åsbrink & Werner, 1966).

Refinement of the extinction corrected data with anisotropic thermal parameters for all atoms resulted in a final reliability index $R=\sum||F_o|-|F_c||/\sum|F_o|=$ 0·029. The final parameters are given in Tables 3 and 4. Observed and calculated structure amplitudes are listed in Table 5.

Table 3. *Fractional atomic coordinates for* $CuWO_4$

All atoms in point position 2(*i*) of space group $P\bar{1}$. E.s.d.'s are given in brackets.

	x	*y*	*z*
Cu	0·49533 (16)	0·65976 (13)	0·24481 (15)
W	0·02106 (4)	0·17348 (3)	0·25429 (4)
O(1)	0·2491 (10)	0·3535 (8)	0·4245 (10)
O(2)	0·2145 (10)	0·8812 (7)	0·4309 (9)
O(3)	0·7353 (10)	0·3803 (8)	0·0981 (9)
O(4)	0·7826 (9)	0·9079 (8)	0·0533 (9)

As mentioned above, there had been some doubt concerning the oxygen content of the phase. Although the isotropic *B* values obtained in the course of the refinement were normal and did not indicate vacancies on any specific oxygen position – the B_O values were equal within their standard deviations – a few refinement cycles were performed in which an occupancy parameter for each oxygen position was also refined. In this case the program *ORFLS* by Busing, Martin & Levy (1962) was used. The positional parameters did not change significantly and the following values were obtained for the occupancy parameters (standard deviations in parentheses): 0·94 (±4), 1·01 (±4), 0·89 (±4) and 1·03 (±4) for the oxygen atom positions 1 through 4. The deviations from unity are hardly significant and cannot be used as a proof for oxygen deficiency. The B_O values, which are strongly correlated with the corresponding occupancy parameters (correlation coefficients 0·79–0·82), were much more divergent after this refinement.

Description

As mentioned above, our preliminary investigation of this crystal structure suggested that it is a distorted version of the wolframite type and this is definitely confirmed by the present refinement.

The wolframite type structure is adopted by a number of tungstates of AWO_4 stoichiometry, *A* being a sufficiently small divalent cation. At least four compounds with this structure have been studied by single-crystal methods, namely $NiWO_4$ (Keeling, 1957), $CdWO_4$ (Chichagov, Ilyukhin & Belov, 1966), $MnWO_4$ (Dachs, Stoll & Weitzel, 1967) and $FeWO_4$ (Ülkü, 1967). The last structure has been refined from X-ray and neutron diffraction data to a high degree of accuracy and is well suited for a comparison with $CuWO_4$.

The normal wolframite structures are monoclinic, space group $P2/c$, with both metal atoms situated on twofold axes. They can be described as a framework of oxygen atoms in an approximately hexagonal close-packing with the cations occupying half of the octahedral sites. Cations of each kind form layers which are interleaved between the oxygen sheets in alternating sequence (Fig. 2). Infinite zigzag chains are formed by edge-sharing octahedra containing like cations (Fig. 1).

The above description applies also to the $CuWO_4$ structure. The more irregular coordination required by the copper atoms compared with iron, for example (see below), is achieved primarily by a shear (not to be confused with 'crystallographic shear') parallel to **b** along each copper plane by which the oxygen layers surrounding the copper atoms become slightly displaced with respect to each other. This is evident in Figs. 1 and 2. The displacement destroys the twofold symmetry and is directly reflected in the deviation of the angle γ from 90°.

Table 4. *Thermal parameters*

The β values refer to the temperature factor $\exp\,[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$.

R(*i*), *i*=1,3, are the r.m.s. components of thermal displacement (in Å) along the principal axes of the ellipsoid of thermal vibration (calculated with the program *ORFFE* by Busing, Martin & Levy, 1964). E.s.d.'s in parentheses.

	β_{11} ($\times 10^5$)	β_{22} ($\times 10^5$)	β_{33} ($\times 10^5$)	β_{12} ($\times 10^5$)	β_{13} ($\times 10^5$)	β_{23} ($\times 10^5$)	*R*(1)	*R*(2)	*R*(3)
Cu	587 (27)	429 (18)	428 (27)	184 (17)	−159 (22)	−109 (18)	0·060 (5)	0·066 (4)	0·110 (3)
W	452 (11)	238 (7)	272 (10)	26 (5)	−79 (6)	17 (5)	0·051 (2)	0·063 (1)	0·078 (1)
	($\times 10^4$)	($\times 10^4$)	($\times 10^4$)	($\times 10^4$)	($\times 10^4$)	($\times 10^4$)			
O(1)	85 (16)	55 (10)	61 (14)	−4 (10)	−13 (12)	−12 (10)	0·075 (20)	0·093 (16)	0·110 (17)
O(2)	91 (16)	34 (9)	57 (15)	24 (10)	2 (13)	−8 (10)	0·057 (24)	0·085 (14)	0·116 (14)
O(3)	85 (16)	50 (10)	45 (14)	19 (10)	−4 (12)	−8 (10)	0·070 (19)	0·077 (21)	0·117 (15)
O(4)	79 (15)	60 (10)	35 (13)	3 (10)	0 (12)	2 (10)	0·065 (13)	0·088 (15)	0·107 (14)

It is evident from Fig. 2 that the pseudo-hexagonal oxygen layers are fairly smooth; the oxygen positions lie within slices which are 0·23$_5$ Å thick. In FeWO$_4$ the corresponding value is 0·19 Å. The separation of the oxygen layers, defined as the distance between the mean planes, is different across the tungsten and copper layers. The separation of the planes surrounding the tungsten atoms is very nearly the same in CuWO$_4$ and FeWO$_4$, namely 2·207 and 2·204 Å respectively, but the difference between the divalent ions gives rise to a small difference in the distances between the planes around these ions; they are 2·523 and 2·458 Å respectively.

