

The Crystal Structure of Zirconium Cupferrate, $\text{Zr}(\text{C}_6\text{H}_5\text{N}_2\text{O}_2)_4$

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The crystal structure of zirconium cupferrate, $\text{Zr}(\text{C}_6\text{H}_5\text{N}_2\text{O}_2)_4$, has been determined by three-dimensional X-ray methods. Zirconium cupferrate forms orthorhombic crystals belonging to the space group *Pbcn*. The crystals have the cell dimensions $a=16.746 \text{ \AA}$, $b=11.208 \text{ \AA}$, and $c=14.444 \text{ \AA}$ and contain four formula units per unit cell.

Intensity data were collected with an automatic single crystal diffractometer using $\text{MoK}\alpha$ radiation.

A three-dimensional electron density calculation based on the zirconium positions revealed the positions of all the light atoms. The structure was refined by means of least squares full matrix and block diagonal methods using a total of 1117 independent reflexions, a final *R*-value of 0.056 being obtained.

The crystal structure of zirconium cupferrate contains discrete $\text{Zr}(\text{C}_6\text{H}_5\text{N}_2\text{O}_2)_4$ molecules, the ligands being related by a two-fold axis through the zirconium atom. There are thus two structurally independent cupferrate ligands.

Zirconium is eight-fold coordinated by oxygen atoms situated at the vertices of a somewhat irregular dodecahedron with triangular faces. The Zr—O distances range from 2.16₃ to 2.22₃ Å. The distances within the organic ligands also lie within the normal range.

The formation of complexes between Th^{4+} and anions of *N*-nitroso-*N*-phenylhydroxylamine was investigated in 1956 by Dyrssen,¹ and in connection with this work, Neumann, Lundgren and Aurivillius started an investigation of the crystal structures of the corresponding zirconium and hafnium compounds,² since it was realised that the thorium atoms would dominate the X-ray scattering to such a degree that it might be difficult to locate the positions of the light atoms with sufficient accuracy. Crystals of both compounds were prepared, and from Weissenberg photographs taken with CuK radiation they were found to have orthorhombic symmetry, those of the zirconium complex having the approximate cell dimensions:

$$a = 16.7 \pm 0.2 \text{ \AA}, b = 11.2 \pm 0.1 \text{ \AA}, c = 14.4 \pm 0.2 \text{ \AA}.$$

The following reflexions are systematically absent:

$$\begin{array}{ll} h k 0 & \text{with } h + k = 2n + 1 \\ h 0 l & \text{» } l = 2n + 1 \\ 0 k l & \text{» } k = 2n + 1 \end{array}$$

and consequently the structure belongs to space group No. 60 $Pbcn^3$.

Three Patterson projections $P(upw)$, $P(pvw)$, and $P(uvp)$ showed² that the metal atoms occupied special positions on the two-fold axes, *i.e.* 4 Zr in $Pbcn$ 4(c): $\pm(0, y, 1/4)$, $\pm(1/2, 1/2 + y, 1/4)$ with $y = 0.074$.

From this result and from the fact that the organic ligands do not have two-fold symmetry, it was suggested that the complex had a "propeller" arrangement.²

The aim of the present investigation was to determine the positions of the light atoms, C, N, and O, and to refine the structural parameters.

CRYSTAL DATA

Crystals of $Zr(C_6H_5N_2O_2)_4$ were prepared under strongly acidic conditions according to previously described methods.^{4,5} The amount of *zirconium* was determined by ignition to ZrO_2 at 1000°C⁶ and was found to be 14.3 % (calculated value for the 4:1 complex = 14.26 %).

To obtain accurate cell dimensions, Guinier photographs were taken using $Pb(NO_3)_2$ as an internal standard ($CuK\alpha_1$ radiation, $\lambda = 1.54050$ Å, $a_{Pb(NO_3)_2} = 7.8565_7$ Å at 21°C⁷). 85 lines were indexed with generated $\sin^2\theta$ values calculated from the approximate cell dimensions. Using the program POWDER⁸ these lines were refined and the following cell dimensions and standard deviations were obtained:

$$\begin{array}{l} a = 16.7458 \pm 0.0010 \text{ \AA} \\ b = 11.2075 \pm 0.0007 \text{ \AA} \\ c = 14.4440 \pm 0.0007 \text{ \AA} \\ V = 2710.8 \text{ \AA}^3 \end{array}$$

The observed and calculated $\sin^2\theta$ values less than 0.093 are listed in Table 1. The previously reported density² of 1.573 ± 0.002 g/ml indicates that there are $4.01 \approx 4$ formula units in the unit cell.

INTENSITY DATA

The rod-shaped crystal used in this investigation had a cross-section of 0.16×0.12 mm² (a and b directions) and was cut to a length of 0.17 mm.

Reflexions were registered with an automatic single crystal diffractometer (Philips PAILRED), using $MoK\alpha$ radiation, with the b axis of the crystal as rotation axis. Data were collected from the zones $h0l$ - $h12l$ and reflexions were registered within 90° on both sides of the l axis so that both hkl and $\bar{h}k\bar{l}$ were observed. Since the linear absorption coefficient for $Zr(C_6H_5N_2O_2)_4$ is as low as 4.6 cm⁻¹ the $|F_o|^2$ values used in the calculations were obtained by correcting for Lorentz and polarization effects only, using the program DATA P1.⁹

Table 1. Guinier powder data for $Zr(C_6H_5N_2O_2)_4$. $CuK\alpha_1$ radiation. $\lambda=1.54050$ Å.

hkl	$10^6 \sin^2\theta$ calc	$10^6 \sin^2\theta$ obs	F calc	I obs
110	684	683	209	v st
200	846	845	304	v st
111	968	969	112	st
002	1137	1137	76	vw
102	1349	1348	95	m
211	1603	1603	130	st
112	1821	1820	259	v st
020	1889	1890	—	vw
202	1984	1984	239	st
021	2174	2177	50	vw
121	2385	2385	71	w
311	2661	2661	111	w
220	2736	2739	97	vw
221	3020		190	
022	3027	3023	143	st
122	3238		44	
113	3243	3241	60	vw
400	3385	3382	107	vw
312	3514	3515	104	w
222	3873		74	
213	3878	3876	40	vw
321	4078	4074	141	m
411	4142	4144	107	w
004	4550	4550	79	vw
131	4747	4750	57	vw
322	4931		181	
313	4936	4927	60	st
412	4995	4990	61	vw
114	5234	5229	94	w
420	5274	5271	119	vw
231	5382	5381	88	vw
421	5559	5563	249	st
510	5762	5764	132	vw
330	6155	6151	96	vw
422	6412	6418	175	st
331	6439	6434	193	st
314	6926	6927	95	vw
133	7022	7020	77	vw
224	7286	7278	40	vw
233	7657	7659	73	vw
115	7793	7793	70	vw
423	7834	7830	63	vw
431	7920	7921	110	w
522	8316		36	
513	8321	8318	45	vw
611	8373	8376	41	vw
241	8688		71	
333	8714	8709	115	w
025	8999	8997	92	vw
125	9210		39	
612	9226	9209	39	vw

