

The Apatite Structure without an Inversion Center in a New Bismuth Calcium Vanadium Oxide: $\text{BiCa}_4\text{V}_3\text{O}_{13}$

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A new bismuth calcium vanadium oxide, $\text{BiCa}_4\text{V}_3\text{O}_{13}$, with hexagonal symmetry has been synthesized: space group $P6_3$ (#173), $a = 9.819(2)$ Å, $c = 7.033(2)$ Å, $V = 587.2(3)$ Å³, and $Z = 2$. The structure was solved and refined from single crystal X-ray data leading to $R = 0.055$ and $R_w = 0.069$ for 1076 unique reflections. Three different types of Ca sites were found: Ca(1) and Ca(2) coordinate to six O atoms, and Ca(3) coordinates to nine O atoms. There is no Bi site; instead, Bi partially occupies the Ca(1) and Ca(2) sites. The V atom is coordinated to four O atoms and forms a distorted tetrahedron with the V-O bond lengths ranging from 1.693(6) Å to 1.72(1) Å and O-V-O angles varying from 102.5(7)° to 114.7(6)°. The coordination polyhedra of Ca(1) and Ca(3) share faces forming chains along the *c* axis, and the coordination hexahedra of Ca(2) also form a chain along the *c* axis through sharing the corners among themselves. The VO_4 tetrahedra connect the two types of chains forming a three dimensional structure. The $\text{BiCa}_4\text{V}_3\text{O}_{13}$ formula may be written as $\text{A}_3(\text{VO}_4)_3\text{O}$ to emphasize that this structure is essentially the same as the apatite structure, except that the inversion center is missing. Many compounds previously reported to have the apatite structure may actually have the lower symmetry version of this structure found in this study and thus be candidates for ferroelectricity. © 1993 Academic Press, Inc.

Introduction

The $\text{CaO-V}_2\text{O}_5$ system has been studied (1-3) over several decades. The well established compounds in this system are CaV_2O_6 , $\text{Ca}_2\text{V}_2\text{O}_7$, and $\text{Ca}_3(\text{VO}_4)_2$; however, $\text{Ca}_2\text{V}_6\text{O}_{17}$ (4), $\text{Ca}_7\text{V}_4\text{O}_{17}$ (4), and $\text{Ca}_5\text{V}_2\text{O}_{10}$ (5) have also been reported. In the $\text{Bi}_2\text{O}_3\text{-CaO}$ system (6) and the $\text{Bi}_2\text{O}_3\text{-V}_2\text{O}_5$ system (7), the formation of limited bismuth rich solid solutions is reported. Recently, we have investigated the Bi-Ca-V-O system and have identified three new phases ($\text{BiCa}_9\text{V}_7\text{O}_{28}$, $\text{Bi}_4\text{CaVO}_{9.5}$, and $\text{BiCa}_4\text{V}_3\text{O}_{13}$) by means of X-ray diffraction and electron microprobe analysis. In this paper, we re-

port the crystal structure of the new bismuth calcium vanadium oxide, $\text{BiCa}_4\text{V}_3\text{O}_{13}$, in which two crystallographic sites are filled with a mixture of Bi and Ca.

Experimental

A mixture of Bi_2O_3 (99.9%, Aldrich), reagent CaO (J. T. Baker), and V_2O_5 (99.9%, Johnson Matthey) with molar ratio Bi:Ca:V = 1:4:3 was first heated at 700°C for 12 hr and 950°C for 20 hr. It was then heated to 1240°C and held at this temperature for 5 min, followed by cooling to 1200°C at a rate of 15°C/hr, held there for 1 hr, cooled to 1150°C at a rate of 3°C/hr,

TABLE I
CRYSTAL DATA AND INTENSITY COLLECTION FOR $\text{BiCa}_4\text{V}_3\text{O}_{13}$

