

Synthesis and Crystal Structure of RbGdNb₆Cl₁₈

Fakhili Gulo^{1*}, Saronom Silaban^{2*}, Christiane Perrin³¹Study Program of Environmental Science, Postgraduate Program, Sriwijaya University, Palembang 30139, Indonesia²Department of Chemistry, Universitas Negeri Medan, Jl. Willem Iskandar/Pasar V Kota Medan 20221 Sumatera Utara, Indonesia³Université de Rennes, CNRS, ISCR, UMR 6226, Avenue du Général Leclerc, 35042 Rennes Cedex, France*Corresponding authors: fgulo@unsri.ac.id and saronomsilaban@unimed.ac.idDOI: <https://doi.org/10.24198/cna.v11.n2.47103>

Abstract: A new quaternary niobium cluster chloride, RbGdNb₆Cl₁₈ has been prepared by solid state reaction methods. The RbCl, GdCl₃, NbCl₅, and niobium powder were mixed in stoichiometric proportions. This mixture was fed into a sealed quartz tube, and heated at 700°C for 2 days. A single crystal was selected for use in determining the structure of this compound using a single crystal X-ray diffractometer. It crystallizes in the trigonal system, hexagonal setting with space group *R*-3 (No. 148). The unit cell parameters are: $a = 9.3037(2)$ Å, $c = 25.5752(2)$ Å, $V = 1.917.17(7)$ Å³, and $Z = 3$. The structure consists of discrete cluster units, [Nb₆Cl₁₈]⁴⁻ that separated by Rb⁺ and Gd³⁺ cations in a close packed cubic stacking arrangement.

Keywords: *crystal structure, niobium cluster, X-ray diffraction*

Abstrak: Suatu kluster niobium klorida kuaterner baru, RbGdNb₆Cl₁₈ telah disiapkan dengan metode reaksi padat. RbCl, GdCl₃, NbCl₅, dan bubuk niobium dicampur dalam proporsi stoikiometri. Campuran ini dimasukkan ke dalam tabung kuarsa tertutup, dan dipanaskan pada suhu 700°C selama 2 hari. Sebuah kristal tunggal dipilih untuk digunakan dalam menentukan struktur senyawa ini memakai difraktometer sinar-X. Senyawa ini mengkristal dalam sistim trigonal, pengaturan heksagonal dengan kelompok ruang *R*-3 (No. 148). Parameter sel satuannya adalah: $a = 9,3037(2)$ Å, $c = 25,5752(2)$ Å, $V = 1,917,17(7)$ Å³, dan $Z = 3$. Struktur senyawa ini terdiri dari unit cluster diskrit, [Nb₆Cl₁₈]⁴⁻ yang dipisahkan oleh kation Rb⁺ dan Gd³⁺ dalam penataan susunan kubik terkemas rapat.

Kata kunci: *difraksi sinar-X, kluster niobium, struktur kristal*

INTRODUCTION

Halide compounds of the early transition metals in a low oxidation state show a tendency to form octahedral hexanuclear clusters. Aggregates of metal atoms with limited dimensions and high symmetry are called clusters (Perrin *et al.* 2001). In clusters, metal atoms are connected to each other through metal-metal bonds. In cluster core, the distances between metal atoms are not significantly different from those inside metal bulks (Corbett 2000).

The hexanuclear clusters of niobium halides tend to favor structures with an octahedral edge-bridged geometry. The most common structural motif in these compounds is $[Nb_6L_{12}L_6^a]^n-$ cluster unit with L = Cl, Br. In this case, the octahedron of the niobium atoms is surrounded by twelve inner ligands (Lⁱ) and six apical ligands (L^a) (Perrin *et al.* 2001). These cluster units can be present in the form of discrete anions, in the solid state compounds. Discrete cluster units are found in the following various compounds: K₄Nb₆Cl₁₈ (Simon *et al.*, 1968), Ba₂Nb₆Cl₁₈ (Broll &

Schäfer 1970), CsErNb₆Br₁₈ (Cordier *et al.* 1993), K₂SrNb₆Cl₁₈ (Duraisamy & Lachgar 2002), KYNb₆Cl₁₈ (Duraisamy & Lachgar 2003) and Cs₂PbNb₆Cl₁₈ (Gulo *et al.* 2001). The octahedral cluster units can be linked to each other by sharing apical ligands and/or inner ligands to form polymers as observed in compounds: NaNb₆Cl₁₅ (Sägebarth *et al.* 1995) and Nb₆Cl₁₄ (Simon *et al.* 1965).