POSITIONS OF THE ATOMS

A three-dimensional Patterson synthesis was computed with the program DRF⁹ in order to obtain accurate positions of the zirconium atoms. A total of 1173 reflexions were used, all the reflexions originating from the same side of the l axis in reciprocal space. The highest peaks in Patterson space, discounting the origin peak, were situated at $(1/2, 1/2, 0)$ with the height 750, at $(0, 0.15, 1/2)$ and at $(1/2, 0.35, 1/2)$ with the heights 390 and 350, respectively. Assuming these to be Zr–Zr vectors, 4 Zr must be situated in $Pbcn$ 4(c): $\pm(0, y, 1/4)$, $\pm(1/2, 1/2 + y, 1/4)$ with $y = 0.075$.

The light atoms C, N and O should occupy the general positions $Pbcn$ 8(d): $\pm(x, y, z)$, $\pm(1/2 - x, 1/2 - y, 1/2 + z)$, $\pm(1/2 + x, 1/2 - y, \bar{z})$, $\pm(\bar{x}, y, 1/2 - z)$ and each molecule must therefore contain two structurally non-equivalent pairs of ligands. Each ligand was assumed to be bonded to zirconium through oxygen rather than through nitrogen^{10,11} forming a bidentate chelate in accordance with the structure proposed for zirconium tetramandelate, $Zr(C_8H_7O_3)_4$ ^{12,13} and the structures found for zirconium acetylacetonate and $Na_4Zr(C_2O_4)_4(H_2O)_3$.^{14,15}

Structure factors were then calculated taking the contributions from zirconium alone into consideration. The observed structure factors which fell within the range $0.5 < F_o/F_c < 2.0$, were assigned the signs of the corresponding F_{calc} and used to calculate a three-dimensional electron density function. Apart from the Zr peaks, this $\rho(xyz)$ revealed forty light atom positions, whose corresponding vectors could all be found in $P(uvw)$. Since the zirconium atoms only contribute to every other reflexion in compliance with the condition $h + k = 2n$, each light atom position shown in this $\rho(xyz)$ must be accompanied by its mirror image in the planes $(x, y, 1/4)$ and $(x, y, 3/4)$, as is given by the general position $Cmcm$: 16(h).

There are thus two possible alternative groupings of the ligands around the zirconium atom. If the two pairs of ligands within the same molecule are denoted L(1) and L(2), respectively, the two alternative structures are related to each other in the following way. All L(1) parameters are identical in the two cases and the same is true for the x and y parameters of L(2), whereas the

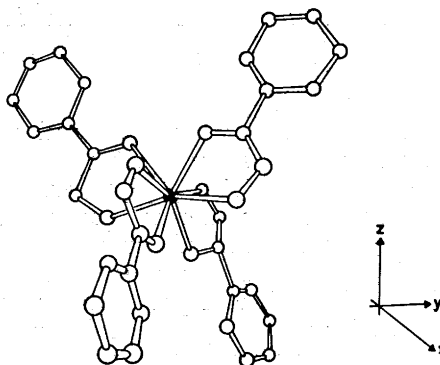


Fig. 1. The $Zr(C_8H_7N_2O_2)_4$ molecule in perspective.

Table 2. Preliminary positions of the light atoms derived from a 3-dimensional electron density calculation, based on the zirconium position.

L(1)				L(2)			
	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
8 C ₁ in <i>Pbcn</i> 8(<i>d</i>):	0.057	0.315	0.477	8 C ₇ in <i>Pbcn</i> 8(<i>d</i>):	0.311	0.368	0.108
8 C ₂ » » » :	0.000	0.275	0.545	8 C ₈ » » » :	0.318	0.409	0.015
8 C ₃ » » » :	0.000	0.325	0.626	8 C ₉ » » » :	0.277	0.364	0.953
8 C ₄ » » » :	0.055	0.434	0.641	8 C ₁₀ » » » :	0.222	0.280	0.967
8 C ₅ » » » :	0.110	0.481	0.573	8 C ₁₁ » » » :	0.206	0.247	0.058
8 C ₆ » » » :	0.108	0.421	0.480	8 C ₁₂ » » » :	0.258	0.283	0.138
8 N ₁ » » » :	0.057	0.254	0.387	8 N ₃ » » » :	0.364	0.420	0.174
8 N ₂ » » » :	0.099	0.290	0.315	8 N ₄ » » » :	0.363	0.382	0.250
8 O ₁ » » » :	0.000	0.150	0.385	8 O ₃ » » » :	0.425	0.500	0.150
8 O ₂ » » » :	0.090	0.222	0.250	8 O ₄ » » » :	0.423	0.433	0.310

z parameters of L(2) are *z* in alternative I and $1/2 - z$ in alternative II. One alternative entails a dodecahedral configuration about the central zirconium atom (cf. Fig. 1) and gave an *R*-value of 0.20 based on the preliminary parameters shown in Table 2. The configuration about zirconium in the other arrangement is either square antiprismatic or dodecahedral, both configurations being considerably distorted. Since this latter arrangement gave a higher *R*-value (0.24) it was abandoned in favour of the former. In addition, 28 reflexions of the 1173 used in the structure factor calculation fell outside the range $0.3 < F_o/F_c < 3.0$ in the first case, whereas, in the second case, this number was 97.

One cycle of least squares full matrix refinement using the program LALS⁹ resulted in an *R*-value of 0.113. At this stage of the investigation the data set of $|F|_{hkl}$ used hitherto was replaced by the mean values of $|F|_{hkl}$ and $|F|_{\bar{h}\bar{k}\bar{l}}$, those reflexions that did not occur twice being eliminated. The *R*-value based on this new set of 1117 structure factors then dropped to 9.7 %.

In the final refinement of the positional and isotropic thermal parameters, individual scale factors for the different layers were also calculated and refined. This was considered to be necessary since the crystal had been exposed continuously to MoK α radiation for more than two months and could have decomposed slightly.

