Available online at www.sciencedirect.com

SCIENCE DIRECT

Journal of Solid State Chemistry 178 (2005) 3066–3073

JOURNAL OF SOLID STATE CHEMISTRY

www.elsevier.com/locate/jssc

Synthesis and structure of $Ba_6Co_6ClO_{16}$, a new cobalt oxychloride with a layered perovskite-related structure

Nathalie Tancret, Pascal Roussel, Francis Abraham*

Laboratoire de Cristallochimie et Physicochimie du Solide, UMR CNRS 8012, ENSCL, Université des Sciences et Technologies de Lille, B. P. 90108, 59652 Villeneuve d'Ascq Cedex, France

Received 27 May 2005; received in revised form 13 July 2005; accepted 19 July 2005
Available online 30 August 2005

Abstract

Well-developed single crystals of the title compound were prepared using a $BaCl_2$ flux and investigated by X-ray diffraction methods using Mo($K\alpha$) radiation and a Charge Coupled Device (CCD) detector. The crystal structure was solved and refined in the hexagonal symmetry with $P\bar{6}m2$ space group, $a = 5.6698(2)$ Å and $c = 14.4654(5)$ Å to a final $R_1 = 0.022$ for 44 parameters with 1418 individual reflections. The structure of $Ba_6Co_6ClO_{16}$, which is related to the 6H-perovkite-type structure of $BaMnO_{2.88}$, is formed by the periodic stacking along [001] of five [BaO_3] layers separated by a [BaOCl] with a (*hhhchc*) stacking sequence. The [BaO_3] stacking creates tetranuclear face sharing octahedra units Co_4O_{15} containing Co(III) connected by dimers of corner-sharing CoO_4 tetrahedra. This new oxychloride belongs to the family of compounds formulated as $[BaOCl]M'_2[Ba_{n+1}M_nO_{3n+3}]$ where n represents the thickness of the octahedral string in hexagonal perovskite slabs.

Keywords: Barium cobalt oxychloride; Hexagonal perovskite; 6H perovskite-type structure; Crystal structure

1. Introduction

The ideal ABX_3 perovskite can be described from the cubic close-packing of AX_3 layers with the B cations occupying the octahedral holes resulting in a three-dimensional framework *ccc* of only corner-sharing octahedra. In opposite, in the ideal hexagonal perovskite ABX_3 the B cations occupy octahedra that are connected by face-sharing to form chains running down the *c*-axis of the hexagonal unit cell, the stacking sequence of the AX_3 layers is *hh*. Intermediate structures called hexagonal perovskite containing different proportions of cubic stacking (corner-sharing octahedra) and hexagonal stacking (face-sharing octahedra) are formed between the two ideal structures. Depending on the *h* and *c* layers stacking sequence, strings of two (*h*), three (*hh*) or four (*hhh*) face-sharing octahedra are corner shared (*c*) or separated by layers of one (*cc*), two (*ccc*), three (*cccc*), … corner-shared octahedra. Many $BaBO_3$ oxides are known corresponding to the different sequences. Furthermore, deficient layers such as BaO_2, BaOCl, BaCl, can be combined to BaO_3 layers to form numerous new compounds derived from hexagonal perovskite [1]. For example, the introduction of double Ba_2Cl_2 layers in an hexagonal perovskite-type arrangement of RuO_6 octahedra allows the formation of the series $[Ba_2Cl_2][Ba_{n+1}Ru_nO_{3n+3}]$ for $n = 2$, 3 [2] or 4 [3] where n represents the thickness of the octahedral string in hexagonal perovskite slabs. The replacement of the middle *h* or *c*-BaO_3 layer in a *chc* or a *ccc* block by a deficient BaO_2 layer results in the creation of two B-cation tetrahedra corner shared (to form a B_2O_7 dimer) or not, respectively. This type of structure is observed, for example, (1) in $Ba_5Fe_5O_{14}$ [4,5] where a *h*-BaO_3 layer is replaced by a BaO_2 layer in a *hhchc* sequence forming trimeric units of three face-shared octahedra cross linked by dimers of corner-shared tetrahedra and (2)

---

*Corresponding author. Fax: +33 3 20 43 68 14
E-mail address: francis.abraham@ensc-lille.fr (F. Abraham).

0022-4596/$ - see front matter © 2005 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2005.07.016

in 12H-$BaCoO_{2.6}$ [6] where a *c*-BaO_3 layer is replaced by a BaO_2 layer in a *hhhccc* sequence forming isolated units of four face-shared octahedral flanked on both boundaries by non-connecting BO_4 tetrahedra to form isolated blocks. A BaOCl layer, deduced from a BaO_2 layer by the substitution of Cl to one O atom, can only replace a *h*-BaO_3 layer to form a B_2O_7 dimer of two corner-shared tetrahedra. For BaO_3 and BaOCl stacking, up today, only $Ba_5B_5ClO_{13}$ compounds have been evidenced in which units of three face-shared octahedra are connected by B_2O_7 units. In these compounds B is Co [7] or a combination of two [8,9] or three metals [10]. For B = Co, the $Ba_5Co_5ClO_{13}$ compound is obtained [7] and can be described as the term $n = 3$ of a series $Ba_{n+2}Co_nCo_2ClO_{3n+4}$.

