

BRIEF COMMUNICATIONS

A New Nine-Coordination System: Pentagonal Interpenetrating Tetrahedral Polyhedron

D. F. MULLICA,* C. K. C. LOK, AND DAVID A. GROSSIE

*Departments of Chemistry and Physics, Baylor University,
Waco, Texas 76798*

Received August 14, 1985; in revised form October 28, 1985

A new nine-coordination geometry has been discovered. Monazite-type compounds, such as $LnPO_4$ ($Ln = La, Ce, Pr, Nd, Sm, Eu, \text{ and } Gd$), $LnAsO_4$ ($Ln = La, Ce, Pr, \text{ and } Nd$), $\alpha\text{-PbSeO}_4$ (Rooseveltite), $BiPO_4$, $PbCrO_4$ (Crocoite), $\alpha\text{-PbSeO}_4$, $PuPO_4$, $LaVO_4$, $SrCrO_4$, $SrSeO_4$, and $ThSiO_4$, exhibit this new nine-coordination geometry. The new geometric form is best described as a pentagonal interpenetrating tetrahedral polyhedron (PITP). © 1986 Academic Press, Inc.

The purpose of this communication is to report the establishment of a new nine-coordination system. The new system is commonly observed in monazite-type compounds with the chemical formula MXO_4 , where M is a metal ion and XO_4 is a tetrahedral-type counterion. This new ninefold coordination geometry contains a central metal ion surrounded by five oxygen atoms on an equatorial plane, with two oxygen atoms above and two oxygen atoms below the pentagonal plane. These apical oxygen atoms are tetrahedrally arranged. This new nine-coordinated system was first encountered while gathering structural data on monazite-type lanthanoid orthophosphates ($LnPO_4$). This structural information is being employed at the Oak Ridge National Laboratory to relate crystal morphology to the stability and strength of polycrystalline ceramics so as to generate new

host materials for the safe disposal of nuclear wastes (1).

Previously, there were only two nine-coordination geometries reported in the literature, the monocapped square antiprism (MSAP) and the tricapped trigonal prism (TTP). Recently, it has been verified that the synthetic lanthanoid orthophosphates ($LnPO_4$, where $Ln = La, Ce, Pr, Nd, Sm, Eu, \text{ and } Gd$), which crystallize in a monazite-type structure (monoclinic, $P2_1/n$, No. 14), have the new ninefold geometry. The stereochemistry associated with the rigidity of monoclinic $LnPO_4$ is best described as a pentagonal interpenetrating tetrahedral polyhedron (PITP) with a point group symbol of C_2 (Fig. 1). The tridecilateral polyhedron contains 9 vertices, 20 edges, 12 triangular faces, and 1 quadrilateral face. A detailed dialectical description of PITP, MSAP, and TTP may be found elsewhere (2-4).

Besides the $LnPO_4$ series, numerous

* To whom all correspondence should be addressed.

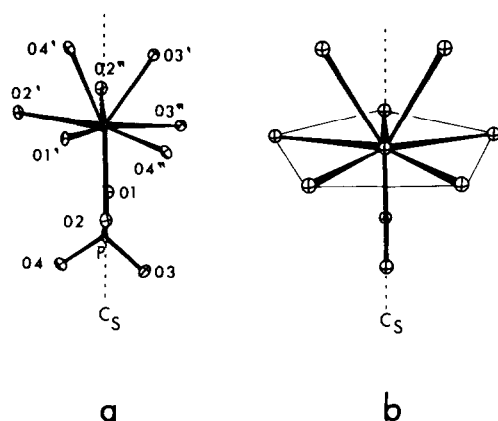


FIG. 1. (a) LnPO_4 coordination group showing C_5 symmetry. (b) Idealized PITP (pentagonal interpenetrating tetrahedral polyhedron) demonstrating the plane of symmetry, C_5 .

other compounds isostructural with the monazite-type structure have the new nine-coordination geometry (PITP). Some of these compounds include: $\alpha\text{-BiAsO}_4$ (Rooseveltite), BiPO_4 , LaAsO_4 , CeAsO_4 , PrAsO_4 , NdAsO_4 , PbCrO_4 (Crocoite),

SrCrO_4 , PuPO_4 , $\alpha\text{-PbSeO}_4$, SrSeO_4 , ThSiO_4 , and LaVO_4 . A comparison of cell parameters of the monoclinic MXO_4 compounds having a monazite-type lattice is presented in Table I.