After three additional cycles of least squares full matrix refinement, using a weighting scheme recommended by Cruickshank¹⁶ ($w = [50 + |F_o| + 0.006 |F_o|^2]^{-1}$), an *R*-value of 0.075 was obtained.

The isotropic thermal parameters were then converted into anisotropic parameters and the refinement was continued with least squares block diagonal methods, since, if allowance was made for anisotropic temperature coefficients, the total number of parameters was greater than the upper limit of 159 accepted by the computer in full matrix least squares calculations. After five cycles of refinement, the *R*-value converged to 0.061. Assuming a bond distance of 1.08 Å between carbon and hydrogen in the benzene rings, the positions of

the hydrogen atoms were calculated using the program HYDROGENS.¹⁷ Each hydrogen atom was given an isotropic temperature coefficient of 2.5, which is about the same as those obtained for the carbon atoms.

Three more cycles of refinement, in which the hydrogen atom parameters were included in structure factor calculations but not in the refinement, yielded a final R -value of 0.056. The hydrogen atom positions were then adjusted slightly but the R -value and the standard deviations were not altered by further refinement. The atomic scattering factors used for H, C, N, and O were those given in the International Tables⁷ and for Zr those of Cromer and Waber.¹⁸

The calculated parameters of the hydrogen atoms are listed in Table 3 and the resulting atomic coordinates and anisotropic temperature coefficients of the other atoms together with their standard deviations in Tables 4 and 5. Calculated and observed structure factors are given in Table 6.

The accuracy of the structure was tested by means of a three-dimensional ($F_o - F_c$) Fourier synthesis which showed a maximum electron density of $0.5 \text{ e}/\text{\AA}^3$. Distances and angles within the molecule, shown schematically in Fig. 2, were calculated with the program DISTAN⁹ and are given in Table 7. Within the limits of the standard deviations all distances and angles lie in the normal range.

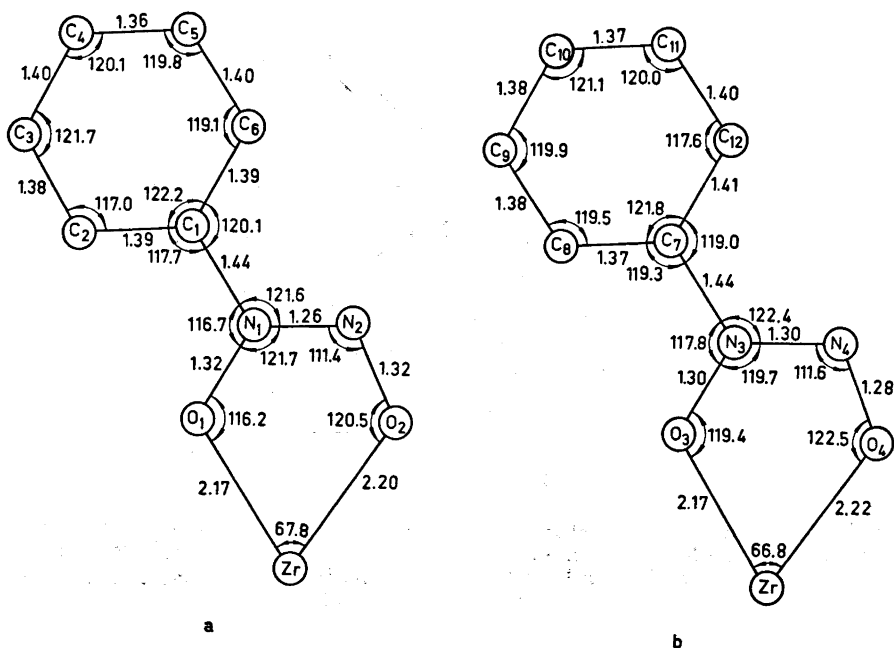


Fig. 2. Schematic representation of the two structurally independent ligands. a: L(1) b: L(2).

Table 3. Calculated positions of hydrogen atoms.

	<i>x</i>	<i>y</i>	<i>z</i>
H ₁	0.4673	0.2983	0.4673
H ₂	0.4732	0.1970	0.3155
H ₃	0.4464	0.0147	0.2057
H ₄	0.1420	0.4462	0.0825
H ₅	0.1436	0.4476	0.4314
H ₆	0.1384	0.0180	0.4989
H ₇	0.2230	0.1077	0.3782
H ₁₀	0.3171	0.2666	0.4185
H ₁₁	0.1650	0.1716	0.0796
H ₁₂	0.2539	0.2546	0.2023

DISCUSSION OF THE STRUCTURE

The crystal consists of discrete molecules of $Zr(C_6H_5N_2O_2)_4$ (cf. Fig. 1), packed as illustrated in Fig. 3. The shortest intermolecular distances, which are about 3.3 Å and are outlined in Fig. 3, occur between structurally non-equivalent ligands and correspond to normal van der Waals contacts.

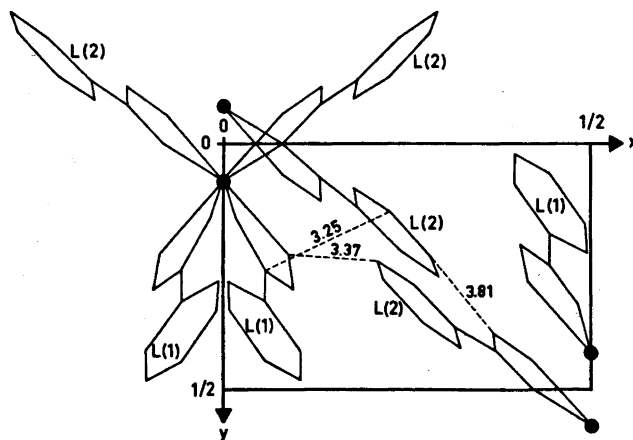


Fig. 3. Projection of the structure on the *xy*-plane to illustrate the packing of ligands belonging to molecules centered at $(0, y, 1/4)$, $(0, \bar{y}, 3/4)$, $(1/2, 1/2 + y, 1/4)$ and $(1/2, 1/2 - y, -1/4)$. The broken lines (distances in Å) indicate the shortest distances between adjacent molecules.

Table 4. Atomic coordinates expressed as fractions of the cell edges. Standard deviations are given within parentheses.