Coordination

Interatomic distances and bond angles are listed in Table 6. When hexavalent tungsten is surrounded by six oxygen atoms, the coordination is generally irregular. This is seen to be the case also in the present structure. The range for the six W–O distances is almost the same as in monoclinic WO$_3$ where it is 1·757–2·162 Å according to a recent refinement (Kihlborg, to be published). The higher symmetry of FeWO$_4$ makes the W–O distances pairwise equivalent, being 1·792 (±5), 1·905 (±6) and 2·124 (±5) Å according to Ülkü's parameters based on neutron diffraction data. These distances should be compared with the mean values of the two shortest, the two intermediate, and the two longest W–O bonds in CuWO$_4$: 1·788, 1·916 and 2·118 Å respectively. In the threefold symmetrical tungsten coordination in Cu$_3$WO$_6$ the distances are 1·791 (±16) and 2·084 (±12) Å (Gebert & Kihlborg, 1969). The corresponding mean values of the three shortest and the three longest bonds in CuWO$_4$

Table 5. *Observed and calculated structure amplitudes*

The column headings are the index h, $10\cdot|F_{\rm obs}|$ and $10\cdot|F_{\rm calc}|$·

H,-8,0		
-4	471	475
-3	586	553
-2	613	588
0	425	422
1	399	398
2	410	409
H,-7,0		
-5	138	139
-4	323	321
-2	116	116
-1	179	170
1	398	405
2	223	217
3	412	415
H,-6,0		
-5	208	199
-4	599	610
-3	399	405
-2	838	846
-1	503	478
0	938	951
1	535	538
2	947	956
3	480	474
4	715	699
H,-5,0		
-5	579	581
-4	625	626
-3	793	802
-2	654	665
-1	702	705
0	461	463
1	577	575
2	321	314
3	375	366
H,-4,0		
-6	199	173
-5	279	274
-4	123	128
-3	319	318
-2	147	114
-1	100	94
0	766	811
1	203	193
2	526	509
3	425	414
4	801	778
5	450	436
6	527	499
H,-3,0		
-7	344	343
-6	261	261
-5	709	705
-4	360	344
-3	1015	1072
-2	663	679
-1	1306	1477
0	637	643
1	1383	1517
2	698	674
3	926	1099
4	458	443
5	844	806
6	316	305
H,-2,0		
-7	486	496
-6	612	630
-5	599	617
-4	858	872
-3	743	737
-2	948	1012
-1	626	631
0	871	898
1	350	343
2	596	599
4	197	180
5	173	170
H,-1,0		
-7	160	167
-6	283	298
-4	219	232
-3	231	233
-1	815	801
0	439	385
1	1110	1065
2	583	568
3	868	855
4	604	582
5	863	816
6	577	548
7	551	508
H, 0,0		
-7	155	157
-6	549	546
-5	419	411
-4	1193	1209
-3	529	518
-2	1128	1209
-1	942	866
1	1097	866
2	1308	1209
3	556	518
4	1253	1209
5	428	411
6	590	546
7	160	157
H, 1,0		
-7	485	508
-6	522	548
-5	777	816
-4	570	582
-3	849	855
-2	564	568
-1	1065	1065
0	446	385
1	851	801
3	240	233
4	239	232
6	288	298
H, 2,0		
-5	160	170
-4	195	180
-2	594	599
-1	348	343
0	938	898
1	644	631
2	977	1012
3	745	737
4	899	872
5	645	617
6	668	630
7	528	496
H, 3,0		
-6	288	305
-5	809	806
-4	441	443
-3	1072	1099
-2	683	674
-1	1379	1517
0	656	643
1	1406	1477
2	695	679
3	1001	1072
4	341	344
5	722	705
6	268	261
7	361	343
H, 4,0		
-6	483	499
-5	433	436
-4	755	778
-3	414	414
-2	511	509
-1	198	193
0	795	811
1	108	94
2	121	114
3	312	318
4	120	128
5	271	274
6	180	173
H, 5,0		
-2	313	314
-1	577	575
0	475	463
1	717	705
2	666	665
3	813	802
4	614	626
5	568	581
6	506	497
H, 6,0		
-4	687	699
-3	476	474
-2	932	956
-1	533	538
0	950	951
1	489	478
2	844	846
3	402	405
4	600	610
H, 7,0		
-3	410	415
-2	214	217
-1	401	405
1	180	170
2	112	116
4	327	321
5	132	139
H, 8,0		
-2	414	409
-1	406	398
0	430	422
1	439	434
2	597	588
3	564	553
4	469	475
H,-8,1		
-4	187	178
-2	442	421
-1	224	209
0	531	535
1	277	280
2	583	596
H,-7,1		
-5	544	530
-4	408	424
-3	674	677
-2	593	576
-1	824	829
0	517	518
1	692	707
2	403	407
3	595	607
H,-6,1		
-4	364	353
-3	364	374
-2	321	310
-1	452	446
0	126	124
4	174	171
H,-5,1		
-6	123	115
-5	314	311
-3	491	491
-2	207	211
-1	874	907
0	416	412
1	872	888
2	501	496
3	935	939
4	461	460
5	685	673
H,-4,1		
-6	642	630
-5	500	497
-4	825	847
-3	641	649
-2	1120	1171
-1	703	720
0	1112	1175
1	555	537
2	934	923
3	384	384
4	651	647
5	153	152
H,-3,1		
-7	381	386
-6	541	541
-5	457	445
-4	465	459
-3	335	333
-2	477	478
-1	294	281
0	148	145
1	113	111
2	199	190
3	222	251
4	276	268
5	327	318
6	430	416
H,-2,1		
-6	251	256
-4	622	627
-3	459	451
-2	1077	1129
-1	133	157
0	1191	1315
1	1009	1022
2	1413	1475
3	496	468
4	979	936
5	617	601
6	796	767
H,-1,1		
-7	536	548
-6	391	404
-5	843	907
-4	680	721
-3	1145	1259
-2	640	667
-1	1512	1642
0	826	765
1	1325	1390
2	468	457
3	947	963
4	169	159
5	468	453
H, 0,1		
-7	448	436
-6	415	414
-5	438	441