One important feature of these monazite-type compounds is that the repulsion method of points-on-a-sphere (5, 6), which has been so successful in explaining the geometry of coordination compounds, fails to predict the existence of this particular geometric structure. The failure of the points-on-a-sphere method can be understood quite readily. The forces exerted on the pentagonal plane by the two oxygen atoms above the plane cannot balance the forces exerted by the two oxygen atoms below the plane, due to their tetrahedral arrangement. In order to restore equilibrium, according to the points-on-a-sphere method, the pentagonal plane has to be destroyed producing either a MSAP or a TTP. Since the experimentally determined structure around the nine-coordinated metal ion shows a

TABLE I
CELL DIMENSIONS OF MONAZITE-TYPE COMPOUNDS

| Compounds | <i>a</i> (Å) | <i>b</i> (Å) | <i>c</i> (Å) | β (°) | Ref. |
|-------------------------|-----------------|-----------------|-----------------|----------------|--------|
| LaPO_4 | 6.825(4) | 7.057(2) | 6.482(2) | 103.21(4) | 2 |
| CePO_4 | 6.777(3) | 6.993(3) | 6.445(3) | 103.54(4) | 7 |
| PrPO_4 | 6.741(3) | 6.961(4) | 6.416(3) | 103.63(3) | 4 |
| NdPO_4 | 6.722(1) | 6.933(3) | 6.390(2) | 103.72(2) | 4 |
| SmPO_4 | 6.669(1) | 6.868(2) | 6.351(1) | 103.92(2) | 3 |
| EuPO_4 | 6.639(3) | 6.823(3) | 6.318(3) | 104.00(4) | 3 |
| GdPO_4 | 6.621(2) | 6.823(2) | 6.310(2) | 104.16(2) | 3 |
| LaAsO_4 | 7.0078 | 7.212 | 6.7670 | 104.48 | 8 |
| CeAsO_4 | 6.9596 | 7.1576 | 6.7378 | 104.72 | 8 |
| NdAsO_4 | 6.897 | 7.094 | 6.6849 | 104.90 | 8 |
| PrAsO_4 | 6.929 | 7.119 | 6.715 | 104.80 | 8 |
| LaVO_4 | 7.047(1) | 7.286(1) | 6.725(1) | 104.85(1) | 9 |
| $\alpha\text{-BiAsO}_4$ | 6.879(1) | 7.159(1) | 6.732(1) | 104.84(1) | 10 |
| SrSeO_4 | 6.853(1) | 7.352(1) | 7.102(2) | 103.43(1) | 11 |
| | 7.087(4) | 7.317(4) | 6.862(8) | 103.55(5) | 12 |
| $\alpha\text{-PbSeO}_4$ | 7.153(3) | 7.403(3) | 6.957(3) | 103.27(5) | 12 |
| PbCrO_4 | 7.118(4) | 7.434(4) | 6.794(4) | 102.42(3) | 12, 13 |
| SrCrO_4 | 7.081(10) | 7.388(10) | 6.771(10) | 103.42(8) | 12 |
| BiPO_4 | 6.752 | 6.933 | 6.468 | 103.70 | 8 |
| PuPO_4 | 6.73 | 7.00 | 6.42 | 103.80 | 8 |
| ThSiO_4 | 6.784(2) | 6.974(3) | 6.500(3) | 104.92(3) | 14 |