In chemistry of niobium cluster halides with monovalent and rare earth as counter-cations, two structure types have been found: **R** type and **P** type. KLuNb₆Cl₁₈ crystallized with space group, *R*-3 is called **R** type (Ihmaïne *et al.* 1988) and CsLuNb₆Cl₁₈ crystallized with space group, *P*-31c is named **P** type (Ihmaïne *et al.* 1989). These two structure types have also been encountered in the centered zirconium cluster halide chemistry, for instance K₂Zr₇(H)Cl₁₈ (**R**) (Imoto *et al.* 1981) and CsLaZr₆(Fe)Cl₁₈ (**P**) (Zhang & Corbett 1993). The coexistence of these two phases (**R** and **P** types) is due to the difference in cation size.

The use of metal clusters as building units for

supramolecular materials is very advantageous due to their unique structural, chemical, physical properties (Zhou & Lachgar 2007). Transition metal clusters have high potential impact and performance in biotechnology, photovoltaic, solar control, catalytic, photonic and sensory applications (Nguyen *et al.* 2022). Several research groups are actively exploring the use of octahedral transition metal clusters, as building units in investigating the effects of metal-metal bonding on their physicochemical properties.

The Charge-transfer antiperovskite (CT) solids have been derived from molybdenum cluster units by electrocrystallization (Hiramatsu *et al.* 2015). In addition, octahedral cluster units of niobium have been widely used as raw materials for the preparation of novel compounds with new structures and magnetic properties (Naumov *et al.* 2003; Zhang *et al.* 2011; Zhou *et al.* 2011).

Up to now, no structure of octahedral niobium cluster of halides with rubidium and gadolinium metals as counter-cations has been reported. Here, we describe the preparation and structural characterization of RbGdNb₆Cl₁₈ containing octahedral clusters that are connected to each other through Rb⁺ and Gd³⁺ cations.

MATERIAL AND METHODS

Preparation

The compound RbGdNb₆Cl₁₈ is prepared from stoichiometrically proportional mixing of RbCl,

GdCl₃, NbCl₅, and niobium powder. This mixture was placed in silica tube in dry boxes (gloved boxes) under an atmosphere of argon gases. The silica tube containing this sample was sealed under vacuum. Then, the sample was heated slowly at a rate of 15 °C per minute to 700°C. A temperature of 700°C was maintained for 2 days, followed by slow cooling to room temperature. This compound was found in the form of microcrystalline powder that has dark brown color and is stable in air at room temperature. Several suitable single crystals for structural determination were obtained during synthesis.

Data Collection

A good single crystal of RbGdNb₆Cl₁₈ has been selected and used in the determination of structure with X-ray diffraction method. Data were collected using the Enraf Nonius KappaCCD diffractometer at room temperature. The Denzo program from the KappaCCD software package was used to perform the identification, correction for Lorentz-polarization, and integration of 11,697 reflections in hexagonal symmetry. A total of 1,874 reflections were obtained from frames scaling and combining of equivalent, redundant, and Friedel reflections in the *r*3 point group.

Structure Determination

The SHELXS-97 program with a direct method has been used to resolve the structure of this

Table 1. Crystal data and structure refinement for RbGdNb₆Cl₁₈

| Empirical formula | RbGdNb ₆ Cl ₁₈ |
|-----------------------------------|--|
| Formula weight | 1438.28 g.mol ⁻¹ |
| Temperature | 293(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Trigonal |
| Space group | <i>R</i> -3 (No. 148), hexagonal setting |
| Unit cell dimensions | a = 9.3037(2) Å b = 9.3037(2) Å c = 25.5752(6) Å |
| Volume | 1917.17(7) Å ³ |
| Z | 3 |
| Density (calculated) | 3.737 g.cm ⁻³ |
| Absorption coefficient | 8.917 mm ⁻¹ |
| F(000) | 1959 |
| Crystal size | 0.15 x 0.12 x 0.10 mm ³ |
| Theta range for data collection | 2.39 to 34.97 °. |
| Index ranges | 0 ≤ h ≤ 14; -12 ≤ k ≤ 0; -41 ≤ l ≤ 40 |
| Reflections collected | 1874 |
| Independent reflections | 1874 |
| Reflections observed (>2σ) | 1683 |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 1874 / 0 / 43 |
| Goodness-of-fit on F ² | 1.134 |
| Final R indices [I>2σ(I)] | R ₁ = 0.0254; wR ₂ = 0.0511 |
| R indices (all data) | R ₁ = 0.0309; wR ₂ = 0.0533 |
| Largest diff. peak and hole | 1.746 and -1.060 e.Å ⁻³ |

compound in the centrosymmetric space group $R\bar{3}$ (Sheldrick 2018^b). The method of least squares of full matrices and Fourier synthesis of F_2 have been applied in the refinement by using the SHELXL-97 program (Sheldrick 2018^a). Anisotropic displacement factors have been applied in the refinement of the all atoms. Rubidium atoms are randomly distributed with an occupancy factor of 0.1726(8) or 51% giving 1.035 Rb per formula. Therefore, we round the formula of this compound to $\text{RbGdNb}_6\text{Cl}_{18}$. The highest residual peak of $1.76 \text{ e.}\text{\AA}^{-3}$ is located at 1.00 \AA from the Cl2 atom while the largest residual hole of $-1.05 \text{ e.}\text{\AA}^{-3}$ lies at 0.68 \AA from the Nb atom.