Majority of the prepared compounds contains mixed valence transition metals and exhibits unusual electronic properties correlated to the crystal structure. In the present paper we report the powder synthesis, the crystal growth and the crystal structure determination of a new oxychloride $Ba_6Co_6ClO_{16}$ that contains tetrameric units of face-shared CoO_6 octahedra connected by dimeric units of corner shared CoO_4 octahedra and is the term $n = 4$ of the predicted series.

2. Experimental

$Ba_6Co_6ClO_{16}$ single crystals were grown by a flux method using a procedure similar to that described by Yamaura et al. [7] for the synthesis of $Ba_5Co_5ClO_{13}$ single crystals. Typically, a 2 g mixture of $BaCO_3$ (Fisher, 99%), Co_3O_4 (Fluka, Assay >71% (KT) Co) and $BaCl_2 \cdot 2H_2O$ (Prolabo, Rectapur) with the 3:1:6 ratio was well ground in an agate mortar and heated in air at 1000 °C in an alumina crucible for 48 h. The crucible was then slowly cooled to 850 °C at 0.5 °C/min and finally quenched to room temperature. The excess of $BaCl_2$ was dissolved in hot water and two types of black shiny crystals were extracted from the preparation. Several single crystals were tested on a Bruker Smart CCD X-ray diffractometer. The needle-shaped crystals correspond to the previously reported $Ba_5Co_5ClO_{13}$ compound. The plate-like crystals also give an hexagonal cell with the same *a* parameter, $a \approx 5.67$ Å, but with lower *c* parameter, $c \approx 14.45$ Å and correspond to the new $Ba_6Co_6ClO_{16}$ compound.

Pure powder of $Ba_6Co_6ClO_{16}$ was synthesized by solid state reaction between the same reactants in stoechiometric ratio 11:4:1, at 900 °C during 24 h. Several intermediate regrindings were realized in order to homogenize the mixture. The resulting dark powder was examined by X-ray diffraction using a Huber G670 diffractometer with Guinier geometry, equipped with front-monochromator using Cu$K\alpha_1$ radiation ($\lambda = 1.54056$ Å).

Energy dispersive spectroscopy realized on several crystals revealed the presence of all elements introduced in the preparation: Ba, Co, Cl and O. Measurements were performed on a JEOL JSM-5300 scanning microscope equipped with an IMIX system of Princeton Gamma Technology, at 15 kV. Quantitative analysis realized on several points lead to the following ratio: Ba/Cl = 6.58(13) and Co/Cl = 6.62(12).

Redox chemical analysis was realized on the powder compound. A precise amount of $Ba_6Co_6ClO_{16}$ powder sample (≈0.08 g) was dissolved into a mixture of 100 mL of 2 N hydrochloric acid and 50 mL of 1 N phosphoric acid, with an excess of $FeCl_2$ solution (20 mL, 0.0974 N). Chemical reactions were:

$$Co^{3+} + Fe^{2+} \rightarrow Co^{2+} + Fe^{3+}$$

$$\text{and} \quad Co^{4+} + Fe^{2+} \rightarrow Co^{2+} + Fe^{3+}$$

leading to the global reaction: $Co^{x+} + (x-2)\,Fe^{2+} \rightarrow Co^{2+} + (x-2)\,Fe^{3+}$.

The proportioning of the excess of Fe^{2+} was realized with a $K_2Cr_2O_7$ solution (0.0167 N) in presence of a redox indicator according to

$$6\,Fe^{2+} + Cr_2O_7^{2-} + 14\,H^+ \rightarrow 6Fe^{3+} + 2\,Cr^{3+} + 7\,H_2O.$$

The oxidation state of cobalt was deduced from the difference between initial Fe^{2+} ions and Fe^{2+} ions titrated after the previous reaction. The results lead to a mean oxidation degree for cobalt of +3.33 (Table 1). So, the formula of the studied compound can be written $Ba_6Co_6ClO_{15.5}$ showing a weak deficiency in oxygen atoms. This hypothesis will be confirmed by structural considerations in the last part of this paper.