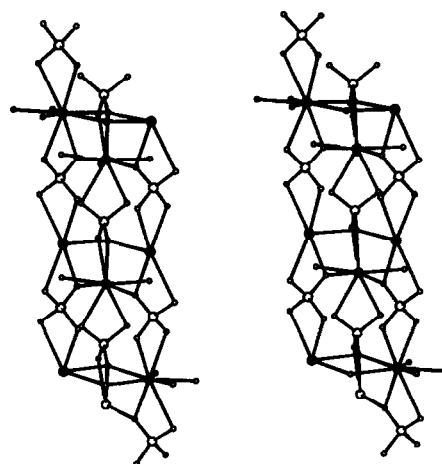


FIG. 2. Monoclinic MXO_4 : a stereoscopic drawing showing the interlocking mechanisms of the chain-like strands. (The large solid circles represent central metal ions (M), while the large open circles are X atoms and the small open circles are oxygen atoms.) For clarity, the stereoview displays only two surrounding strands instead of five.

pentagonal plane with an interpenetrating tetrahedron, the obvious conclusion is that the traditional repulsion method of points-on-a-sphere is inadequate in describing the interactions between all nine oxygen atoms. The rigidity associated with the PITP geometry of these monazite-type structures may be attributed to the bidentate bonding of the tetrahedral anionic groups. The lanthanoid metal atoms are apically and rigidly linked together in a chain-like fashion by the bidentate bonding. The apical bidentate bonding accounts for four of the nine oxygen atoms in the nine-coordinated polyhedron. The five remaining equatorial oxygen atoms forming the pentagonal plane of the polyhedron are bridged to five surrounding chain-like strands (Fig. 2). The bridging secures and supports the pentagonal plane in a locking-device manner so that planarity exists with negligible distortion. This interaction is termed the "locking effect."

A theoretical and experimental research program related to this new and interesting nine-coordination system is ongoing.

Acknowledgments

This work was supported in part by the The Robert A. Welch Foundation (Grant AA-668) and Baylor University.

References

1. B. C. SALES, C. W. WHITE, AND L. A. BOATNER, *Nucl. Chem. Waste Manage.* **4**, 281 (1983), and references therein.
2. D. F. MULLICA, W. O. MILLIGAN, DAVID A. GROSSIE, G. W. BEALL, AND L. A. BOATNER, *Inorg. Chim. Acta* **95**, 231 (1984).
3. D. F. MULLICA, DAVID A. GROSSIE, AND L. A. BOATNER, *Inorg. Chim. Acta* **109**, 105 (1985).
4. D. F. MULLICA, DAVID A. GROSSIE, AND L. A. BOATNER, *J. Solid State Chem.* **58**, 71 (1985).
5. L. J. GUGGENBERGER AND E. L. MUETTERTIES, *J. Amer. Chem. Soc.* **98**, 7221 (1976).
6. T. A. CLAXTON AND G. C. BENSON, *Canad. J. Chem.* **44**, 157 (1966).
7. G. W. BEALL, L. A. BOATNER, D. F. MULLICA, AND W. O. MILLIGAN, *J. Inorg. Nucl. Chem.* **43**, 101 (1981).
8. R. W. G. WYCKOFF, "Crystal Structures," Vol. 3, 2nd ed., p. 35, Interscience, New York (1965).
9. C. E. RICE AND W. R. ROBINSON, *Acta Crystallogr. Sect. B* **32**, 2232 (1976).
10. D. BEDLIVY AND K. MEREITER, *Acta Crystallogr. Sect. B* **38**, 1559 (1982).
11. H. PREVOST-CZESKLEBA AND H. ENDRES, *Acta Crystallogr. Sect. C* **40**, 18 (1984).
12. C. W. F. T. PISTORIUS AND M. C. PISTORIUS, *Z. Kristallogr.* **117**, 259 (1962).
13. S. QUARENI AND R. DE PIERI, *Acta Crystallogr.* **19**, 287 (1965).
14. M. TAYLOR AND R. C. EWING, *Acta Crystallogr. Sect. B* **34**, 1074 (1978).