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Zr	0	0.07529(10)	1/4
C ₁	0.0575(5)	0.3175(8)	0.4751(7)
C ₂	0.4932(7)	0.2234(8)	0.0440(6)
C ₃	0.4911(8)	0.1642(8)	0.1276(7)
C ₄	0.4441(7)	0.0624(10)	0.1407(7)
C ₅	0.3956(7)	0.0232(9)	0.0718(9)
C ₆	0.1057(6)	0.4170(9)	0.4870(7)
C ₇	0.3152(6)	0.3709(8)	0.1053(7)
C ₈	0.3204(6)	0.4115(9)	0.0163(7)
C ₉	0.2276(7)	0.1379(10)	0.4491(8)
C ₁₀	0.2813(7)	0.2259(11)	0.4722(9)
C ₁₁	0.2099(7)	0.2370(9)	0.0623(9)
C ₁₂	0.2590(7)	0.2840(9)	0.1314(7)
N ₁	0.0576(5)	0.2546(7)	0.3883(6)
N ₂	0.0958(5)	0.2929(9)	0.3193(6)
N ₃	0.3677(4)	0.4194(7)	0.1745(5)
N ₄	0.3665(5)	0.3839(7)	0.2602(6)
O ₁	0.0190(3)	0.1521(5)	0.3859(4)
O ₂	0.0876(4)	0.2217(6)	0.2473(6)
O ₃	0.4188(4)	0.4998(6)	0.1487(4)
O ₄	0.4184(4)	0.4390(6)	0.3092(4)

Table 5. Anisotropic temperature coefficients for Zr(C₆H₅N₂O₂)₄. The temperature coefficient is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$. Standard deviations are given within parentheses.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zr	0.00226(3)	0.00438(7)	0.00202(5)	0	0.00020(13)	0
C ₁	0.0014(3)	0.0022(7)	0.0017(5)	0.0003(8)	-0.0008(7)	0.0015(10)
C ₂	0.0025(4)	0.0041(7)	0.0013(4)	-0.0005(13)	-0.0019(9)	-0.0005(9)
C ₃	0.0034(5)	0.0041(7)	0.0032(5)	0.0000(13)	0.0027(11)	-0.0007(11)
C ₄	0.0029(4)	0.0050(8)	0.0022(5)	-0.0017(11)	-0.0004(8)	-0.0017(12)
C ₅	0.0030(4)	0.0040(8)	0.0042(7)	-0.0022(11)	-0.0012(10)	-0.0020(14)
C ₆	0.0028(4)	0.0022(6)	0.0028(6)	-0.0011(11)	0.0007(8)	0.0005(12)
C ₇	0.0021(4)	0.0025(6)	0.0025(5)	0.0011(9)	0.0008(8)	-0.0007(11)
C ₈	0.0028(4)	0.0037(7)	0.0022(5)	-0.0006(11)	0.0015(8)	0.0000(12)
C ₉	0.0026(4)	0.0063(10)	0.0022(6)	-0.0004(11)	-0.0012(8)	-0.0012(13)
C ₁₀	0.0021(4)	0.0057(9)	0.0045(7)	-0.0003(11)	0.0001(10)	-0.0016(15)
C ₁₁	0.0027(4)	0.0031(8)	0.0046(7)	-0.0016(10)	0.0005(9)	-0.0009(13)
C ₁₂	0.0024(4)	0.0037(7)	0.0024(5)	-0.0011(10)	-0.0002(8)	-0.0002(12)
N ₁	0.0011(3)	0.0037(6)	0.0023(4)	-0.0009(7)	0.0005(6)	-0.0003(9)
N ₂	0.0018(3)	0.0068(8)	0.0020(4)	-0.0021(9)	0.0009(7)	0.0024(11)
N ₃	0.0015(2)	0.0021(5)	0.0015(4)	-0.0006(8)	-0.0004(5)	0.0002(9)
N ₄	0.0034(3)	0.0054(6)	0.0017(5)	-0.0002(8)	0.0016(8)	0.0028(12)
O ₁	0.0016(3)	0.0029(4)	0.0015(3)	-0.0025(5)	0.0003(4)	-0.0004(7)
O ₂	0.0030(3)	0.0065(5)	0.0015(3)	-0.0027(7)	0.0017(8)	-0.0004(14)
O ₃	0.0022(2)	0.0040(5)	0.0014(3)	-0.0018(7)	-0.0007(5)	0.0022(8)
O ₄	0.0024(3)	0.0044(5)	0.0018(3)	-0.0027(7)	-0.0003(5)	-0.0003(8)

Table 6. Continued.