Color	Dark yellow
Size, mm	0.1 × 0.1 × 0.3
Crystal system	Hexagonal
Space group	$P6_3$ (No. 173)
a (Å)	9.819 (2)
c (Å)	7.033(2)
Volume (Å ³)	587.2(3)
Z	2
Formula weight	730.12
Calculated density, g/cc	4.129
Diffractometer	Rigaku AFC6R
Radiation	MoK α ($\lambda = 0.71069$ Å) graphite-monochromated
Temperature	23°C
μ (Mo), cm ⁻¹	189.17
Maximum 2θ (°)	80.0
Data collected	$-15 \leq h \leq 15, -22 \leq k \leq 22, -9 \leq l \leq 9$
Scan method	ω - 2θ
Scan speed (°/min)	16.0 in ω , and 32 in 2θ
No. of data collected	5704
No. unique data with $F_0^2 > 3\sigma(F_0^2)$	1076
R_{int}	0.104
Absorption correction	DIFABS
Transmission factors, range	0.81–1.21
Refinement method	full-matrix least-squares on $ F $
Parameters varied	54
Data/parameter ratio	19.93
R	0.055
R_w	0.069
Goodness of fit indicator	1.99

then cooled to 600°C at 15°C/hr, and finally furnace cooled to room temperature. The main product from this procedure is clear light yellow crystals with composition around Ca : Bi : V = 9 : 1 : 7. Only a few dark yellow needle crystals were separated. The chemical composition of several needle crystals was analyzed using an SX-50 microprobe. The standards were Bi_2O_3 , $\text{CaMgSi}_2\text{O}_6$, and $\text{Pb}_3\text{Cl}(\text{VO}_4)_3$ for Bi, Ca, and V respectively. The average of these results gave the stoichiometry of the title compound.

Single crystal X-ray diffraction data were collected on a Rigaku AFC6R diffractom-

eter. Details of the data collection, reduction, and refinement are summarized in Table 1. The cell dimensions were determined by a least-squares analysis of 15 reflections in the range $11.6^\circ \leq 2\theta$ (MoK α) $\leq 35.3^\circ$ that had been centered on the diffractometer. The intensity data were collected using the ω - 2θ scan technique; a scan width of $\Delta\omega = (1.47 + 0.3 \tan \theta)^\circ$ was used. The intensities of three standard reflections, monitored every 300 reflections throughout data collection, exhibited excursions of less than 2.5%.

The structure was solved and refined with computer programs from the TEXSAN

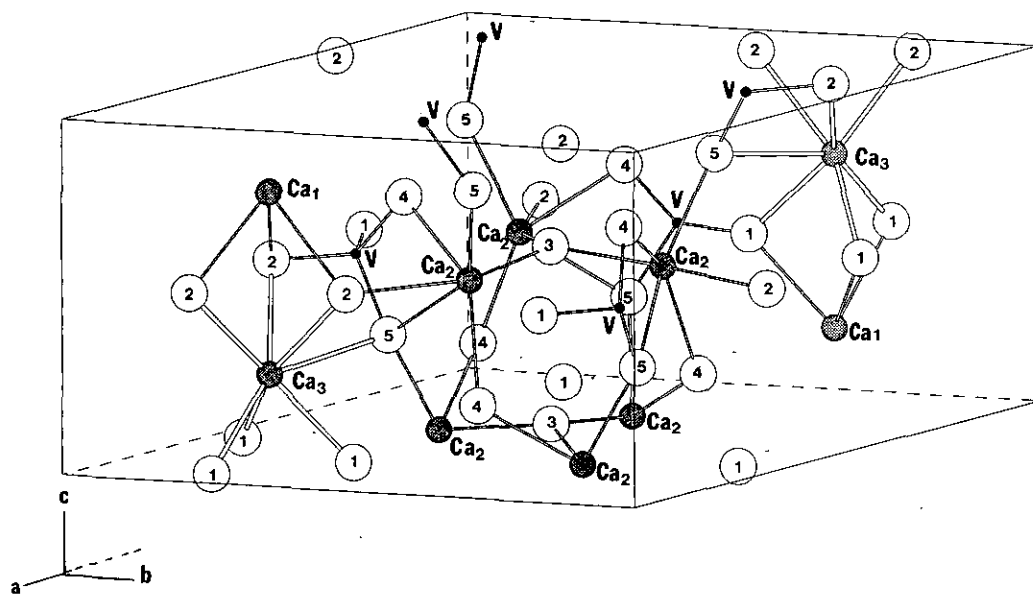


FIG. 1. Contents of a unit cell of $\text{BiCa}_4\text{V}_3\text{O}_{13}$, where large circles with numbers are oxygen atoms.

