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The Crystal Structure of Vanadium(IV) Oxide Sulphate, $VOSO_4$

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The crystal structure of vanadium(IV)oxide sulphate has been determined from three-dimensional X-ray data. The structure is orthorhombic, space group *Pnma*. The elementary cell contains four formula units and has the dimensions

$a = 7.3710 \pm 0.0012$ Å
$b = 6.2692 \pm 0.0008$ Å
$c = 7.0821 \pm 0.0009$ Å

The structure may be described in terms of distorted vanadium-oxygen octahedra which are joined by sharing corners to form chains running parallel to the *a* axis. The VO_6 octahedra of the chains are also pairwise connected by a sulphate group via corner sharing. The two remaining oxygen atoms of each SO_4 teterahedron partake in linking with two further chains of VO_6 octahedra, thus bringing about a three-dimensional framework. The structure is discussed and compared with some other compounds containing distorted transition metaloxygen octahedra.

Within a research program being conducted at this Institute and intended to provide accurate structural data needed for discussions of the bonding conditions in some groups of transition metal compounds of simple stoichiometry, a report has recently been published on the structure of molybdenum(V)oxide phosphate, $MoOPO_4$.[1] In continuation to this work crystal structure studies were started on three compounds of analogous composition, *viz.* $NbOPO_4$, $VOPO_4$, and $VOSO_4$. Reports of the results obtained for the two first-mentioned phases will shortly appear elsewhere. This article will describe the investigation of the structure of $VOSO_4$.

The preparation and analysis of $VOSO_4$ was reported in 1928 by Sieverts and Müller.[2] Their method of heating V_2O_5 with concentrated sulphuric acid was the one used to prepare the material used for this investigation. However, in order to obtain crystals large enough for the X-ray study, heating was prolonged for about two weeks. Vanadium oxide sulphate crystallizes in the shape of light green rods with a length to width ratio of approximately 5:1.

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X-RAY DATA AND COMPUTING METHODS

The powder pattern of $VOSO_4$ was completely indexed on the basis of a primitive orthorhombic unit cell. The cell parameters were calculated from a photograph taken with strictly monochromatized Cu$K\alpha_1$ radiation in a focusing camera of the Guinier type. Potassium chloride (a = 6.29228 Å)[3] was used as an internal standard. Least-squares refinement gave the following unit-cell dimensions (25°C):

$$a = 7.3710 \pm 0.0012 \text{ (Å)}$$
$$b = 6.2692 \pm 0.0008 \text{ (Å)}$$
$$c = 7.0821 \pm 0.0009 \text{ (Å)}$$
$$V = 327.3 \text{ (Å}^3\text{)}$$

Table 1. X-ray powder data observed for $VOSO_4$. Cu$K\alpha_1$ radiation. $\lambda_{CuK\alpha_1}$ = 1.54050 Å.

h k l	$10^5 \sin^2\Theta$ obs	$10^5 \sin^2\Theta$ calc	I obs	h k l	$10^5 \sin^2\Theta$ obs	$10^5 \sin^2\Theta$ calc	I obs
1 0 1	2273	2275	s+	0 0 4	18938	18926	w(d)
0 1 1	2690	2692	s+	4 1 0		18981	
1 1 1	3778	3784	m	2 3 1	19145	19136	vw
2 0 0	4376	4368	vvw	1 3 2	19406	19409	w
0 0 2	4734	4732	s+	1 0 4	20019	20018	vvvw
2 0 1	5540	5551	vvs+	3 0 3	20492	20474	vw
1 0 2	5827	5824	s+	3 2 2	20593	20598	vw
0 2 0	6031	6038	vs+	3 1 3	21956	21983	vw
2 1 1	7058	7060	w	4 0 2	22200	22203	w
1 1 1	7333	7333	m	2 3 2	22675	22685	w
1 2 1	8308	8313	w	4 1 2	23710	23712	vvw
2 0 2	9112	9099	vvw	0 4 0	24148	24152	s+
2 2 0	10416	10406	vw	2 1 4	24800	24804	m
2 2 1	11591	11589	w(d)*	1 2 4	26103	26056	vvw
1 2 2	11856	11862	m	3 2 3	26483	26512	w
0 1 3	12158	12156	w	3 3 2	28173	28145	vvw
3 1 1	12528	12520	vvw	4 1 3	29672	29627	m(d)
1 1 3	13258	13248	vvw(d)	2 4 1		29703	
3 0 2	14562	14559	vvw	4 3 0	31076	31057	vvw(d)
0 3 1	14761	14769	vs+	0 1 5		31082	
2 0 3	15002	15014	m	1 1 5	32200	32174	vw(d)
2 2 2	15136	15138	vvw	4 3 1		32240	
3 2 0	15874	15866	vvw	2 3 4	36858	36880	vvw
1 3 1		15861		5 3 0	40878	40885	vvw(d)
2 1 3	16534	16523	vw	3 1 5		40910	
4 0 0	17465	17472	vw	2 4 1	41639	41624	vw
				0 3 5	43152	43158	vvw