2.1. Crystal structure determination

A black plate-like crystal of $Ba_6Co_6ClO_{16}$ was selected, mounted on a glass fiber and aligned on a Bruker X8 CCD 4 K diffractometer. The X-ray intensity data were measured at room temperature using a Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) selected by a graphite monochromator. A strategy based on phi and omega scans has been chosen. According to the cell parameters of the compound and the high quality of the selected crystal, the scan angle and the *Dx* parameter were adjusted to limit the overlapping of reflections, i.e. in our case, the

Table 1
Mean oxidation state for cobalt (x) in $Ba_6Co_6ClO_{16}$

Experiment	m (g)	V (mL)	x
1	0.0746	15.90	3.328
2	0.0894	15.10	3.327
3	0.0998	14.50	3.336
4	0.0852	15.30	3.335

scan angle and the Dx parameter were fixed, respectively, to 0.5°/frame and 40 mm. The diffracted intensities were collected up to $2\theta = 92°$ (coverage of 99.75% achieved at $\theta = 45.87°$). A total of 9 runs (2 ω scans and 7φ scans), i.e. 4770 frames, was recorded, leading to a redundancy of 16.22 in the $P\bar{6}m2$ space group. The Saint 7.12 software [11] was used to extract reflection intensities from the collected frames and the SADABS 2004/1 program [12] was used to correct absorption effects using a semi-empirical method based on redundancy. Hexagonal unit-cell was refined leading to $a = 5.6698(2)$ Å and $c = 14.4654(5)$ Å, integrating 1418 individual reflections (22,870 observed reflections; redundancy 16.22).

The structure was determined in the $P\bar{6}m2$ space group by direct methods using SIR97 program [13] which allowed to localize heavy atoms (Ba, Co and Cl). Oxygen atoms positions were found by difference Fourier map calculations. The structure was refined by means of the JANA2000 Software package [14]. Anisotropic displacement parameters were attributed to all atoms in the last cycles of refinement, leading to the good R values given in Table 2.

Table 2
Crystal data, intensity collection and structure refinement parameters for $Ba_6Co_6ClO_{16}$

Empirical formula	$Ba_6Co_6ClO_{16}$
Formula mass	1469.1
Temperature (K)	298
Wavelength (Å)	Mo $K\alpha$ [0.71073]
Crystal system	hexagonal
Space group	$P\bar{6}m2$ (No. 187)
Unit cell dimensions (Å)	$a = 5.6698(2)$
(from single crystal)	$c = 14.4654(5)$
Cell volume (Å^3)	402.71(2)
Z	1
Density (calculated) (g cm^{-3})	6.056
Absorption coefficient (mm^{-1})	20.649
F(000)	643
Crystal size	$90 \times 150 \times 25$
Theta range for data collection	2.82–45.87
Index range	$-11 \leqslant h \leqslant 11$; $-11 \leqslant k \leqslant 11; -29 \leqslant l \leqslant 28$
Reflections collected	23068
Reflections observed	22870
Independent reflections	1422 [$R_{int} = 3.41$]
Redundancy	16.22
Criterion for observation	$I > 3\sigma(I)$
Data/restraints/parameters	1418/0/44
Final R indices (R, wR) all	2.21, 3.65
Final R indices (R, wR) obs	2.22, 3.66
Weighting scheme	$1/(\sigma^2(F) + 0.0004\ F^2)$
Largest diff. peak and hole [e$^-$ Å^3]	3.86, −2.00
Extinction method	B-C type 1 Gaussian isotropic [27]
Extinction coefficient	0.133(7)
Absolute configuration parameter	0.50(4)

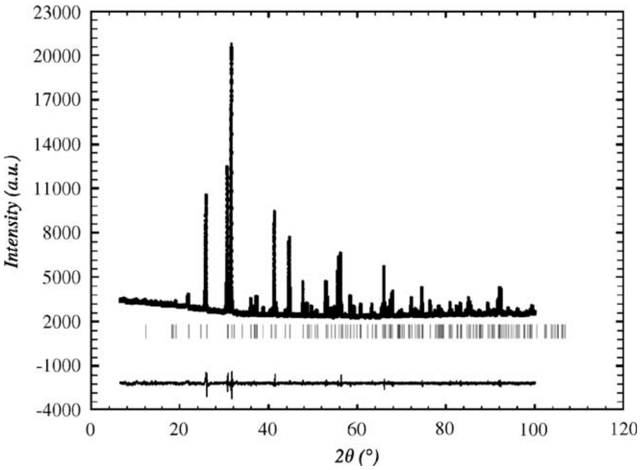


Fig. 1. Observed, calculated XRD patterns and their difference for $Ba_6Co_6ClO_{16}$.