crystallographic software package (8). A trial structure based on the positions of Ca and V which were determined from direct methods, SHELXS (9), was first refined. The O atoms were then located from subsequent analyses of difference electron density maps. The occupancy factors for Ca(1) and Ca(2) atoms were found to be greater than 1, indicating that Bi atoms were mixing

with Ca atoms at these sites. After the refinement of positional parameters, occupational parameters, and isotropic thermal parameters, an empirical absorption correction using the program DIFABS (10) was applied. The data were also corrected for Lorentz and polarization effects. Final least-squares on $|F|$ with anisotropic thermal parameters on all the heavy atoms and

TABLE II
POSITIONAL PARAMETERS AND B_{eq} FOR $\text{BiCa}_4\text{V}_3\text{O}_{13}$

Atom	x	y	z	B_{eq}^a	Occupancy
Ca/Bi(1)	$\frac{1}{2}$	$\frac{2}{3}$	0.2503	1.2(1)	0.9/0.1
Ca/Bi(2)	0.2252(1)	0.9963(1)	0.0030(9)	2.68(4)	0.7/0.3
Ca(3)	$\frac{1}{2}$	$\frac{2}{3}$	-0.2611(6)	1.8(2)	1
V	0.0297(1)	0.6269(1)	-0.003(1)	0.94(4)	1
O(1)	-0.1647(6)	0.5045(6)	0.003(3)	1.5(2)	1
O(2)	0.1341(7)	0.5307(7)	-0.001(3)	2.5(3)	1
O(3)	0	0	-0.460(3)	3.0(3)	1
O(4)	0.078(1)	0.760(1)	0.180(2)	1.7(1)	1
O(5)	0.097(1)	0.739(1)	-0.203(2)	1.7(1)	1

$$^a B_{\text{eq}} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i a_j.$$

TABLE III
ANISOTROPIC THERMAL PARAMETERS ($\times 10^{-3} \text{ \AA}^2$)
FOR THE ATOMS OF $\text{BiCa}_4\text{V}_3\text{O}_{13}$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca/Bi(1)	16(2)	16	14(3)	8	0	0
Ca/Bi(2)	42.7(6)	17.7(4)	34.3(8)	9.8(4)	-16(3)	1(1)
Ca(3)	2.8(2)	2.8	11(3)	14	0	0
V	9.8(5)	12.3(5)	11.8(6)	4.1(4)	3(1)	6(1)
O(1)	17(2)	21(3)	12(3)	4(2)	1(6)	0(6)
O(2)	23(3)	20(3)	56(6)	15(2)	15(8)	22(7)

two oxygen atoms resulted in $R = 0.055$ and $R_w = 0.069$.

Description of the Structure

One unit cell of the $\text{BiCa}_4\text{V}_3\text{O}_{13}$ structure is shown in Fig. 1. The atomic positions and isotropic thermal factors are given in Table II, and the anisotropic thermal parameters are given in Table III. Selected bond distances and angles are given in Table IV.

Three different types of Ca atoms were found in $\text{BiCa}_4\text{V}_3\text{O}_{13}$. The Ca(2) atom is in the general position and coordinates to six O atoms forming an irregular hexacoordination polyhedron (Fig. 2). These polyhedra

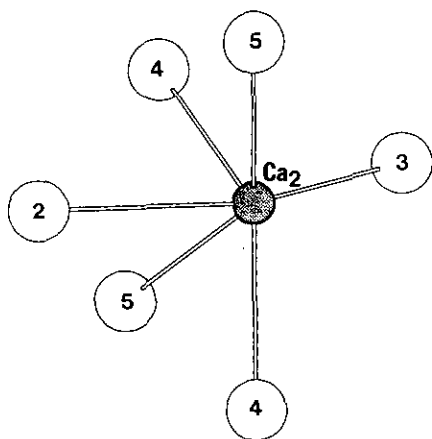


FIG. 2. Coordination of Ca(2) atom.