-4	381	373
-3	407	404
-2	287	281
-1	123	120
1	259	245
2	323	306
3	454	443
4	414	400
5	539	516
6	453	426
7	478	450
H, 1,1		
-7	221	229
-5	481	496
-4	283	284
-3	974	976
-2	420	422
-1	1257	1432
0	810	794
1	1486	1583
2	820	813
3	1362	1326
4	645	617
5	842	823
6	506	481
7	637	608
H, 2,1		
-6	690	721
-5	417	422
-4	971	982
-3	791	806
-2	1341	1461
-1	151	311
0	1082	1153
1	743	744
2	1182	1287
3	78	91
4	462	453
6	337	323
7	152	148
H, 3,1		
-6	262	272
-5	299	294
-4	323	326
-3	270	272
0	251	248
1	213	209
2	433	435
3	372	385
4	601	615
5	478	470
6	506	501
H, 4,1		
-5	220	221
-4	615	634
-3	354	352
-2	929	944
-1	635	637
0	1139	1704
1	694	696
2	1084	1101
3	639	644
4	838	884
5	517	521
6	597	578
H, 5,1		
-5	694	706
-4	481	490
-3	849	864
-2	408	406
-1	937	953
0	415	410
1	762	766
2	146	152
3	561	565
5	198	202
6	147	143
H, 6,1		
-4	127	124
-3	116	102
-2	119	117
-1	247	250
0	264	255
1	322	312
2	215	207
3	537	535
4	463	465
H, 7,1		
-3	546	551
-2	434	434
-1	753	774
0	563	561
1	772	771
2	513	507
3	671	677
4	474	483
5	533	530
H, 8,1		
-2	506	572
-1	289	292
0	545	545
1	152	162
2	353	351
H,-8,2		
-3	501	480
-2	479	463
-1	424	422
0	513	513
1	342	345
H,-7,2		
-4	189	192
-2	165	161
-1	205	190
0	119	121
1	389	394
2	155	163
3	442	430
H,-6,2		
-4	597	594
-3	345	353
-2	768	794
-1	527	517
0	933	959
1	515	532
2	840	857
3	414	423
4	705	707
H,-5,2		
-6	471	460
-5	621	632
-4	622	616
-3	656	670
-2	505	510
-1	688	693
0	490	493
1	539	545
2	202	191
3	259	253
5	144	127
H,-4,2		
-6	99	80
-5	268	262
-3	190	192
-2	440	442
-1	170	161
0	392	387
1	193	185
2	789	787
3	525	528
4	594	585
5	391	379
H,-3,2		
-6	235	223
-5	611	598
-4	430	426
-3	1061	1117
-2	570	565
-1	1209	1261
0	708	718
1	1319	1394
2	570	550
3	946	1035
4	479	477
5	739	727
6	229	237
H,-2,2		
-7	419	426
-6	598	611
-5	592	608
-4	780	803
-3	582	589
-2	875	880
-1	553	538
0	792	815
1	269	265
2	457	462
4	174	166
5	187	171
H,-1,2		
-4	199	208
-3	345	349
-2	183	179
0	327	320
1	854	873
2	590	588
3	894	907
4	649	646
5	710	699
6	483	477
H, 0,2		
-6	662	652
-5	412	409
-4	859	870
-3	461	450
-2	1501	1656
-1	956	1018
0	1232	1424
1	415	392
2	1443	1552
3	758	740
4	906	899
5	225	227
6	609	576
H, 1,2		
-6	486	503
-5	607	631
-4	478	480
-3	898	915
-2	523	525
-1	744	792
0	202	194
1	595	611
2	89	104
3	271	258
4	228	230
6	386	372
H, 2,2		
-5	116	115
-4	239	236
-3	136	127
-2	511	504
-1	367	359
0	830	853
1	650	664
2	871	921
3	696	704
4	809	795
5	636	620
6	643	626
H, 3,2		
-6	308	315
-5	713	703
-4	429	425
-3	1060	1105
-2	634	637
-1	1193	1284
0	641	632
1	1205	1337
2	529	522
3	898	961
4	382	399
5	635	637
6	146	151
H, 4,2		
-5	436	432
-4	550	556
-3	238	234
-2	688	692
-1	349	350
0	439	423
1	265	282
2	273	264
3	110	112
5	439	447
6	163	165
H, 5,2		
-5	173	160
-4	150	152
-3	308	317
-2	260	255
-1	548	541
0	550	548
1	740	735
2	639	645
3	676	677
4	566	586
5	583	607
6	534	530
H, 6,2		
-4	712	729
-3	461	467
-2	815	833
-1	468	468
0	903	910
1	487	485
2	770	781
3	320	326
4	514	520
H, 7,2		
-3	489	448
-2	140	146
-1	275	276
1	219	217
2	202	195
4	296	298
H, 8,2		
-1	297	300
0	468	466
1	556	556
2	536	529
3	443	440
H,-8,3		
-2	368	358
-1	186	194
0	513	517
H,-7,3		
-4	442	442
-3	702	688
-2	513	501
-1	675	673
0	456	462
1	688	703
2	393	404
H,-6,3		
-5	375	379
-4	307	309
-3	416	422
-2	309	299
-1	197	189
1	112	103
3	152	151
H,-5,3		
-5	263	256
-3	522	518
-2	318	323
-1	717	726
0	353	350
1	867	883
2	528	533
3	771	779
4	411	417
H,-4,3		
-6	536	523
-5	441	442
-4	797	828
-3	625	621
-2	964	964
-1	575	569
0	949	992
1	514	506
2	831	832
3	308	308
4	512	510
H,-3,3		
-6	402	402
-5	329	324
-4	428	426
-3	390	390
-2	318	306
-1	100	70
1	72	42
2	157	147
3	243	243
4	359	364
5	361	362
H,-2,3		
-6	241	242
-5	147	134
-4	614	628
-3	203	202
-2	770	759
-1	601	581
0	1258	1397
1	576	560
2	929	929
3	619	617
4	1022	1032
5	493	496
6	578	572
H,-1,3		
-6	467	478
-5	781	838
-4	490	507
-3	971	1023
-2	666	711
-1	1242	1301
0	507	494
1	1052	1097
2	389	387
3	725	735
4	115	124
5	435	432
H, 0,3		
-6	334	331
-5	358	353
-4	348	348
-3	288	280
-2	164	163
1	269	263
2	280	268
3	456	446
4	398	398
5	513	505
6	398	389
H, 1,3		
-5	502	522
-4	249	246
-3	748	748
-2	471	471
-1	1110	1231
0	681	682
1	1166	1241
2	672	690
3	1039	1046
4	601	582
5	820	808
6	450	443
H, 2,3		
-6	594	612
-5	482	493
-4	975	987
-3	511	499
-2	894	908
-1	526	527
0	1195	1356