H 5 12	2	42	-33	4	41	-45	H 7 6	8	61	-57	5	40	-41	14	-	11
1 33	3	23	-25	5	-	-14	1 90	10	36	-33	6	54	-53	15	-	15
2 -	4	-	-24	6	57	-61	2 39	12	43	-45	7	-	-12	H 9 2	15	2
3 -	5	-	-18	7	-	-19	3 82	14	-	-27	8	49	51	1	-	15
4 -	6	-	-17	8	58	-59	4 23	16	33	-31	9	-	-2	2	39	-41
5 27	7	31	32	9	-	15	5 -	17	0	-	10	34	40	3	27	24
6 -	8	56	-55	10	45	-44	6 -	18	H 8 1	11	-	11	-	4	23	-24
7 40	9	-	-49	11	-	-16	7 -	19	1	15	-14	12	48	45	5	26
8 -	10	41	-49	12	6 13	-	8 36	20	2	33	35	H 8 7	0	33	-35	7
9 33	11	-	-20	13	-	-30	9 69	22	3	16	16	0	3	25	-21	8
1 42	12	32	-30	14	-	13	10 -	23	4	39	38	1	25	-21	9	-
2 -	13	-	-11	15	-	-17	11 71	24	5	13	13	2	-	-16	10	-
3 38	14	-	-17	16	-	-17	12 -	25	6	28	26	3	28	28	10	-
4 -	15	-	-17	17	-	-17	13 54	26	7	-	-	4	28	26	11	-
5 -	16	-	-17	18	-	-17	14 -	27	8	-	-1	5	-	-10	12	-
6 67	17	-	-17	19	-	-17	15 36	28	9	-	3	6	-	-9	13	-
7 -	18	-	-17	20	-	-17	16 -	29	10	42	40	7	-	-3	14	-
8 -	19	-	-17	21	-	-17	17 38	30	11	-	17	4	-	-15	15	-
9 -	20	-	-17	22	-	-17	18 -	31	12	39	33	9	-	-14	-	11
10 -	21	-	-17	23	-	-17	19 -	32	13	-	3	9	-	-10	-	9
11 -	22	-	-17	24	-	-17	20 -	33	14	-	30	10	31	-	-	3
12 -	23	-	-17	25	-	-17	21 -	34	15	-	12	11	-	-25	-	4
13 -	24	-	-17	26	-	-17	22 -	35	16	-	13	12	-	-25	-	4
14 -	25	-	-17	27	-	-17	23 -	36	17	-	14	13	-	-25	-	4
15 -	26	-	-17	28	-	-17	24 -	37	18	-	15	14	-	-25	-	4
16 -	27	-	-17	29	-	-17	25 -	38	19	-	16	15	-	-25	-	4
17 -	28	-	-17	30	-	-17	26 -	39	20	-	17	16	-	-25	-	4
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20 -	31	-	-17	33	-	-17	29 -	42	23	-	20	19	-	-25	-	4
21 -	32	-	-17	34	-	-17	30 -	43	24	-	21	20	-	-25	-	4
22 -	33	-	-17	35	-	-17	31 -	44	25	-	22	21	-	-25	-	4
23 -	34	-	-17	36	-	-17	32 -	45	26	-	23	22	-	-25	-	4
24 -	35	-	-17	37	-	-17	33 -	46	27	-	24	23	-	-25	-	4
25 -	36	-	-17	38	-	-17	34 -	47	28	-	25	24	-	-25	-	4
26 -	37	-	-17	39	-	-17	35 -	48	29	-	26	25	-	-25	-	4
27 -	38	-	-17	40	-	-17	36 -	49	30	-	27	26	-	-25	-	4
28 -	39	-	-17	41	-	-17	37 -	50	31	-	28	27	-	-25	-	4
29 -	40	-	-17	42	-	-17	38 -	51	32	-	29	28	-	-25	-	4
30 -	41	-	-17	43	-	-17	39 -	52	33	-	30	29	-	-25	-	4
31 -	42	-	-17	44	-	-17	40 -	53	34	-	31	30	-	-25	-	4
32 -	43	-	-17	45	-	-17	41 -	54	35	-	32	31	-	-25	-	4
33 -	44	-	-17	46	-	-17	42 -	55	36	-	33	32	-	-25	-	4
34 -	45	-	-17	47	-	-17	43 -	56	37	-	34	33	-	-25	-	4
35 -	46	-	-17	48	-	-17	44 -	57	38	-	35	34	-	-25	-	4
36 -	47	-	-17	49	-	-17	45 -	58	39	-	36	35	-	-25	-	4
37 -	48	-	-17	50	-	-17	46 -	59	40	-	37	36	-	-25	-	4
38 -	49	-	-17	51	-	-17	47 -	60	41	-	38	37	-	-25	-	4
39 -	50	-	-17	52	-	-17	48 -	61	42	-	39	38	-	-25	-	4
40 -	51	-	-17	53	-	-17	49 -	62	43	-	40	39	-	-25	-	4
41 -	52	-	-17	54	-	-17	50 -	63	44	-	41	40	-	-25	-	4
42 -	53	-	-17	55	-	-17	51 -	64	45	-	42	41	-	-25	-	4
43 -	54	-	-17	56	-	-17	52 -	65	46	-	43	42	-	-25	-	4
44 -	55	-	-17	57	-	-17	53 -	66	47	-	44	43	-	-25	-	4
45 -	56	-	-17	58	-	-17	54 -	67	48	-	45	44	-	-25	-	4
46 -	57	-	-17	59	-	-17	55 -	68	49	-	46	45	-	-25	-	4
47 -	58	-	-17	60	-	-17	56 -	69	50	-	47	46	-	-25	-	4
48 -	59	-	-17	61	-	-17	57 -	70	51	-	48	47	-	-25	-	4
49 -	60	-	-17	62	-	-17	58 -	71	52	-	49	48	-	-25	-	4
50 -	61	-	-17	63	-	-17	59 -	72	53	-	50	49	-	-25	-	4
51 -	62	-	-17	64	-	-17	60 -	73	54	-	51	50	-	-25	-	4
52 -	63	-	-17	65	-	-17	61 -	74	55	-	52	51	-	-25	-	4
53 -	64	-	-17	66	-	-17	62 -	75	56	-	53	52	-	-25	-	4
54 -	65	-	-17	67	-	-17	63 -	76	57	-	54	53	-	-25	-	4
55 -	66	-	-17	68	-	-17	64 -	77	58	-	55	54	-	-25	-	4
56 -	67	-	-17	69	-	-17	65 -	78	59	-	56	55	-	-25	-	4
57 -	68	-	-17	70	-	-17	66 -	79	60	-	57	56	-	-25	-	4
58 -	69	-	-17	71	-	-17	67 -	80	61	-	58	57	-	-25	-	4
59 -	70	-	-17	72	-	-17	68 -	81	62	-	59	58	-	-25	-	4
60 -	71	-	-17	73	-	-17	69 -	82	63	-	60	59	-	-25	-	4
61 -	72	-	-17	74	-	-17	70 -	83	64	-	61	60	-	-25	-	4
62 -	73	-	-17	75	-	-17	71 -	84	65	-	62	61	-	-25	-	4
63 -	74	-	-17	76	-	-17	72 -	85	66	-	63	62	-	-25	-	4
64 -	75	-	-17	77	-	-17	73 -	86	67	-	64	63	-	-25	-	4
65 -	76	-	-17	78	-	-17	74 -	87	68	-	65	64	-	-25	-	4
66 -	77	-	-17	79	-	-17	75 -	88	69	-	66	65	-	-25	-	4
67 -	78	-	-17	80	-	-17	76 -	89	70	-	67	66	-	-25	-	4
68 -	79	-	-17	81	-	-17	77 -	90	71	-	68	67	-	-25	-	4
69 -	80	-	-17	82	-	-17	78 -	91	72	-	69	68	-	-25	-	4
70 -	81	-	-17	83	-	-17	79 -	92	73	-	70	69	-	-25	-	4
71 -	82	-	-17	84	-	-17	80 -	93	74	-	71	70	-	-25	-	4
72 -	83	-	-17	85	-	-17	81 -	94	75	-	72	71	-	-25	-	4
73 -	84	-	-17	86	-	-17	82 -	95	76	-	73	72	-	-25	-	4
74 -	85	-	-17	87	-	-17	83 -	96	77	-	74	73	-	-25	-	4
75 -	86	-	-17	88	-	-17	84 -	97	78	-	75	74	-	-25	-	4
76 -	87	-	-17	89	-	-17	85 -	98	79	-	76	75	-	-25	-	4
77 -	88	-	-17	90	-	-17	86 -	99	80	-	77	76	-	-25	-	4
78 -	89	-	-17	91	-	-17	87 -	100	81	-	78	77	-	-25	-	4
79 -	90	-	-17	92	-	-17	88 -	101	82	-	79	78	-	-25	-	4
80 -	91	-	-17	93	-	-17	89 -	102	83	-	80	79	-	-25	-	4
81 -	92	-	-17	94	-	-17	90 -	103	84	-	81	80	-	-25	-	4
82 -	93	-	-17	95	-	-17	91 -	104	85	-	82	81	-	-25	-	4
83 -	94	-	-17	96	-	-17	92 -	105	86	-	83	82	-	-25	-	4
84 -	95	-	-17	97	-	-17	93 -	106	87	-	84	83	-	-25	-	4
85 -	96	-	-17	98	-	-17	94 -	107	88	-	85	84	-	-25	-	4
86 -	97	-	-17	99	-	-17	95 -	108	89	-	86	85	-	-25	-	4
87 -	98	-	-17	100	-	-17	96 -	109	90	-	87	86	-	-25	-	4
88 -	99	-	-17	101	-	-17	97 -	110	91	-	88	87	-	-25	-	4
89 -	100	-	-17	102	-	-17	98 -	111	92	-	89	88	-	-25	-	4
90 -	101	-	-17	103	-	-17	99 -	112	93	-	90	89	-	-25	-	4
91 -	102	-	-17	104	-	-17	100 -	113	94	-	91	90	-	-25	-	4
92 -	103	-	-17	105	-	-17	101 -	114	95	-	92	91	-	-25	-	4
93 -	104	-	-17	106	-	-17	102 -	115	96	-	93	92	-	-25	-	4
94 -	105	-	-17	107	-	-17	103 -	116	97	-	94	93	-	-25	-	4
95 -	106	-	-17	108	-	-17	104 -	117	98	-	95	94	-	-25	-	4
96 -	107	-	-17	109	-	-17</										