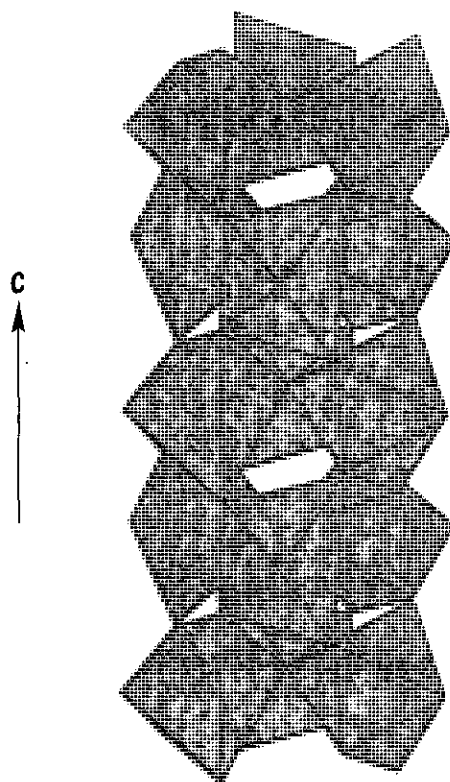


FIG. 3. Chain structure formed from $\text{Ca}(2)\text{O}_6$ polyhedra.

share corners with each other resulting in a chain along the c axis (Fig. 3). This chain is centered on the 6_3 axis.

Both Ca(1) and Ca(3) sit on a threefold symmetric axis with a separation of 3.6 \AA between Ca atoms along this axis. The Ca(1) atom is coordinated by six O atoms, three O(1) atoms forming a triangle 1.76 \AA above Ca(1) and three O(2) atoms forming a triangle 1.76 \AA below Ca(1). This CaO_6 polyhedron has C_3 symmetry and can be described roughly as a trigonal antiprism. Actually, the ideal trigonal antiprism is distorted by having one oxygen triangle rotated by 9.8° with respect to its ideal location. The bond length ($2.43(1) \text{ \AA}$) and bond angle ($72.3(5)^\circ$) formed from O(1) and Ca(1) are very close

TABLE IV
SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°)
FOR $\text{BiCa}_4\text{V}_3\text{O}_{13}$

Ca/Bi(1)–O(1) × 3	2.43(1)	Ca(3)–O(1) × 3	2.34(1)
–O(2) × 3	2.47(2)	–O(2) × 3	2.52(2)
		–O(5) × 3	2.773(9)
Ca/Bi(2)–O(2)	2.575(6)	V –O(1)	1.693(6)
–O(3)	2.245(3)	–O(2)	1.707(6)
–O(4)	2.379(9)	–O(4)	1.72(1)
–O(4)	2.43(1)	–O(5)	1.70(1)
–O(5)	2.63(1)		
–O(5)	2.38(1)		
O(1)–Ca/Bi(1)–O(1)	72.3(5)	O(1)–Ca/Bi(1)–O(2)	152.4(2)
O(1)–Ca/Bi(1)–O(2)	127.5(3)	O(1)–Ca/Bi(1)–O(2)	94.2(5)
O(2)–Ca/Bi(1)–O(2)	74.7(6)		
O(2)–Ca/Bi(2)–O(3)	154.6(2)	O(2)–Ca/Bi(2)–O(4)	75.4(4)
O(2)–Ca/Bi(2)–O(4)	85.6(5)	O(2)–Ca/Bi(2)–O(5)	68.5(4)
O(2)–Ca/Bi(2)–O(5)	81.5(5)	O(3)–Ca/Bi(2)–O(4)	80.5(4)
O(3)–Ca/Bi(2)–O(4)	108.3(6)	O(3)–Ca/Bi(2)–O(5)	94.5(4)
O(3)–Ca/Bi(2)–O(5)	103.4(6)	O(4)–Ca/Bi(2)–O(4)	139.0(4)
O(4)–Ca/Bi(2)–O(5)	65.4(2)	O(4)–Ca/Bi(2)–O(5)	83.8(4)
O(4)–Ca/Bi(2)–O(5)	73.9(3)	O(4)–Ca/Bi(2)–O(5)	129.5(3)
O(5)–Ca/Bi(2)–O(5)	141.2(3)		
O(1)–Ca(3)–O(1)	75.5(5)	O(1)–Ca(3)–O(2)	152.1(2)
O(1)–Ca(3)–O(2)	126.9(3)	O(1)–Ca(3)–O(2)	93.2(5)
O(1)–Ca(3)–O(5)	141.3(4)	O(1)–Ca(3)–O(5)	67.3(3)
O(1)–Ca(3)–O(5)	85.2(3)	O(2)–Ca(3)–O(2)	73.0(7)
O(2)–Ca(3)–O(5)	60.1(3)	O(2)–Ca(3)–O(5)	124.8(6)
O(2)–Ca(3)–O(5)	66.9(3)	O(5)–Ca(3)–O(5)	117.9(1)
O(1)–V(1)–O(2)	113.4(3)	O(1)–V(1)–O(4)	107.8(6)
O(1)–V(1)–O(5)	114.7(6)	O(2)–V(1)–O(4)	113.4(7)
O(2)–V(1)–O(5)	102.5(7)	O(4)–V(1)–O(5)	104.8(6)