1	386	363
2	593	612
4	608	609
6	134	132
H, 3,3		
-5	343	336
-4	173	170
-3	131	99
0	257	249
1	253	243
2	479	486
3	379	393
4	529	547
5	385	388
6	502	506
H, 4,3		
-5	189	196
-4	544	551
-3	397	399
-2	863	873
-1	558	555
0	950	968
1	637	639
2	965	977
3	588	604
4	703	759
5	428	445
H, 5,3		
-4	385	383
-3	721	727
-2	406	411
-1	807	828
1	657	645
2	156	167
3	426	434
5	178	201
H, 6,3		
-2	103	83
-1	230	225
1	343	335
2	400	392
3	535	538
4	295	303
H, 7,3		
-2	435	439
-1	648	647
0	481	472
1	702	696
2	511	517
3	628	632
H, 8,3		
0	435	428
H,-7,4		
-1	261	257
1	279	285
H,-6,4		
-4	478	481
-3	374	380
-2	763	747
-1	463	462
0	766	774
1	443	458
2	740	760
3	414	424
H,-5,4		
-5	521	522
-4	430	436
-3	572	570
-2	512	512
-1	598	599
0	305	305
1	372	372
2	165	159
3	260	260
H,-4,4		
-5	230	223
-2	253	240
0	458	467
1	427	429
2	598	592
3	316	323
4	548	552
H,-3,4		
-6	191	200
-5	623	617
-4	431	429
-3	790	806
-2	496	482
-1	1109	1117
0	607	615
1	993	1003
2	509	505
3	900	912
4	377	386
5	576	579
H,-2,4		
-6	561	565
-5	461	464
-4	606	615
-3	492	498
-2	721	729
-1	394	377
0	552	554
1	155	149
2	343	338
4	168	127
5	210	214
H,-1,4		
-6	189	223
-3	303	297
-2	89	89
-1	496	468
0	419	415
1	744	754
2	540	539
3	696	704
4	535	533
5	619	623
H, 0,4		
-6	528	512
-5	294	299
-4	828	831
-3	615	619
-2	1081	1120
-1	446	430
0	1131	1164
1	766	769
2	1119	1148
3	337	326
4	694	693
5	352	353
H, 1,4		
-6	327	338
-5	572	599
-4	483	497
-3	655	653
-2	277	259
-1	610	609
0	221	194
1	427	408
2	111	122
3	168	170
H, 2,4		
-4	204	212
-3	131	125
-2	427	422
-1	399	397
0	682	669
1	568	553
2	705	737
3	613	630
4	687	681
H, 3,4		
-5	636	629
-4	458	457
-3	889	898
-2	487	479
-1	982	1017
0	573	572
1	979	1009
2	440	445
3	731	794
4	283	299
5	474	481
H, 4,4		
-4	485	490
-3	340	338
-2	532	534
0	291	273
2	258	257
3	334	338
4	119	123
5	296	302
H, 5,4		
-3	275	266
-2	344	348
-1	519	515
0	465	462
1	588	573
2	566	564
3	607	610
4	549	570
H, 6,4		
-3	365	364
-2	709	721
-1	457	461
0	778	760
1	379	373
2	630	620
3	282	286
4	452	461
H, 7,4		
-1	269	260
1	115	113
2	238	235
H,-6,5		
-3	277	282
-2	147	148
-1	153	151
0	122	113
H,-5,5		
-4	146	145
-3	463	463
-2	234	228
-1	577	574
0	428	427
1	718	736
2	384	395
3	641	649
H,-4,5		
-4	643	659
-3	437	444
-2	774	759
-1	521	520
0	767	789
1	381	387
2	615	614
3	223	232
H,-3,5		
-5	352	336
-4	345	338
-3	198	200
-2	125	126
-1	112	112
1	142	83
2	239	242
3	253	251
4	303	309
H,-2,5		
-5	105	114
-4	414	405
-3	255	259
-2	776	794
-1	506	491
0	764	767
1	458	458
2	927	959
3	589	602
4	671	678
H,-1,5		
-5	574	592
-4	448	469
-3	862	898
-2	481	506
-1	833	831
0	441	432
1	809	839
2	256	259
3	531	530
4	120	120
5	325	326
H, 0,5		
-5	306	298
-4	255	245
-3	133	131
-2	121	113
1	274	261
2	258	244
3	412	408
4	344	342
5	442	440
H, 1,5		
-5	357	366
-4	165	216
-3	676	676
-2	488	479
-1	825	843
0	532	511
1	927	929
2	572	602
3	817	839
4	502	507
5	621	620
H, 2,5		
-5	396	402
-4	646	661
-3	393	390
-2	872	899
-1	484	484
0	714	697
1	143	159
2	628	660
3	215	204
4	318	320
H, 3,5		
-3	174	171
-1	216	74
0	290	286
1	205	192
2	401	402
3	313	328
H, 4,5		
-3	377	372
-2	611	657
-1	460	466
0	800	795
1	567	560
2	749	750
3	471	489
4	574	615
H, 5,5		
-3	627	642
-2	339	340
-1	613	592
0	206	212
1	542	524
3	314	306
H, 6,5		
-1	133	125
0	188	177
1	452	438
2	262	255
H,-5,6		
-2	357	345
-1	373	376
0	236	236
1	348	352
H,-4,6		
-2	204	184
-1	200	192
0	420	426
1	252	255
2	408	405
H,-3,6		
-4	297	295
-3	640	657
-2	490	494
-1	805	796
0	420	427
1	804	796
2	467	471
3	656	662
H,-2,6		
-4	544	535
-3	386	390
-2	463	474
-1	241	237
0	415	408
1	123	115
2	232	232
H,-1,6		
-3	164	158
-2	158	164
-1	460	457
0	361	359
1	510	497
2	433	431
3	580	584
H, 0,6		
-4	686	669
-3	392	386
-2	737	747
-1	533	532
0	975	971
1	438	436
2	686	668
3	373	372
4	665	675
H, 1,6		
-4	271	274
-3	440	434
-2	275	276
-1	478	463
1	246	236
H, 2,6		
-3	149	150
-2	381	367
-1	355	341
0	515	487
1	482	470
2	558	583
3	506	521
H, 3,6		
-3	655	640
-2	432	428
-1	817	811
0	452	441
1	733	712
2	350	356
3	556	590
H, 4,6		
-2	298	284
0	359	339
H, 5,6		
0	417	405
1	528	507
H,-2,7		
-2	506	515
-1	316	316
0	643	650
1	519	512
H,-1,7		
-2	324	342
-1	647	667
0	403	359
1	531	527
2	178	177
H, 0,7		
1	231	225
2	200	200
H, 1,7		
-2	324	322
-1	614	603
0	496	479
1	710	712
2	428	456
H, 2,7		
-1	233	230
0	561	528
1	280	273
H, 3,7		
0	186	179