Table 6. Continued.

1	H	9	8	1	H	9	12	7	-	-21	7	-	-13	8	25	-19	5	-	-10	H	12	3	-8
2	-	-	24	2	-	-	0	8	65	-63	8	45	-47	9	32	33	6	-	-2	0	-	-	-4
3	-	-	-10	3	-	-	-6	9	-	-10	9	-	-2	1	22	-27	7	33	-26	1	-	-	-15
4	-	-	-25	4	-	-	-16	10	44	-46	10	37	-34	2	16	-17	8	-	-9	2	-	-	-16
5	-	-	0	5	41	-49	1	H	9	13	0	H	10	8	0	2	22	-20	1	H	11	7	3
6	-	-	5	6	35	37	1	35	37	0	38	40	0	1	10	0	3	22	-20	2	64	-67	4
7	36	-31	2	7	35	32	2	-	-10	1	30	32	2	28	-30	5	4	22	-28	3	93	-31	5
8	-	-	16	8	3	35	32	3	-	8	3	-	8	3	-	11	6	-	-9	4	93	-31	6
9	-	-	-14	9	-	-	-	4	-	10	4	-	10	4	-	11	6	-	-9	4	11	-23	7
10	-	-	-2	10	-	-	-	5	-	0	5	-	0	5	-	12	7	-	-12	6	32	-31	8
11	-	-	3	11	-	-	-	6	27	27	6	-	-14	6	-	16	8	-	-4	7	32	-31	9
								7	-	-6	7	-	-6	7	-	18	9	-	-18	8	-	-	10
								8	-	-4	8	-	-4	8	-	10	9	-	-18	9	-	-	11
								9	-	-12	9	-	-12	9	-	11	9	-	-18	10	-	-	12
								10	-	0	10	-	0	10	-	12	10	-	-18	11	-	-	13
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Table 7. Distances and angles in the Zr cupferrate molecule.

O ₁ -N ₁	1.318 ± 0.009 Å	O ₃ -N ₃	1.297 ± 0.010 Å
O ₄ -N ₂	1.318 ± 0.012 Å	O ₄ -N ₃	1.279 ± 0.011 Å
N ₁ -N ₂	1.259 ± 0.012 Å	N ₃ -N ₄	1.301 ± 0.012 Å
N ₁ -C ₁	1.438 ± 0.013 Å	N ₃ -C ₇	1.438 ± 0.013 Å
C ₁ -C ₂	1.387 ± 0.014 Å	C ₇ -C ₈	1.365 ± 0.015 Å
C ₂ -C ₃	1.378 ± 0.013 Å	C ₈ -C ₉	1.377 ± 0.015 Å
C ₃ -C ₄	1.400 ± 0.016 Å	C ₉ -C ₁₀	1.376 ± 0.017 Å
C ₄ -C ₅	1.357 ± 0.016 Å	C ₁₀ -C ₁₁	1.374 ± 0.018 Å
C ₅ -C ₆	1.396 ± 0.016 Å	C ₁₁ -C ₁₂	1.396 ± 0.016 Å
C ₆ -C ₁	1.387 ± 0.014 Å	C ₁₂ -C ₇	1.406 ± 0.014 Å
O ₁ -Zr-O ₂	67.8 ± 0.3°	O ₃ -Zr-O ₄	66.8 ± 0.3°
Zr-O ₁ -N ₁	116.		

The molecule can be roughly described in terms of two planes, intersecting at the central zirconium atom to make an angle of approximately 80° . Each plane consists of two ligands, L(1) and L(2), which point upwards in the z direction in one plane and downwards in the other. Each ligand L(1) and L(2) is in fact composed of two different planes, *e.g.* in L(1), the five-membered ring $\text{Zr}-\text{O}_1-\text{N}_1-\text{N}_2-\text{O}_2$ and the six-membered ring $\text{C}_1-\text{C}_2-\text{C}_3-\text{C}_4-\text{C}_5-\text{C}_6$. The best fitting planes through the ring systems and the mean plane for the dodecahedron trapezoid, $\text{Zr}-\text{O}_1-\text{O}_2-\text{O}_3-\text{O}_4$, were determined by least squares calculations with the program PLANEFIT⁹ for a molecule with Zr situated in (0,0.0753,1/4). The planes are given in cartesian coordinates (Ångströms) in Table 8, together with angles between those planes which

Table 8. Best fitting planes through different ring systems in the zirconium cupferrate molecule. Zr situated in (0,0.0753,1/4).