to those formed from O(2) and Ca(1) atoms (2.47(2) and 74.7(6)).

Three O(1) atoms, three O(2) atoms, and three O(5) atoms are bound to the Ca(3) atom and form a C_3 symmetric nanocoordinate polyhedron which is quite different from the C_{4v} or D_{3h} nanocoordinate polyhedron described by Muetterties and Wright (11). The triangle formed from O(2) atoms sits above the Ca(3) atom with a distance of 1.83 Å while the triangle of O(1) atoms is 1.86 Å below the Ca(3) atom. The triangle formed from three O(5) atoms is 0.41 Å above the Ca(3) atom, and the O(5) triangle is twisted by 35° around the C_3 axis with

respect to the O(2) triangle. As expected from the repulsion between these two triangles, the Ca(3)–O(2) and Ca(3)–O(5) bond lengths are longer than the Ca(3)–O(1) bond length. The average Ca–O bond length around the nine-coordinated Ca(3) (2.54 Å) is longer than that around six-coordinated Ca(1) (2.45 Å) and Ca(2) (2.44 Å). The polyhedra of Ca(1)O₆ and Ca(3)O₉ share faces forming chains along the C_3 axes (Fig. 4).

The V atom is coordinated to four O atoms and forms a distorted tetrahedron with V–O bond lengths ranging from 1.693(6) Å to 1.72(1) Å and O–V–O angles

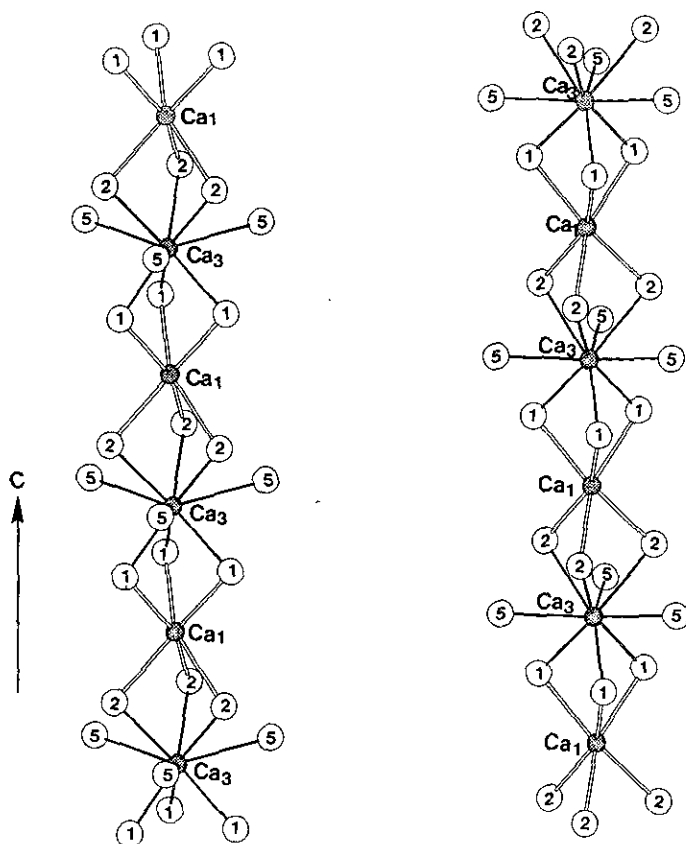


FIG. 4. The chain structure of $\text{Ca}(1)\text{O}_6\text{-Ca}(3)\text{O}_9$.

varying from $102.5(7)^\circ$ to $114.7(6)^\circ$. Each VO_4 tetrahedron shares one O(2) corner with a $\text{Ca}(1)\text{O}_6$ hexahedron, one O(4)-O(5) edge with a $\text{Ca}(2)\text{O}_6$ hexahedron, and one O(2)-O(5) edge with a $\text{Ca}(3)\text{O}_9$ polyhedron and connects the chains formed from Ca atoms.