are 1·807 and 2·075 Å. There is thus a close similarity between the W–O bond lengths in these structures despite the difference in symmetry.

The copper coordination is subjected to the Jahn–Teller distortion typical for divalent copper and which gives rise to a considerable lengthening of two opposite Cu–O bonds. The details of the coordination should be evident from Table 6 and Fig. 3. The same type of distortion, even more pronounced, is present in CuO. In that case the Cu–O distances are 1·9509 (±26), 1·9608 (±13) and 2·7840 (±37) Å, each occurring twice (Åsbrink & Norrby, 1970). In $CuMoO_4$, of a structure entirely different from the present one (Abrahams, Bernstein & Jamieson, 1968), two of the three non-equivalent copper atoms have a similar 4+2 coordination, while the third is five-coordinated. The equatorial Cu–O distances around the former atoms range from 1·933 to 1·980 Å, with an average of 1·956 Å which is almost exactly the same as in CuO. The corresponding average in $CuWO_4$ is 1·976 Å. The long Cu–O bonds in $CuMoO_4$ fall within the range 2·213–2·619 Å with an average of 2·312 Å, only slightly shorter than in the tungstate. Cu_3WO_6 has five-coordinated copper atoms with the oxygen atoms forming a somewhat distorted trigonal bipyramid (Gebert & Kihlborg, 1969). Here, the five Cu–O distances range from 1·921 to 2·243 Å with a next-nearest oxygen atom not closer than 3·10 Å.