2.2. Powder crystal structure refinement

The structure of $Ba_6Co_6ClO_{16}$ was also refined from powder X-ray diffraction data with the Rietveld profile refinement technique [15] by means of the FullProf program [16]. First, the "pattern matching" option included in the program was applied to the whole diagram allowing to modelize the profile. The peak shape was represented by a pseudo-Voigt function with an asymmetry correction at low angles. In order to describe the angular dependence of the peak full-width at half-maximum (H), the formula of Caglioti et al. [17] was used: $H^2 = U\tan^2\theta + V\tan\theta + W$, where U, V and W were parameters refined in the process. The calculations involved the refinement of 2-theta zeropoint, background level by a polynomial function and cell parameters too. In a second step, atomic coordinates and thermal parameters were added and the structure was refined by the Rietveld method. The agreement between observed and calculated data was indicated by the reliability factors ($Rw_p = 0.111$, $R_p = 0.194$, $R_F = 0.039$, $R_{Bragg} = 0.035$ and $R_{exp} = 0.113$) and by the plot of observed and calculated patterns represented in Fig. 1. The results of the refinement show the quality of the determined structure and that prepared powder is a pure phase of $Ba_6Co_6ClO_{16}$ without $Ba_5Co_5ClO_{13}$ since all peaks are unambiguously indexed.

3. Results and discussion

3.1. Crystal structure description

The atomic coordinates and isotropic displacement parameters for $Ba_6Co_6ClO_{16}$ deduced from the single crystal refinement are listed in Table 3. Selected bond lengths and charge distribution calculations results [18–20] are reported in Table 4.

Table 3
Atomic coordinates and isotropic displacement parameters for $Ba_6Co_6ClO_{16}$.
Anisotropic displacement parameters

	Wyck.	Occ	x	y	z	U_{eq}
Ba(1)	2*g*	1	0	0	0.79691(2)	0.00585(5)
Ba(2)	2*i*	1	−1/3	−2/3	0.35377(2)	0.00614(6)
Ba(3)	1*c*	1	1/3	−1/3	0	0.01211(9)
Ba(4)	1*b*	1	0	0	1/2	0.00909(8)
Co(1)	2*h*	1	1/3	−1/3	0.75454(5)	0.00339(9)
Co(2)	2*h*	1	1/3	−1/3	0.58322(4)	0.00274(8)
Co(3)	2*i*	1	−1/3	−2/3	0.87867(4)	0.0062(1)
Cl	1*a*	1	0	0	0	0.0258(6)
O(1)	6*n*	1	0.1859(2)	−0.6282(4)	0.6667(1)	0.0080(5)
O(2)	6*n*	1	0.0169(5)	−0.4915(2)	0.8329(2)	0.0097(4)
O(3)	3*k*	1	0.0348(4)	−0.4826(2)	1/2	0.0043(5)
O(4)	1*e*	0.19(6)	0.731(2)	−0.269(2)	0	0.0304(4)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba1	0.00608(7)	0.00608(7)	0.0054(1)	0.00304(3)	0	0
Ba2	0.00650(7)	0.00650(7)	0.0054(1)	0.00325(3)	0	0
Ba3	0.0142(1)	0.0142(1)	0.0078(2)	0.00712(5)	0	0
Ba4	0.00630(8)	0.00630(8)	0.0147(2)	0.00315(4)	0	0
Co1	0.00383(9)	0.00383(9)	0.0025(2)	0.00192(5)	0	0
Co2	0.0036(1)	0.0036(1)	0.0011(2)	0.00179(5)	0	0
Co3	0.0073(1)	0.0073(1)	0.0039(2)	0.00366(6)	0	0
Cl1	0.0331(8)	0.0331(8)	0.0112(9)	0.0166(4)	0	0
O1	0.0102(5)	0.0090(8)	0.0044(6)	0.0045(4)	0.0008(3)	0.0016(5)
O2	0.0053(6)	0.0101(5)	0.0119(7)	0.0026(3)	0.0041(7)	0.0021(3)
O3	0.0011(7)	0.0052(6)	0.0050(7)	0.0006(4)	0	0
O4	0.031(4)	0.031(4)	0.014(4)	0.005(5)	0	0

Note. The U_{eq} values are defined by

$$U_{eq} = 1/3\left(\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j\right).$$

The anisotropic displacement factor exponent takes the form

$$-2\pi^2\left[h^2 a^{*^2} U_{11} + \cdots + 2\,h\,ka^* b^* U_{12}\right].$$

Table 4
Selected bond distances d (Å) and charge distribution (CD) in $Ba_6Co_6ClO_{16}$