Plane No.	Atoms defining the plane	Mean plane in Cartesian coordinates (Å)
1	$\text{Zr}-\text{O}_1-\text{O}_2-\text{O}_3-\text{O}_4$	$-0.7020X + 0.6896Y - 0.1779Z = -0.0005$
2	$\text{Zr}-\text{O}_1-\text{N}_1-\text{N}_2-\text{O}_2$	$-0.7769X + 0.5896Y - 0.2210Z = -0.3746$
3	$\text{Zr}-\text{O}_3-\text{N}_3-\text{N}_4-\text{O}_4$	$-0.6684X + 0.7135Y - 0.2101Z = -0.1563$
4	$\text{O}_1-\text{N}_1-\text{N}_2-\text{O}_2$	$-0.8226X + 0.4905Y - 0.2876Z = -1.0216$
5	$\text{O}_3-\text{N}_3-\text{N}_4-\text{O}_4$	$-0.6689X + 0.7131Y - 0.2100Z = -0.1544$
6	$\text{C}_1-\text{C}_2-\text{C}_3-\text{C}_4-\text{C}_5-\text{C}_6$	$-0.7367X + 0.5888Y - 0.3327Z = -0.8904$
7	$\text{C}_7-\text{C}_8-\text{C}_9-\text{C}_{10}-\text{C}_{11}-\text{C}_{12}$	$-0.6848X + 0.7071Y - 0.1764Z = 0.1101$

Angles between the planes					
1-2:	7.6°	4-5:	16.2°	5-7:	2.1°
1-3:	3.0°	2-4:	7.3°	6-7:	11.6°
1-4:	14.8°	3-5:	0.0°	2-7:	8.9°
1-5:	3.0°	2-6:	6.8°	3-6:	10.8°
1-6:	10.8°	3-7:	2.2°	4-7:	16.1°
1-7:	1.4°	4-6:	7.9°	5-6:	10.7°
2-3:	9.5°				

Plane No.	Deviations from the best fitting plane (Å × 10 ³)	
	for atoms defining the plane	for other atoms
1	$\text{Zr}(-59), \text{O}_1(-39), \text{O}_2(49), \text{O}_3(51), \text{O}_4(-2)$	
2	$\text{Zr}(74), \text{O}_1(-99), \text{N}_1(68), \text{N}_2(46), \text{O}_2(-89)$	
3	$\text{Zr}(-4), \text{O}_3(-2), \text{N}_3(5), \text{N}_4(-5), \text{O}_4(3)$	
4	$\text{O}_1(-8), \text{N}_1(14), \text{N}_2(-14), \text{O}_2(7)$	Zr(397)
5	$\text{O}_3(-3), \text{N}_3(5), \text{N}_4(-5), \text{O}_4(3)$	Zr(-2)
6	$\text{C}_1(-7), \text{C}_2(18), \text{C}_3(-19), \text{C}_4(9), \text{C}_5(2), \text{C}_6(-2)$	$\text{O}_1(-195), \text{O}_2(85), \text{N}_1(-6), \text{N}_2(108)$
7	$\text{C}_7(-19), \text{C}_8(16), \text{C}_9(3), \text{C}_{10}(-20), \text{C}_{11}(17), \text{C}_{12}(3)$	$\text{O}_3(-75), \text{O}_4(-144), \text{N}_3(-61), \text{N}_4(-110)$

together constitute an approximately planar half of the molecule. Atoms defining the planes deviate from their respective planes by less than one standard deviation in all cases except for the dodecahedron trapezoid and the five-membered ring of L(1) (*cf.* Table 8).

Each zirconium is eight-fold coordinated by oxygen atoms situated at the vertices of a somewhat distorted dodecahedron with triangular faces of approximate symmetry $D_{2d}-\bar{4}2m$ (*cf.* Fig. 4). The *a priori* choice of a neutral eight-coordinated bidentate complex to achieve either an antiprismatic or a dodecahedral configuration is according to facts outlined by Hoard and Silverton¹⁹ almost impossible to predict.

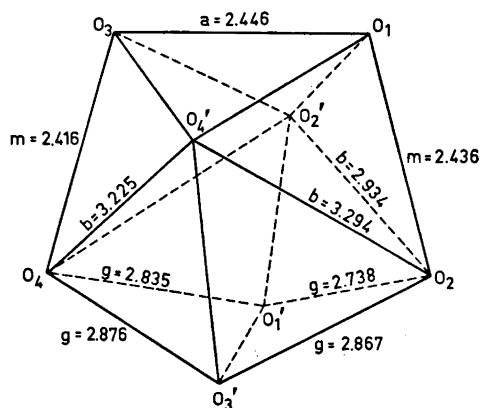


Fig. 4. The eight-fold configuration of oxygen atoms about zirconium in $Zr(C_6H_5N_2O_2)_4$. The letters are those used by Hoard and Silverton¹⁹ to indicate distances that ought to be equal according to the ideal $\bar{4}2m$ symmetry.

The eight oxygen atoms form two equivalent trapezoids (O_1, O_2, O_3, O_4) lying in two planes which deviate by 2.8° from the ideal case in which they would be mutually perpendicular. Within the ZrO_8 polyhedron there are two types of $Zr-O$ distances denoted by $M-A$ and $M-B$, respectively, where B refers to oxygen atoms at the base of the trapezoids. According to Duffey,²⁰ $M-A$ orbitals have a larger fraction of d -character. Hence σ -bonding to the A atoms should be stronger than to the B atoms and the $M-A$ bonds should presumably be shorter than the $M-B$ bonds. This is the case in $Zr(C_6H_5N_2O_2)_4$ but the opposite is true for $Na_4Zr(C_2O_4)_4(H_2O)_3$ ¹⁵ and $Zr_2(OH)_2(SO_4)_3(H_2O)_4$.²¹ Distances within these different polyhedra together with the lengths of the dodecahedron edges, labeled in accordance with Hoard and Silverton,¹⁹ are compared in Table 9 with the hard sphere model (HSM) and the most favourable model (MF) proposed by the same authors. Due to the minimisation of the repulsive energy between the ligands in a molecule the edges of the polyhedron differ significantly from those of the hard sphere model, *e.g.* the long O_4-O_3' distance ($g = 2.88 \text{ \AA}$).