All oxygen atoms are bonded to three metal atoms in a triangular arrangement. The oxygen atoms lie fairly close to the triangular planes; the distances to these planes are 0·184, 0·189, 0·140 and 0·272 Å for the oxygen atoms 1 to 4 respectively.

The deviation from closest packing of the anions is demonstrated by the considerable divergence of the close O–O distances. There are only 8 or 9 oxygen neighbours within 3·0 Å and the twelfth-nearest oxygen atom, completing the coordination sphere, is found at a distance up to 3·33 Å. With three exceptions, all oxygen atoms are more than 2·67 Å apart. The two shortest O–O separations, 2·411 and 2·507 Å, are along those edges in the WO_6 octahedron which are shared with equivalent octahedra. Shortening of such edges is a well-known phenomenon in polyhedra around high-valence cations when no electrons are available for direct metal–metal bonding. The effect should be less pronounced in the copper–oxygen polyhedra because of the probably lower charge on the copper atoms. Although the third shortest O–O distance (2·625 Å) is along one of the shared edges in the CuO_6 octahedron, the other shared edge, O(1)–O(1), is seen from Table 6 to be considerably *longer* than normal. This shortening and lengthening of the shared edges can be considered as being mainly an effect of the parallel displacement of the oxygen layers around the copper atoms, mentioned above. In $FeWO_4$ the same shared-edge shortening is observed within the tungsten polyhedra (O–O, 2·436 Å) but is much less pronounced in the FeO_6 octahedra where the O–O distances along the common edges are 2·918 Å, insignificantly shorter than the average length of the edges in these octahedra, 2·985 Å.

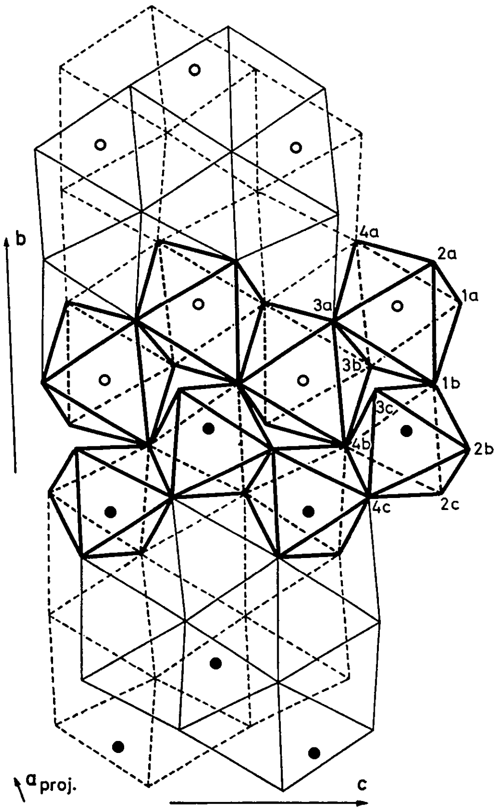

Fig. 1. The structure of $CuWO_4$ projected on to the *bc* plane. Three pseudo-hexagonal oxygen layers are indicated as triangular nets: in the upper part of the Figure two layers surrounding copper atoms (open circles) and in the lower part two layers enclosing tungsten atoms (filled circles). The top layer (full lines) of the upper part continues as the bottom layer (hatched lines) in the lower half of the Figure. For clarity the unit-cell axes have been displaced from the origin which is situated halfway between the two upper left tungsten atoms. The **a** direction is into the plane of the paper.