* d = diffuse.

A comparison of observed and calculated $\sin^2\Theta$ values is given in Table 1. The density of $VOSO_4$ was determined experimentally by its apparent loss of weight in benzene. It was found to be 3.30 which compares favourably with the theoretical value of 3.308 based on four formula units in the unit cell.

Rotation photographs about the needle axis of the crystal showed this to be the crystallographic b axis. Weissenberg photographs of the layer lines $h0l$—$h3l$ were taken with Cu$K\alpha$ radiation of a well shaped rod of the following dimensions: 0.030 mm × 0.019 mm × 0.117 mm. The use of Mo$K\alpha$ radiation did not significantly increase the number of visible reflections.

The reflections were recorded photographically with the multiple film technique. The relative intensities were estimated visually by comparison with an intensity scale obtained by photographing a reflection with different exposure times. A total of 198 independent reflections were assigned an intensity.

Computational work involved in refinement of lattice constants (Program No. 6018), absorption correction (No. 6019), Lorentz-polarization correction (No. 6024), Fourier summations (No. 6015), least-squares refinement (No. 6023) and calculation of interatomic distances (No. 6016) were performed on the electronic computers FACIT EDB and BESK. The numbers refer to the list of crystallographic computer programs.[4]

The linear absorption coefficient, $\mu = 314.7$ cm^{-1}, was used in calculating an absorption factor for each reflection. This factor (AF) ranged in value from 0.44 to 0.61 in the formula $I = I_{obs}/AF$. The numerical values of the AF's are included in a document which reproduces all the data involved in this investigation.[5]

STRUCTURE DETERMINATION

The reflections systematically absent in the photographs are $hk0$ with h = odd and $0kl$ with $k + l$ = odd. This is characteristic of two space groups No. 62 *Pnma* and No. 33 $Pn2_1a$. The higher symmetry, *Pnma*, was taken as the starting point of the structure investigation. The result thus obtained was found to be throughout consistent. It was not significantly improved by lowering the symmetry.

In No.62 *Pnma* the following point positions are possible:

4(a): 000; $0\frac{1}{2}0$; $\frac{1}{2}0\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; 4($b$): $00\frac{1}{2}$; $0\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}00$; $\frac{1}{2}\frac{1}{2}0$;
4(c): $\pm (x\frac{1}{4}z)$; $\pm (\frac{1}{2} + x, \frac{1}{4}, \frac{1}{2}-z)$
8(d): $\pm (x, y, z,)$; $\pm (\frac{1}{2} + x, \frac{1}{2}-y, \frac{1}{2}-z)$; $\pm (\bar{x}, \frac{1}{2} + y, \bar{z})$; $\pm (\frac{1}{2}-x, \bar{y}, \frac{1}{2} + z)$

Assuming the structure to be an ordered one, the four vanadium and the four sulphur atoms in the unit cell must occupy two of the fourfold positions 4(a)—4(c). Moreover, since there are also twenty oxygen atoms in the cell, *i.e.* an odd multiple of four, at least four oxygen atoms must likewise occupy one of these positions. Atoms situated in the positions 4(a) and 4(b) would give rise to maxima at $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}0$ and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ in the Patterson function. As such maxima are lacking in the sections $P(u0w)$ and $P(u\frac{1}{2}w)$ illustrated in Figs. 1 and 2 it is concluded that the vanadium and sulphur atoms and some of the oxygen atoms are situated in point positions 4(c).