	d (Å)		CD		d (Å)		CD
Ba(1)–Cl	2.9378(3)	Ba(1)	2.17	Ba(2)–O(1) (6*x*)	2.857(2)	Ba(2)	2.07
Ba(1)–O(1) (3*x*)	2.623(2)			Ba(2)–O(3) (3*x*)	2.782(1)		
Ba(1)–O(2) (6*x*)	2.884(2)			Ba(2)–O(2) (3*x*)	3.201(3)		
Ba(3)–O(2) (6*x*)	2.874(3)	Ba(3)	1.79	Ba(4)–O(3) (6*x*)	2.840(2)	Ba(4)	2.04
Ba(3)–O(4) (6*x*)	3.01(2)			Ba(4)–O(1) (6*x*)	3.024(2)		
Ba(3)–Cl (3*x*)	3.274						
Co(1)–O(1) (3*x*)	1.926(2)	Co(1)	3.84	Co(2)–O(1) (3*x*)	1.885(2)	Co(2)	3.57
Co(1)–O(2) (3*x*)	1.923(3)			Co(2)–O(3) (3*x*)	1.897(2))		
Co(3)–O(2) (3*x*)	1.843(3)	Co(3)	2.94	Co(1)–Co(2)	2.4782(9)		
Co(3)–O(4)	1.865(5)			Co(2)–Co(2)	2.4076(8)		
				O(4)–O(4) (2*x*)	1.09(2)		
		Cl	−1.01				
		O(1)	−1.95			O(2)	−1.72
		O(4)	−1.37			O(3)	−1.98

A view of the structure, in projection along [010] is given in Fig. 2. The structure of $Ba_6Co_6ClO_{16}$ can be derived from the 6H-polytype hexagonal structure with a stacking sequence (*hhhchc*) adopted for example by $BaMnO_{2.88}$ [21] by the replacement of the *h*-[BaO_3] layer of the *chc* part by a *h*′-[BaOCl] layer where *h* represents an hexagonal layer, i.e. a layer between two layers of the same type and *c* represents a cubic layer, i.e. a layer, between two layers of different types; in *h*′ Ba occupy the same positions than in *h*, the two O_3 triangles are replaced by a O and a Cl atom (Fig. 3). The oxygen atoms of this stacking create octahedral and tetrahedral sites occupied by Co atoms leading to the formation of a three-dimensional framework of polyhedra built from tetrameric Co_4O_{15} units of edge-shared octahedra linked by Co_2O_7 units of two corner-shared CoO_4 tetrahedra. The structure is correlated to that of $Ba_5Co_5ClO_{13}$ [7] which can be deduced from the 10H-polytype hexagonal structure with a stacking sequence $(hhchc)_2$, adopted for example by $BaMnO_{2.81}$ [21], by the replacement of the *h*-[BaO_3] layer of the *chc* part by a *h*′-[BaOCl] layer leading to trimeric Co_3O_{12} units of edge-shared octahedra linked by Co_2O_7 units. Starting from the same $(hhchc)_2$ sequence or from (*hhccc*), the replacement of the central [BaO_3] layer of the *chc* or *ccc* part by a [BaO_2] layer leads to the structure of $BaVO_{2.8}$ [22] or $BaFeO_{2.8}$ [23,24], respectively (Fig. 4). Tetrameric-containing compounds are fewer, however $BaCoO_{2.6}$ [6] corresponds to the (*hhhcc*′*c*) sequence ($c' = [BaO_2]$), whereas up today no example of (*hhhch*′*c*) sequence ($h' = [BaO_2]$), is known.