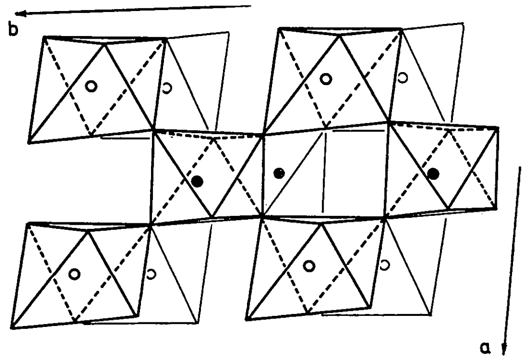

Fig. 2. The structure of $CuWO_4$ depicted as linked octahedra, viewed along the *c* axis. Open and filled circles represent copper and tungsten atoms, respectively.

The root-mean-square components of thermal vibrations along the ellipsoid axes are given in Table 4. It is seen that the anisotropy is rather small for the tungsten atoms and hardly significant for the oxygen atoms due to the large standard deviations. The values for the copper atom, however, indicate a thermal ellipsoid of nearly rotational symmetry and with one axis considerably longer than the other two. This long ellipsoid axis is directed approximately perpendicular to the plane of Fig. 3. The vibrational amplitude for the copper atom is thus highest perpendicular to the short Cu–O bonds. This is reasonable and was found to be the case also in CuO (Åsbrink & Norrby, 1970).

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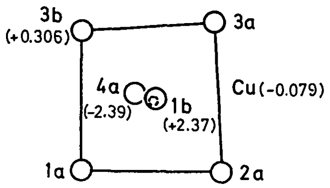

Fig. 3. The coordination around copper projected on to the plane defined by the centres of the oxygen atoms (1*a*), (2*a*) and (3*a*). The values in parentheses are the distances, in Å, of the other atoms above (+) or below (−) this plane.

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Table 6. *Interatomic distances and bond angles*

The Table gives metal–oxygen and metal–metal distances (in Å) as well as the bond angles (in degrees) at the metal atoms and the corresponding oxygen–oxygen separation (in Å). The standard deviations in the last digit are in brackets.

			Within CuO_6 octahedra				
Cu–O(2*a*)	1·961 (4)	O(1*b*)–Cu–O(1*a*)	89·7 (2)	3·135 (9)	O(2*a*)–Cu–O(4*a*)	101·2 (2)	3·332 (6)
–O(1*a*)	1·967 (5)	O(1*b*)–Cu–O(2*a*)	87·2 (2)	3·064 (6)	O(3*b*)–Cu–O(3*a*)	82·6 (2)	2·625 (9)
–O(3*a*)	1·978 (5)	O(1*b*)–Cu–O(3*b*)	79·5 (2)	2·865 (6)	O(3*b*)–Cu–O(4*a*)	92·1 (2)	3·131 (6)
–O(3*b*)	1·997 (5)	O(1*b*)–Cu–O(3*a*)	85·7 (2)	3·033 (7)	O(3*a*)–Cu–O(4*a*)	94·5 (2)	3·179 (6)
–O(4*a*)	2·340 (5)	O(1*a*)–Cu–O(2*a*)	90·4 (2)	2·788 (6)	O(1*b*)–Cu–O(4*a*)	171·5 (2)	4·777 (6)
–O(1*b*)	2·450 (5)	O(1*a*)–Cu–O(3*b*)	88·5 (2)	2·765 (7)	O(1*a*)–Cu–O(3*a*)	170·6 (2)	3·932 (7)
		O(1*a*)–Cu–O(4*a*)	88·8 (2)	3·026 (7)	O(2*a*)–Cu–O(3*b*)	166·7 (2)	3·932 (6)
		O(2*a*)–Cu–O(3*a*)	97·5 (2)	2·963 (6)			
			Within WO_6 octahedra				
W–O(1*b*)	1·760 (5)	O(1*b*)–W–O(2*c*)	94·3 (2)	2·784 (6)	O(2*b*)–W–O(4*c*)	82·4 (2)	2·769 (6)
–O(4*b*)	1·816 (5)	O(1*b*)–W–O(2*b*)	98·4 (2)	2·840 (6)	O(3*c*)–W–O(4*c*)	84·7 (2)	2·743 (6)
–O(3*c*)	1·845 (4)	O(1*b*)–W–O(3*c*)	103·2 (2)	2·826 (6)	O(3*c*)–W–O(4*b*)	98·0 (2)	2·762 (6)
–O(2*b*)	1·988 (4)	O(1*b*)–W–O(4*b*)	100·9 (2)	2·757 (7)	O(4*c*)–W–O(4*b*)	76·4 (2)	2·507 (9)
–O(2*c*)	2·028 (4)	O(2*c*)–W–O(2*b*)	73·8 (2)	2·411 (9)	O(1*b*)–W–O(4*c*)	172·0 (2)	3·959 (6)
–O(4*c*)	2·208 (5)	O(2*c*)–W–O(4*c*)	78·2 (2)	2·676 (6)	O(2*c*)–W–O(3*c*)	159·5 (2)	3·811 (6)
		O(2*c*)–W–O(4*b*)	88·9 (2)	2·697 (6)	O(2*b*)–W–O(4*b*)	155·0 (2)	3·714 (6)
		O(2*b*)–W–O(3*c*)	93·0 (2)	2·781 (6)			