In $P(u0w)$ and $P(u\frac{1}{2}w)$ there are three peaks at $P(0.50, 0, 0)$, $P(0.16, \frac{1}{2}, 0.50)$ and $P(0.32, \frac{1}{2}, 0.50)$ which regarding their heights and positions could be interpreted as corresponding to the V—V vectors. The four maxima at

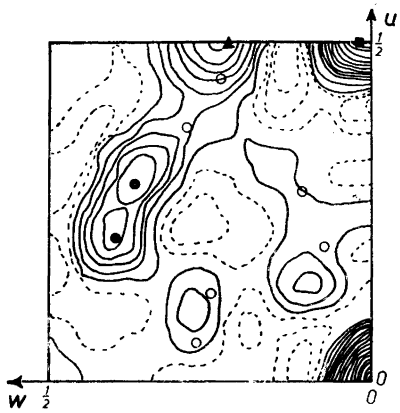

Fig. 1. The Patterson section $P(u0w)$ for $VOSO_4$. The V—V (■), V—S (▲), V—O (○) and S—S (●) vectors have been indicated for the final structure. Dashed lines indicate negative values.

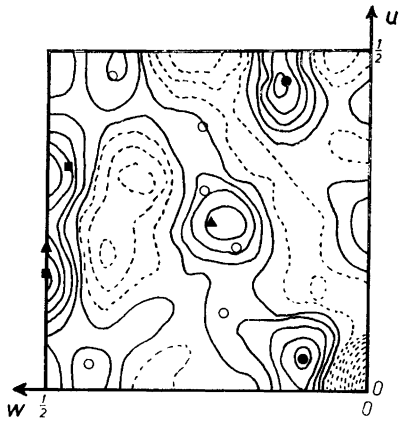

Fig. 2. The Patterson section $P(u\frac{1}{2}w)$ for $VOSO_4$. The vectors have been indicated as in Fig. 1. Dashed lines indicate negative values.

$P(0.23, 0, 0.39)$, $P(0.30, 0, 0.36)$, $P(0.05, \frac{1}{2}, 0.10)$ and $P(0.45, \frac{1}{2}, 0.14)$ were analogously ascribed to V—S vectors. Using these two sets of vectors approximate parameter values were derived for the vanadium and sulphur atoms. The remaining moderate peaks $P(0.50, 0, 0.24)$; $P(0.22, \frac{1}{2}, 0.50)$ and $P(0.24, \frac{1}{2}, 0.22)$ were found to be in agreement with S—S vectors required by the proposed structure.

The three-dimensional electron density section $\varrho(x\frac{1}{4}z)$ (Fig. 3) was then calculated, using the signs of the observed structure factors derived from the vanadium and sulphur contributions only. (At this and subsequent calculations atomic scattering curves for un-ionized atoms were used. The real

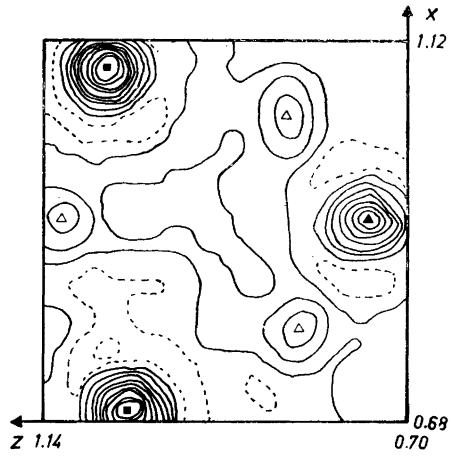

Fig. 3. The electron density section $\varrho(x\frac{1}{4}z)$ for $VOSO_4$. The final positions of the vanadium (■), sulphur (▲) and oxygen (△) atoms have been marked. Dashed lines indicate negative values.

part of the anomalous dispersion correction [6] was applied to the scattering curves.[7]) In addition to these atoms the section also showed the positions of twelve of the twenty oxygen atoms occupying three sets of point positions 4(*c*). The remaining eight oxygen atoms were found to be situated in a position 8(*d*) with parameters obtained from a series of Fourier sections $\varrho(xyz)$, where y was varied from 0.00 to 0.50.