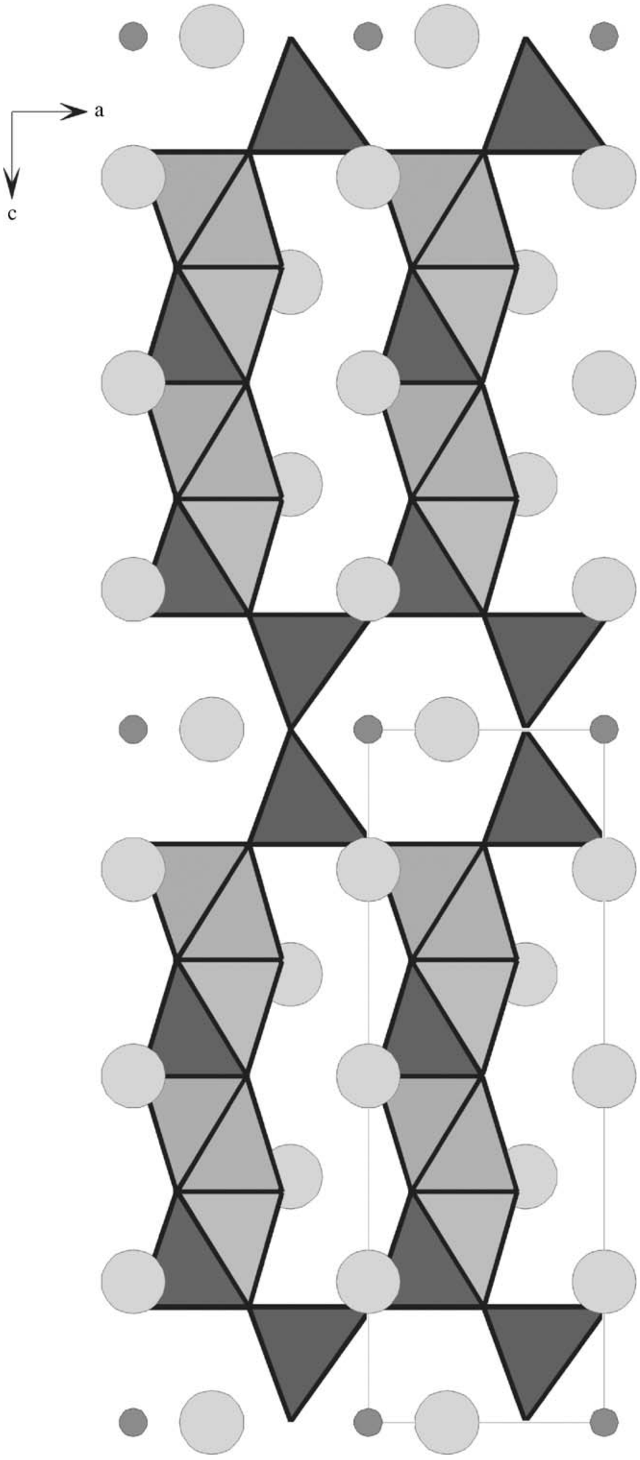


Fig. 2. Schematic crystal structure of hexagonal $Ba_6Co_6ClO_{16}$ view along [010] showing the four shared-octahedra chains pillared by Co_2O_7 dimers of corner-shared tetrahedra.

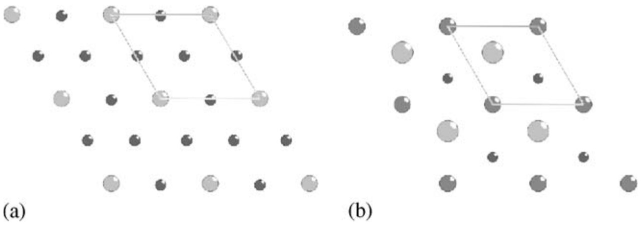


Fig. 3. Relations between [BaO_3] and [BaOCl] layers.

The Ba^{2+} and Cl^- ions occupy the cavities created by the three-dimensional network of CoO_6 and CoO_4 polyhedra. Ba(2) and Ba(4) occupy a classical environment of 12 oxygen atoms (Fig. 5a) with Ba–O distances comprised between 2.782(1) and 3.201(3) Å for Ba(2) and 2.840(2) and 3.024(2) Å for Ba(4). The environment of Ba(1) can be deduced from that of Ba(2) or Ba(4) by replacing an O_3 triangle by one chlorine atom (Fig. 5b). Ba(1) is then surrounded by 9 oxygen atoms localized from 2.623(2) to 2.884(2) Å and a chlorine atom at 2.9378(3) Å. The last barium Ba(3) is in a geometry close to that of Ba(2) and Ba(4) but three oxygen atoms are replaced by three chlorine atoms on the equatorial plane (Fig. 5c). Ba–O distances range from 2.874(3) to 3.01(2) Å and Ba–Cl distances are equal to 3.274 Å. But the environment of Ba(4) is quite particular because there is a disorder around the O(4) atom which occupies the vertex of a little triangle around the three-fold axis (Table 4). Indeed, refinement is improved if the corner-shared oxygen atom is distributed over three-fold axis related positions. As already observed in layered

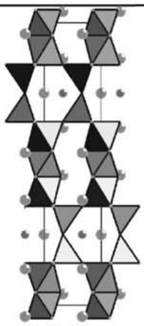
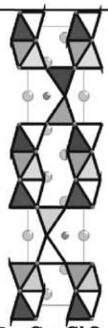
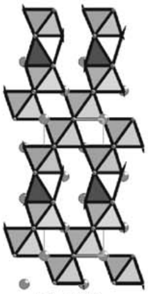
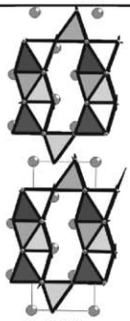
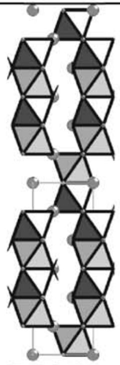
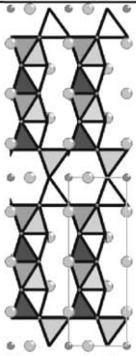
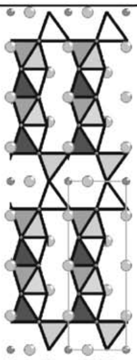
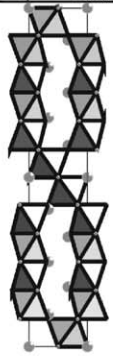
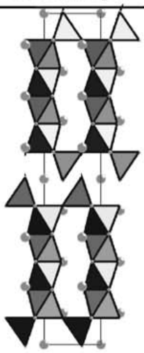
	h' or c' = $[BaO_3]$	h' or c' = $[BaO_2]$	h' or c' = $[BaOCl]$
(hhch'c)$_2$ – 10H	 $BaMnO_{2.81}$	 $BaFeO_{2.654}$	 $Ba_5Co_5ClO_{13}$
(hhcc'c) – 5H	 $BaVO_3$	 $BaVO_{2.8}$	
(hhhch'c) – 6H	 $BaMnO_{2.88}$	 No example	 $Ba_6Co_6ClO_{13}$
(hhhch'c)$_2$ – 12H	 No example	 $BaCoO_{2.6}$	