Between polyhedra

Cu–Cu	2·986 (2)	W–W	3·172 (1)	O(1)–W	1·760 (5)	O(3)–W	1·845 (4)
–Cu	3·150 (2)	–W	3·212 (1)	–Cu	1·967 (5)	–Cu	1·978 (5)
				–Cu	2·450 (5)	–Cu	1·997 (5)
Cu–W, W–Cu	3·437 (1)						
	3·468 (1)			O(2)–Cu	1·961 (4)	O(4)–W	1·816 (5)
	3·507 (1)			–W	1·988 (4)	–W	2·208 (5)
	3·524 (1)			–W	2·028 (4)	–Cu	2·340 (5)
	3·549 (1)						
	3·636 (1)						
	3·826 (1)						
	4·117 (1)						

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The Structure of 3,4:7,8-Dibenzotricyclo[4.2.0.0^{2,5}]octa-3,7-diene

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The structure of 3,4:7,8-dibenzotricyclo[4.2.0.0^{2,5}]octa-3,7-diene has been studied by single-crystal diffraction techniques. This compound ($C_{16}H_{12}$) crystallizes in the monoclinic space group $P2_1/c$, with $a=10\cdot716$, $b=7\cdot706$, $c=6\cdot719$ Å, $\beta=98\cdot37°$, $Z=2$. The structure was determined by the symbolic addition procedure and was refined by block-diagonal least squares methods to a final R value of 0·069, including hydrogen atoms. The molecule is in the *anti* configuration, with two planar benzocyclobutene systems on opposite sides of a planar central cyclobutane ring. The bridgehead bond, common to two four-membered rings, is found to be unusually long, 1·593 Å.

Introduction

Since the early fifties, transition metal complexes and complex intermediates have become widely used for producing many organic compounds which would have been difficult or impossible to make otherwise. In producing benzocyclobutadiene and cyclobutadiene (Emerson, Watts & Pettit, 1965) by such methods many new and interesting compounds have been isolated. Three dimers of benzocyclobutadiene have been so prepared (Emerson *et al.*, 1965; Avram, Dinu & Nenitzescu, 1959; Cava & Napier, 1957). Formation of these dimeric products of benzocyclobutadiene is dependent upon different transition metals which act as catalysts. The title compound, hereinafter referred to as DBTCO, is the one of these dimers which was prepared using nickel tetracarbonyl as a catalyst (Avram *et al.*, 1959; Cava & Napier, 1957). This compound has so far only been isolated in one configuration, which has been shown by Griffin & Weber (1961) to be *anti*.

In other systems containing four-membered rings, the ring is in either the planar or the puckered conformation, and often exhibits unusually long carbon–carbon bond distances (Adman & Margulis, 1968). Fusion of other rings to four-membered rings seems to have varying effects on the cyclobutane ring geometry, depending on the nature of the fusing rings (Margulis, 1965; Einstein, Hosszu, Longworth, Rahn & Wei, 1967; Adman, Gordon & Jensen, 1968; Camerman, Weinblum & Nyburg, 1969; Camerman & Nyburg, 1969; Barnett & Davis, 1970). The present investigation was undertaken to determine the effect on ring geometry of fusion of cyclobutane with two highly strained four-membered rings.

Experimental

Suitable crystals for X-ray studies were obtained by recrystallization of a sample of DBTCO, kindly supplied by Professor R. Pettit, from an aqueous acetone solution. These crystals are clear, light gray bulky plates. The crystal used was approximately $0\cdot068\times0\cdot126\times0\cdot194$ mm with [001] parallel to the φ axis of the goniometer. All X-ray studies were carried out using a General Electric XRD-5 diffractometer equipped with a single crystal orienter, with Cu $K\alpha$ radiation, and at ambient room temperature (~21 °C).

Plots of the intensity weighted reciprocal lattice were used to determine the crystal symmetry. Cell constants were obtained from least-squares refinement using 27 independent 2θ measurements.

Crystal data

3,4:7,8-Dibenzotricyclo[4.2.0.0^{2,5}]octa-3,7-diene, $C_{16}H_{12}$. $a=10\cdot716\,(2)$, $b=7\cdot706\,(1)$, $c=6\cdot719\,(1)$ Å, $\beta=98\cdot37\,(2)°$. Systematic absences: $h0l$, $l=2n+1$; $0k0$, $k=2n+1$. Space group: $P2_1/c$ (No. 14). $Z=2$; $F(000)=216$; $V=548\cdot86$ Å^3; $\mu=5\cdot38$ (Cu $K\alpha$). λ(Cu $K\alpha_{\text{mean}}=1\cdot54178$, Cu $K\alpha_1=1\cdot54050$, Cu $K\alpha_2=1\cdot5433$ Å).

Three-dimensional single-crystal intensity data were collected by the stationary-crystal stationary-counter method to the limit $2\theta=130°$ (Cu $K\alpha_1$), using a balanced nickel–cobalt filter pair. Of the 925 in-