



## STEREOACTIVE LONE-PAIR BEHAVIOR OF Pb IN THE CRYSTAL STRUCTURE OF BIDEAUXITE: $Pb^{2+}_2 Ag^+ Cl_3 F (OH)$

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### ABSTRACT

The crystal structure of bideauxite,  $Pb^{2+}_2 Ag^+ Cl_3 F (OH)$ , cubic,  $a$  14.1273(6) Å,  $V$  2819.2(4) Å<sup>3</sup>,  $Fd\bar{3}m$ ,  $Z = 16$ ,  $D_{calc} = 6.26$  g.cm<sup>-3</sup>, has been solved by direct methods and refined to an  $R$  index of 2.8% for 324 observed ( $5\sigma$ ) reflections measured with  $MoK\alpha$  X-radiation. There is one unique  $Ag$  site surrounded by an octahedral array of Cl anions, and one  $Pb$  site surrounded by nine anions with a very asymmetrical distribution of bonds and bond-lengths characteristic of stereoactive lone-pair behavior of  $Pb^{2+}$ . Four ( $AgCl_6$ ) octahedra link by sharing corners to form an  $[Ag_4Cl_{18}]$  cluster, and these clusters link by sharing corners to form a three-dimensional chequerboard arrangement, with  $[Pb_4(OH)_2 F_2 Cl_{18}]$  clusters filling the interstices. The structure of bideauxite is not related to those of the paragenetically related minerals boléite and pseudoboléite.

*Keywords:* bideauxite, crystal-structure refinement, hydroxy-chloride.

### SOMMAIRE

Nous avons résolu la structure cristalline de la bideauxite,  $Pb^{2+}_2 Ag^+ Cl_3 F (OH)$ , cubique,  $a$  14.1273(6) Å,  $V$  2819.2(4) Å<sup>3</sup>,  $Fd\bar{3}m$ ,  $Z = 16$ ,  $D_{calc} = 6.26$  g.cm<sup>-3</sup>, par méthodes directes jusqu'à un résidu  $R$  de 2.8% en utilisant 324 réflexions observées en diffraction X ( $5\sigma$ ) mesurées avec rayonnement  $MoK\alpha$ . Il y a un site unique  $Ag$  entouré d'anions Cl définissant un agencement octaédrique, et un site  $Pb$  entouré de neuf anions ayant une distribution très asymétrique de liaisons et de longueurs de liaison, signes d'une paire isolée d'électrons stéréoactifs sur l'ion  $Pb^{2+}$ . Quatre octaèdres ( $AgCl_6$ ) sont liés par partage d'un coin pour former un agencement  $[Ag_4Cl_{18}]$ , et ces agencements à leur tour sont liés par partage de coins pour former un réseau tridimensionnel en damier, avec des agroupements  $[Pb_4(OH)_2 F_2 Cl_{18}]$  dans les interstices. La structure de la bideauxite n'a pas de rapport avec celles des minéraux boléite et pseudoboléite de la même paragenèse.

(Traduit par la Rédaction)

*Mots-clés:* bideauxite, affinement de la structure cristalline, hydroxy-chlorure.

### INTRODUCTION

Bideauxite is a lead-silver fluor-hydroxy-chloride mineral,  $Pb_2 Ag Cl_3 (F,OH)_2$ , described by Williams (1970) from the Mammoth - St. Anthony mine, Tiger, Pinal County, Arizona. It is transparent when fresh and becomes lavender on exposure to strong light. It occurs as crystals up to 7 mm in maximum dimension. Bideauxite overgrows crystals of boléite and, in turn, is overgrown by matlockite and leadhillite, with associated sugary anglesite and surficial cerussite (Bideaux 1980). Among the secondary minerals of lead, halides are rare; a typical occurrence is in ancient metallurgical

slags, such as Laurion, Greece. Recently, a similar paragenesis with rare lead oxychlorides was discovered in the Etruscan metallurgical slags of Baratti beach, southern Tuscany, Italy (Franzini & Perchiazzi 1992).

Both Canadian (MC and FCH) and Italian (SM, MP and NP) groups have long-term interests in the crystal chemistry of lead-(copper) oxide-hydroxy-chloride minerals (Hawthorne 1985, Hawthorne & Groat 1986, Cooper & Hawthorne 1995, Merlino *et al.* 1993, 1994, 1995, 1996, Pasero & Perchiazzi 1996, Kutzke *et al.* 1999). In view of our interest in these minerals, both groups have solved the structure of bideauxite; we present the joint results here.

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