Fig. 4. Correlation between structures built from $[BaO_3]$ only layers stacking and structures obtained by the replacement of one $[BaO_3]$ by a deficient $[BaO_2]$ or a $[BaOCl]$ layer.

hexagonal perovskite-type compounds containing M_2O_7 dimeric units, the shared oxygen is not well localized, in $Ba_5Co_5ClO_{13}$ its isotropic displacement parameter is large [7], in $Ba_5Fe_4PtClO_{12.5}$ it is only half occupied [8]. Cl^- is coordinated by five Ba atoms forming a trigonal bipyramid (Fig. 5d).

In the Co_4O_{15} unit of face shared octahedra, the Co(2)–Co(2) distance for the two central octahedra

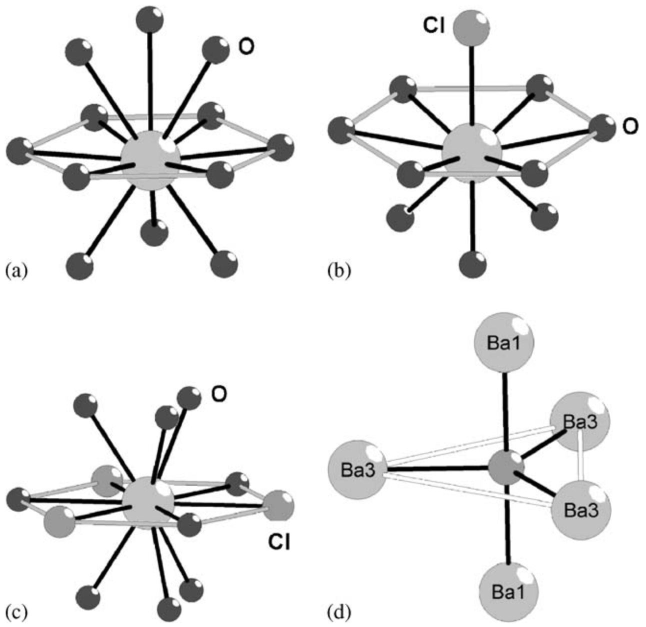


Fig. 5. Environment of (a) Ba(2) and Ba(4), (b) Ba(1), (c) Ba(3) and (d) Cl in $Ba_6Co_6ClO_{16}$.

(2.408 Å) is significantly shorter that the Co(1)–Co(2) distance between terminal octahedra (2.478 Å), these distances are comparable to the corresponding values obtained in $BaCoO_{2.6}$ [6]. The composition of the oxychloride is rather stochiometric $Ba_6Co_6ClO_{16}$, however disorder of the O(4) atom, large isotropic parameter for Cl and for some O atoms could indicate the possibility of non-stoechiometry. The average Co valence calculated for $Ba_6Co_6ClO_{16}$ is +3.5 and mixed valence for Co ions in both octahedral and tetrahedral sites could be possible. Nevertheless Co^{3+} has a strong preference for octahedral coordination and, using average Co–O bond lengths, a valence ordered site model for the Co ions can be proposed. For the octahedral cobalt, the average Co–O bond distances are 1.891 and 1.925 Å for Co(2) and Co(1), respectively, which well agree with the Co^{3+}–O from the sums of ionic radii of 1.895 and 1.934 Å for low-spin and high-spin Co^{3+} ion, respectively [25]. Though the Co(3)–O average bond distance for the tetrahedral cobalt considering only O(4) (1.865 Å) is higher than the calculated value from ionic radii considering Co^{4+} (1.75 Å), it is comparable to the obtained value in some tetrahedral Co^{4+} containing compounds (for example 1.81 Å in Na_4CoO_4 [26]). So, if we assume that the octahedral sites contain only Co^{3+} and the tetrahedral sites only Co^{4+} as in the 12H-$BaCoO_{2.6}$ [6], then the ideal composition is $Ba_6Co_6ClO_{15.5}$ involving oxygen vacancies. Such oxygen vacancies can be achieved by half-occupancy of the shared oxygen site in the [BaOCl] layer as in $Ba_5Fe_4PtClO_{12.5}$ [8]. Oxygen vacancies can also be accommodated in the $[BaO_3]$ layers as in several $BaCoO_x$ compounds and in many hexagonal or perovskite oxides as Brownmillerite-type compounds. The required composition of the layers for $Ba_6Co_6ClO_{15.5}$ is $[BaO_{2.9}]$. This hypothesis is in agreement with redox chemical analysis previously discussed.