A refinement of the coordinates so obtained was then performed using the least-squares technique. Initially all 198 of the independent reflections measured were included in the calculations, but after some cycles ten strong, low-angle reflections were omitted as suffering from extinction. The refinement was considered as complete when the parameter shifts were less than five per cent of the standard deviations, at which stage the discrepancy index, R, was down to 0.100.

Hughes' weighting function $w = 1/h^2$ $|F_{obs}, \min|^2$ for $|F_{obs}| \leq h|F_{obs}, \min|$ and $w = 1/|F_{obs}|^2$ for $|F_{obs}| > |F_{obs}, \min|$ with $h = 4$ was used in the refinement. A weight analysis obtained in the last cycle is given in Table 2.

Table 2. Weight analysis obtained in the final cycle of the least-squares refinement of $VOSO_4$. w = weighting factor, $\Delta = ||F_{obs}| - |F_{calc}||$

Interval sin Θ	Number of independent reflections	$\overline{w\,\Delta^2}$	Interval F_{obs}	Number of independent reflections	$\overline{w\,\Delta^2}$
0.00–0.46	36	1.09	0– 5	0	–
0.46–0.58	31	1.09	5–10	13	0.69
0.58–0.67	18	0.77	10–15	22	2.56
0.67–0.74	22	0.84	15–20	27	1.00
0.74–0.79	21	0.26	20–25	30	0.97
0.79–0.84	12	0.73	25–30	32	0.93
0.84–0.89	15	1.00	30–35	26	0.56
0.89–0.93	15	1.68	35–40	17	0.55
0.93–0.97	10	1.52	40–45	10	0.25
0.97–1.00	8	1.63	45–50	11	0.93

A list of the observed and calculated structure factors is included in a document [5] which may be obtained from the secretary of this Institute.

A three-dimensional difference synthesis calculated over the unique part of the unit cell at points 0.2 Å apart showed no maxima higher than about twenty per cent of the heights of the oxygen peaks in the electron density functions. From these calculations as well as from a computation of the interatomic distances which were found to be of reasonable lengths (see below), further evidence was obtained that the atomic parameters arrived at in the last cycle and listed in Table 3 present an adequate description of the structure of $VOSO_4$.

Table 3. The structure of $VOSO_4$.

Space group: No. 62, *Pnma*

Unit cell dimensions: $a = 7.3710 \pm 0.0012$ Å
$b = 6.2692 \pm 0.0008$ Å
$c = 7.0821 \pm 0.0009$ Å

Cell contents: 4 $VOSO_4$
4 V, 4 S, 4 O_2, 4 O_3 and 4 O_4 in 4(*c*): $\pm(x,\frac{1}{4},z)$; $\pm(\frac{1}{2}+x,\frac{1}{4},\frac{1}{2}-z)$
8 O_1 in 8(*d*); $\pm(x,y,z)$; $\pm(\frac{1}{2}+x,y,\frac{1}{2}-z)$ $\pm(x,\frac{1}{2}-y,z)$; $\pm(\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}-z)$

Atom	$x \pm \sigma(x)$	$y \pm \sigma(y)$	$z \pm \sigma(z)$	$B \pm \sigma(B)$ Å^2
V	0.1658 ± 0.0005	¼	0.2327 ± 0.0005	0.88 ± 0.06
S	0.8761 ± 0.0006	¼	0.8669 ± 0.0006	0.81 ± 0.08
O_2	0.7187 ± 0.0018	¼	0.9896 ± 0.0020	1.3 ± 0.2
O_3	0.0399 ± 0.0018	¼	0.9799 ± 0.0017	0.8 ± 0.2
O_4	0.3719 ± 0.0022	¼	0.1647 ± 0.0025	1.7 ± 0.3
O_1	0.1251 ± 0.0015	0.5733 ± 0.0029	0.2569 ± 0.0016	1.8 ± 0.2

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The crystals of $VOSO_4$ are built up of chains, parallel to the *a*-axis and formed by distorbed VO_6 octahedra linked together by sharing opposite corners. The VO_6 octahedra of the chains are also pairwise connected by a sulphate group *via* corner sharing. The two remaining oxygen atoms of each SO_4 tetrahedron partake in linking with two further chains of VO_6 octahedra, thus giving a threedimensional network. Schematic drawings showing the links between the octahedra and tetrahedra are given in Fig. 4.