Most of the oxygen atoms are coordinated by three cations. Only O(3) sits on the three-fold axis, thus bonding to three Ca(2) atoms. The O(2) and O(5) atoms are bound to four cations in an approximate tetrahedral arrangement.

Discussion

Disordering between Ca and Bi atoms is a common phenomenon in the new phases

discovered in the Bi-Ca-O system. In $\text{BiCa}_4\text{V}_3\text{O}_{13}$, the Bi atoms were found to be mixed with Ca atoms at those positions with coordination number six to the oxygen atoms but not at the nine-coordinate position. This is not surprising because Bi^{3+} may be regarded as smaller than Ca^{2+} . In $\text{Ba}_2\text{Bi}^{3+}\text{Bi}^{5+}\text{O}_6$ (12), the $\text{Bi}^{3+}\text{-O}$ distances for this six coordinate Bi are 2.31 Å, significantly shorter than either the average Ca(1)-O or the average Ca(3)-O distance in $\text{BiCa}_4\text{V}_3\text{O}_{13}$ (Table IV). None of the Ca atoms sits at a center of symmetry; thus, all these sites offer Bi^{3+} some opportunity to distort through hybridization of its 6s and 6p levels. This will be especially easy because the Bi-O distances are longer than

optimal. Given the two sites of six-coordination with about the same average distances, Bi^{3+} has shown some tendency to prefer the site of lower symmetry (Table II).

The formula for $\text{BiCa}_4\text{V}_3\text{O}_{13}$ may be written as $\text{A}_5(\text{VO}_4)_3\text{O}$ to emphasize the more covalent bonding within the VO_4 tetrahedra. The oxygen atom not bound to vanadium is the oxygen atom on the 6_3 axis. Assuming pentavalent vanadium, the average oxidation state of A is 2.2. Thus, A must be mixed valent or a mixture of cations as it is in $\text{BiCa}_4\text{V}_3\text{O}_{13}$. Another possibility would be $\text{Ca}_5(\text{VO}_4)_3\text{F}$. This is an apatite type of formula, and indeed one of the most studied apatites is $\text{Ca}_5(\text{PO}_4)_3\text{F}$ (13). Apatite is also hexagonal with the same Z and similar cell dimensions ($a = 9.37 \text{ \AA}$ and $c = 6.88 \text{ \AA}$ for $\text{Ca}_5(\text{PO}_4)_3\text{F}$). However, the space group for apatite is $P6_3/m$, and there are only two types of Ca atom. If a mirror plane is inserted midway between Ca(1) and Ca(2) of the $\text{BiCa}_4\text{V}_3\text{O}_{13}$ structure, this structure is converted to the apatite structure and these two Ca sites merge to become one site. The coordination of this Ca to oxygen is best described as 9, and all the O atoms are now bound to four cations. The lower symmetry in the structure of $\text{BiCa}_4\text{V}_3\text{O}_{13}$ may be related to the site selective distribution of Bi atoms on the Ca sites. Systematic absences for the apatite and $\text{BiCa}_4\text{V}_3\text{O}_{13}$ structures are the same.

About 100 compounds have been reported to have the apatite structure based on their compositions and X-ray powder patterns (13). However, it is likely that some of these compounds actually have the lower symmetry $\text{BiCa}_4\text{V}_3\text{O}_{13}$ structure. They are, therefore, candidates for ferroelectricity. A monoclinic distortion of the apatite structure has been reported (14) for

$\text{Ca}_5(\text{PO}_4)\text{Cl}$. However, the reported space group is $P2_1/b$ with a center of symmetry. This structure transforms to the hexagonal apatite structure above 200°C . Careful consideration was given to the possibility of an acentric structure for either the hexagonal or the monoclinic version of $\text{Ca}_5(\text{PO}_4)\text{Cl}$. The conclusion was that both are centric (15).

Acknowledgments

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