4. Conclusion

Single crystals of the term $n = 4$ of the series $[BaOCl]M'_2[Ba_{n+1}M_nO_{3n+3}]$ have been isolated for $M = M' = Co$. The $[Ba_{n+1}Co_nO_{3n+3}]$ slab contains Co_4O_{15} entities resulting from face-shared octahedra connected by Co_2O_7 entities formed from corner-shared tetrahedra. The mean oxidation state of Co is +3.5. The term $n = 3$ has previously been reported for $M = M' = Co$ but also for other M, M' couples. Other terms together with intergrowth structures of mixed terms are expected using other synthesis conditions or other M,M' couples, in fact five face-shared octahedra strings exist in 19*R*-$BaMnO_3$ [21]. Neutrons diffraction experiments are also planed to precisely locate the O(4) atoms and to check the hypothesis of oxygen vacancies in $[BaO_3]$ layers.

References

[1] J. Darriet, M.A. Subramanian, J. Mater. Chem. 5 (4) (1995) 543.
[2] N. Tancret, P. Roussel, F. Abraham, J. Solid State Chem. 177 (2004) 806.
[3] J. Wilkens, Hk. Müller-Buschbaum, Acta Chem. Scand. 45 (1991) 812.
[4] M.I. Gómez, G. Lucotti, J.A. de Morán, P.J. Aymonino, S. Pagola, P. Stephens, R.E. Carbonio, J. Solid State Chem. 160 (2001) 17.
[5] J.L. Delattre, A.M. Stacy, T. Siegrist, J. Solid State Chem. 177 (2004) 925.
[6] A.J. Jacobson, J.L. Hutchinson, J. Solid State Chem. 35 (1980) 334.
[7] K. Yamaura, D.P. Young, T. Siegrist, C. Besnard, C. Svensson, Y. Liu, R.J. Cava, J. Solid State Chem. 158 (2001) 175–179.
[8] W. Leib, H. Mueller-Buschbaum, Z. Anorg. Allg. Chem. 551 (1987) 7–12.
[9] N. Tancret, P. Roussel, F. Abraham, J. Solid State Chem. 177 (2004) 1023.
[10] M. Neubacher, H. Mueller-Buschbaum, J. Alloys Comp. 183 (1992) 18–23.
[11] Bruker Analytical X-ray system, "SAINT+, Version 7.12", Madison, USA, 2004.
[12] G.M. Scheldrick, SADABS, Bruker-Siemens Area Detector Absorption and Other Correction, Version 2004/1, Goetingen, Germany, 2004.
[13] A. Altomare, M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, SIR97 A Package for Crystal Structure Solution by Direct Methods and Refinement, Bari, Rome, Italy, 1997.
[14] V. Petricek, M. Dusek, L. Palatinus, The Crystallographic Computing System JANA2000, Praha, Czech Republic, 2005.
[15] (a) H.M. Rietveld, Acta Crystallogr. 22 (1967) 151;
(b) H.M. Rietveld, Acta Crystallogr. 25 (1969) 589.

[16] (a) J. Rodriguez-Carvajal, FULLPROF: A program for rietveld refinement and pattern matching analysis, Abstracts of the Satellite Meeting on Powder Diffraction of the XV Congress of the IUCr, Toulouse, France, 1990, p. 127;
(b) C. Caglioti, A. Paoletti, E.P. Ricci, Nucl. Instrum. Methods 3 (1958) 223.
[17] C. Caglioti, A. Paoletti, E.P. Ricci, Nucl. Instrum. Methods 3 (1958) 223.
[18] R. Hoppe, S. Voigt, H. Glaum, J. Kissel, H.P. Müller, K. Bernet, J. Less-Common Metals 156 (1989) 105.
[19] M. Nespolo, G. Ferraris, H. Ohashi, Acta Crystallogr. B 55 (1999) 902.
[20] M. Nespolo, G. Ferraris, G. Ivaldi, R. Hoppe, Acta Crystallogr. B 57 (2001) 652.
[21] T. Negas, R.S. Roth, J. Solid State Chem. 3 (1971) 323.
[22] G. Liu, J.E. Greedan, J. Solid State Chem. 110 (1994) 274.
[23] M.I. Gomez, G. Lucotti, J.A. de Moran, P.J. Aymonono, S. Pagola, P. Stephens, R.E. Carbonio, J. Solid State Chem. 160 (2001) 17.
[24] J.L. Delattre, A.M. Stacy, T. Siegrist, J. Solid State Chem. 177 (2004) 928.
[25] R.D. Shannon, Acta Crystallogr. Sect. A. 32 (1976) 751.
[26] M. Jansen, Z. Anorg. Allg. Chem. 417 (1975) 35.
[27] P.J. Becker, P. Coppens, Acta Cryst. A 30 (1974) 148.