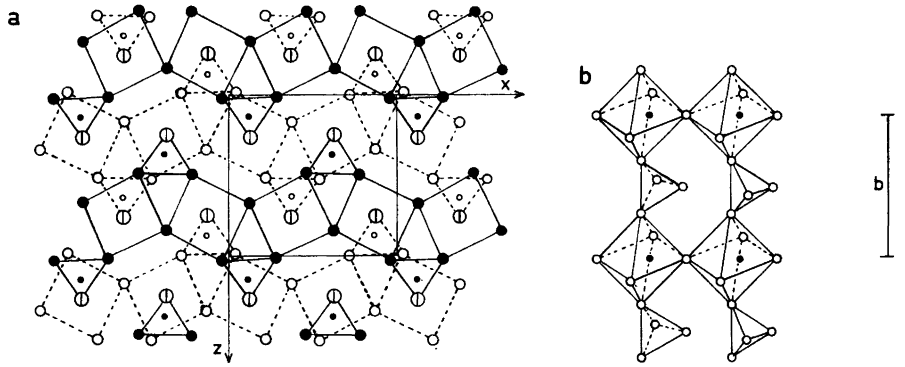

Fig. 4. Schematic drawings showing the structure of $VOSO_4$. a) The structure viewed along [010] showing the zig-zag chains formed by VO_6 octahedra linked together by sharing corners and also showing the links between the SO_4 tetrahedra and VO_6 octahedra. Open and full circles denote atoms (large circles oxygen and small ones sulphur) situated in two separate planes $b/2 = 3.13$ Å apart. Lined open circles denote oxygen atoms shared between VO_6 octahedra and SO_4 tetrahedra as shown in Fig. 4b. The vanadium atoms have not been indicated. b) The linking in the *y*-direction between VO_6 octahedra and SO_4 tetrahedra. Only two VO_6 octahedra in each chain (*cf.* 4a) have been indicated. Full circles denote vanadium atoms and open ones oxygen atoms. The sulphur atoms have not been indicated.

Table 4. Interatomic distances (Å) and standard deviations ($\pm \sigma$ in Å) in $VOSO_4$.

VO_6-octahedron:	
V — 2 O_1	= 2.056 ± 0.018
V — O_2	= 2.005 ± 0.015
V — O_3	= 2.016 ± 0.013
V — 2 O_4	= 1.594 ± 0.017; 2.284 ± 0.017
2 O_1 — O_2	= 2.794 ± 0.018
2 O_1 — O_3	= 2.890 ± 0.017
4 O_1 — O_4	= 2 × 2.800 ± 0.019; 2 × 2.811 ± 0.019
O_2 — 2 O_4	= 2.891 ± 0.021 ; 2.696 ± 0.022
O_3 — 2 O_4	= 2.775 ± 0.021 ; 2.805 ± 0.021
SO_4-tetrahedron:	
S — 2 O_1	= 1.412 ± 0.016
S — O_2	= 1.449 ± 0.014
S — O_3	= 1.449 ± 0.014
O_1 — O_1	= 2.215 ± 0.026
2 O_1 — O_2	= 2.366 ± 0.018
2 O_1 — O_3	= 2.349 ± 0.017
O_2 — O_3	= 2.369 ± 0.019
O—O < 3.5 Å outside the polyhedra:	
O_1 — 2 O_2	= 3.220 ± 0.018
O_1 — 2 O_3	= 3.133 ± 0.017
O_1 — 2 O_4	= 3.094 ± 0.019
O_2 — 2 O_4	= 3.386 ± 0.022
O_3 — 2 O_3	= 3.202 ± 0.019

The interatomic distances and standard deviations (σ) in $VOSO_4$ are given in Table 4. A complete list of bond angles is given in the document.[5] From the table we can see that all distances are reasonable and consistent with previous knowledge of the vanadium(IV) [8] and sulphate [9] structural chemistry. It is also obvious that the structure, although described as a network formed by octahedra and tetrahedra, owes much of its stability to its rather close packing of oxygen atoms. As we can see every oxygen atom is surrounded by ten to twelve oxygen atoms at distances of 2.4—3.4 Å.