In order to minimise the interaction with L(2) ligands from neighbouring molecules (*cf.* Fig. 3) and at the same time ensure that there is sufficient separation between the L(1) ligands in one molecule ($O_2-N_1' = 3.14 \text{ \AA}$), repulsion presumably occurs along the z axis between the L(1) ligands. This

Table 9. Interatomic distances (in Å) within the ZrO₆ polyhedra in Zr(C₆H₅N₃O₂)₄ and in some structurally related compounds.

	M—A		M—B	
	Zr—O ₁	2.168 ± 0.006	Zr—O ₂	2.201 ± 0.007
	Zr—O ₃	2.169 ± 0.007	Zr—O ₄	2.222 ± 0.007
Average		2.168		2.212
Zr(C ₆ H ₅ N ₃ O ₂) ₄ ⁴⁻		2.230		2.168
Zr ₂ (OH) ₂ (SO ₄) ₃ (H ₂ O) ₄		2.202		2.185
	<i>a</i>		<i>m</i>	
	O ₁ —O ₂	2.446 ± 0.009	O ₁ —O ₃	2.436 ± 0.010
			O ₃ —O ₄	2.416 ± 0.009
Average		2.446		2.426
Zr(C ₆ H ₅ N ₃ O ₂) ₄ ⁴⁻		2.570		2.563
Zr ₂ (OH) ₂ (SO ₄) ₃ (H ₂ O) ₄		2.78		2.49
HSM		2.63		2.63
MF		2.57		2.57
	<i>g</i>		<i>b</i>	
	O ₄ —O ₃ '	2.876 ± 0.010	O ₂ —O ₂ '	2.934 ± 0.014
	O ₂ —O ₂ '	2.867 ± 0.010	O ₂ —O ₄ '	3.294 ± 0.010
	O ₄ —O ₁ '	2.835 ± 0.009	O ₄ —O ₄ '	3.225 ± 0.014
	O ₃ —O ₁ '	2.738 ± 0.010		
Average		2.829		3.151
Zr(C ₆ H ₅ N ₃ O ₂) ₄ ⁴⁻		2.735		3.19
Zr ₂ (OH) ₂ (SO ₄) ₃ (H ₂ O) ₄		2.72		3.21
HSM		2.63		3.29
MF		2.72		3.27

would lead to a reduction of the O₂—O₂' distance ($b = 2.93$ Å) and a consequent shortening of the O₁—O₃ distance ($a = 2.45$ Å) to relieve the strain within the five-membered ring Zr—O₁—N₁—N₂—O₂. Such an assumption would also explain the exceptionally long *g* edges, O₂—O₃' (2.87 Å) and O₄—O₁' (2.84 Å), as well as the fact that zirconium lies 0.40 Å above and below, respectively, the best fitting planes through O₁—N₁—N₂—O₂. The plane containing O₂—Zr—O₂' is almost perpendicular to the *z* axis so that it is possible that there is interaction between the filled *d_{xy}*-orbital of zirconium and the oxygen πp -orbitals leading to repulsion between the O₂ atoms. This is supported by the fact that for the L(2) ligands, where such an interaction is impossible, zirconium lies only 0.002 Å above and below the plane O₃—N₃—N₄—O₄ (cf. Table 8).

Configurations and average Zr—O distances for some oxygen containing zirconium and hafnium compounds with seven- or eight-fold coordination are summarised in Table 10. It is apparent that the Zr—O distances obtained for zirconium cupferrate, ranging from 2.168 to 2.222 Å, are in good agreement with those found in other eight-fold coordinated zirconium compounds.

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Table 10. Structural characteristics of some oxygen containing zirconium and hafnium compounds.

Compound	Coord. No. of metal	Configuration	Bond dist. Zr(Hf)–O(Å)	Ref.
ZrO ₂ (cubic)	8	cubic	2.20	22
ZrO ₂ (tetr.)	8	dodecahedron	2.26	23
ZrO ₂ (mon.)	7	combination of tetrahedron + triangle	2.065–2.455	24
HfO ₂ (isomorphous with ZrO ₂)	8	square antiprism	2.04 — 2.26	25
ZrOCl ₂ (H ₂ O) ₈	8	square antiprism	2.24	25
ZrSiO ₄	8	dodecahedron	2.09 — 2.37	26
Zr(SO ₄) ₂ (H ₂ O) ₄	8	dodecahedron	2.22	26
Zr(SO ₄) ₂ (H ₂ O) ₄	8	square antiprism	2.15 — 2.29	27
Zr(IO ₃) ₄	8	square antiprism	2.18	27
Zr ₄ (OH) ₆ (CrO ₄) ₅ (H ₂ O) ₂	8	square antiprism	2.176–2.183	28
Zr ₄ (OH) ₆ (CrO ₄) ₅ (H ₂ O) ₂	7	pentagonal bipyramid	2.21	28
Zr(acetylacetonate) ₄	7	pentagonal bipyramid	2.197–2.216	29
Zr(acetylacetonate) ₄	8	square antiprism	2.14	29
Na ₄ Zr(C ₂ O ₄) ₄ (H ₂ O) ₃	8	square antiprism	1.97 — 2.21	14
Na ₄ Zr(C ₂ O ₄) ₄ (H ₂ O) ₃	8	dodecahedron	2.20	14
Zr(OH) ₂ (NO ₃) ₂ (H ₂ O) ₄	8	dodecahedron	2.181–2.217	15
Zr(OH) ₂ (NO ₃) ₂ (H ₂ O) ₄	8	dodecahedron	2.20	15
Zr ₂ (OH) ₂ (SO ₄) ₃ (H ₂ O) ₄	8	dodecahedron	2.144–2.244	21
Zr ₂ (OH) ₂ (SO ₄) ₃ (H ₂ O) ₄	8	dodecahedron	2.21	21
Hf(OH) ₂ (SO ₄)(H ₂ O)	8	dodecahedron	2.12 — 2.37	21
Hf(OH) ₂ (SO ₄)(H ₂ O)	7	pentagonal bipyramid	2.19	21
Zr(C ₆ H ₅ N ₂ O ₂) ₄	7	pentagonal bipyramid	2.090–2.261	30
Zr(C ₆ H ₅ N ₂ O ₂) ₄	8	dodecahedron	2.12	30
Zr(C ₆ H ₅ N ₂ O ₂) ₄	8	dodecahedron	2.08 — 2.18	
Zr(C ₆ H ₅ N ₂ O ₂) ₄	8	dodecahedron	2.19	
Zr(C ₆ H ₅ N ₂ O ₂) ₄	8	dodecahedron	2.168–2.222	

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