The $S—O_i^j$ distances — all interatomic distances discussed in the following are given with the limits $\pm 2\sigma$ — within the sulphate group are 1.41 ± 0.03 Å (two distances) and 1.45 ± 0.03 Å (two distances) and the O—O distances are 2.22 ± 0.05 Å (one distance) and 2.36 ± 0.04 Å (average value of five distances) from which an average angle O—S—O = 109.4° is calculated. The sulphur-oxygen bond distances found within the SO_4 group are somewhat smaller than the values, ranging from 1.44 Å to 1.53 Å and with an average distance of 1.49 Å obtained from six determinations, given in the *International Tables.*[9]

The coordination polyhedron around vanadium is a distorted octahedron of oxygen atoms (Fig. 5). There are four V—O bonds at about 2.0 Å (average values 2.03 ± 0.03 Å) one at 1.6 Å (1.59 ± 0.03 Å) and the last at 2.3 Å (2.28 ± 0.03 Å). The long and short bonds are opposite each other in the

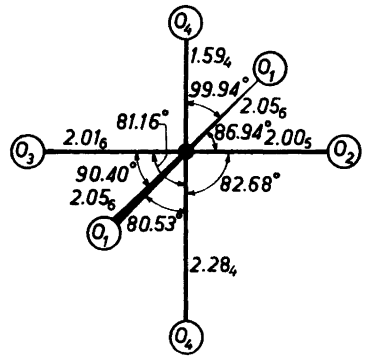

Fig. 5. The coordination of oxygen atoms around the vanadium atom in $VOSO_4$. Open circles denote oxygen atoms and full ones vanadium atoms. Angles related to the others by symmetry have not been indicated.

octahedron. This kind of deformation has been found [8] to be characteristic of most vanadium compounds. In some cases the octahedral coordination is even more distorted and the coordination is better described as a square pyramid. This is the case with vanadyl bisacetylacetonat, $VO(C_5H_7O_2)_2$.[10] In other cases such as VO_2[11] the octahedron is much less distorted with V—O bond distances ranging from 1.76 Å to 2.05 Å. The structure of VO_2, however, consists of edge sharing octahedra, which makes a straight-forward comparison difficult. In $(NH_4)_2V(NCS)_4 \cdot 5H_2O$ [12] on the other hand the long and short V—S bonds (1.62 Å and 2.22 Å) are almost the same as in $VOSO_4$.

The single short bond is also found in some Mo(V) compounds. The oxygen coordination around molybdenum in $MoOPO_4$ [1] is very similar to that found for vanadium in the structure described here. The structures of $VOSO_4$ and $MoOPO_4$ also have many other similarities. They both consist of chains of distorted octahedra running parallel to an axis. Furthermore, the octahedron-tetrahedron connections along the *a* and *b* axes of $MoOPO_4$ are the same as in the *b* axis direction of $VOSO_4$.

One would have predicted that these two compounds should have been structurally isomorphous. Both have a cation capable of octahedral coordination with one unpaired *d* electron. Furthermore, both contain a complex anion with a tetrahedral configuration. The significant difference appears to be the smaller size of the sulphate group compared to the phosphate group. If four chains of octahedra were linked to each smaller sulphate group as they are in $MoOPO_4$ this would bring the oxygen atoms of the chains too close. This problem is eliminated in $VOSO_4$ by alternately rotating each tetrahedron approximately $+90°$ and $-90°$ about the *b* axis so that each tetrahedron now is connected to only three different chains and thus separating the parallel chains.

The new compound $VOMoO_4$ [13] which has the $MoOPO_4$ structure seems to give further evidence that it is the sulphate group which causes $VOSO_4$ not to be isostructural with these two compounds. The vanadium in $VOMoO_4$ is in octahedral coordination with oxygen and the molybdenum is in tetrahedral coordination.

Structural studies on further members of this family of compounds are in progress. Investigations of their magnetic and optical behaviour and of

other physical properties capable of providing additional information about their structural and bonding character are also on the program.

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