Selected data of crystals and structural refinement are presented in Table 1. Atomic coordinates and equivalent isotropic displacement parameters (\AA) are listed in Table 2. Selected bond lengths (\AA) are summarized in Table 3. The structure is visualized with aid of DIAMOND software (K. Brandenburg, 2014).

RESULTS AND DISCUSSION

The new halide compound, $\text{RbGdNb}_6\text{Cl}_{18}$ crystallizes in a trigonal system and its structure is isotypic with those of $\text{KLuNb}_6\text{Cl}_{18}$ (Ihmaine *et al.* 1988) and $\text{Cs}_2\text{PbNb}_6\text{Cl}_{18}$ (Gulo *et al.* 2001). Hexagonal unit-cell of the structure is represented in Figure 1 with the $\text{Nb}_6\text{Cl}_{18}$ units centered on a $\bar{3}$ inversion axis. Gadolinium and rubidium atoms lie at $(1/3 \ 2/3 \ 1/6)$ and $(2/3 \ 1/3 \ z)$ positions in the octahedral and tetrahedral cavities respectively between the cluster units.

The structure is characterized by the presence of $[\text{Nb}_6\text{Cl}_{12}^i\text{Cl}_6^\alpha]^{4-}$ cluster unit of D_{3d} symmetry. The octahedral Nb_6 cluster is edge-bridged by 12 chlorine atoms called inner ligands (Cl^i) and bonded to six

additional chlorine atoms occupying the terminal position denoted by the apical ligand (Cl^a). This discrete cluster unit is shown in Figure 2. Crystallographically, the octahedral Nb_6 cluster is formed from one independent niobium atom located at the base of a pyramidal site built by

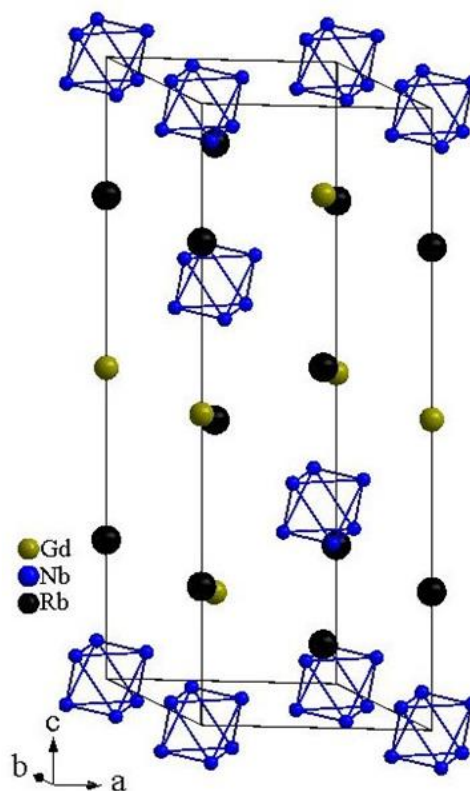


Figure 1. Unit cell of $\text{RbGdNb}_6\text{Cl}_{18}$. The Cl atoms are omitted for clarity.

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (\AA) for $\text{RbGdNb}_6\text{Cl}_{18}$

| Atom | x | Y | z | U_{eq} |
|-------|-----------|-----------|-----------|----------|
| Gd | 1/3 | 2/3 | 1/6 | 0.012(1) |
| Nb | 0.1578(1) | 0.9598(1) | 0.0466(1) | 0.009(1) |
| Cl(1) | 0.4181(1) | 0.1404(1) | 0.0005(1) | 0.015(1) |
| Cl(2) | 0.3650(1) | 0.9164(1) | 0.1065(1) | 0.017(1) |
| Cl(3) | 0.2325(1) | 0.1855(1) | 0.1097(1) | 0.016(1) |
| Rb | 2/3 | 1/3 | 0.1104(1) | 0.029(1) |

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Bond lengths [\AA] for $\text{RbGdNb}_6\text{Cl}_{18}$

| Bond | Length | Bond | Length |
|----------|----------------|----------|-----------------|
| Gd-Cl(2) | 2.6783(6) $6x$ | Nb-Nb | 2.9181(3) $6x$ |
| Nb-Cl(1) | 2.4492(6) | Nb-Nb | 2.9206(4) $6x$ |
| Nb-Cl(1) | 2.4512(6) | Rb-Cl(2) | 3.4706(6) $3x$ |
| Nb-Cl(3) | 2.4553(6) | Rb-Cl(3) | 3.5087(11) $3x$ |
| Nb-Cl(3) | 2.4576(6) | Rb-Cl(1) | 3.5102(10) $3x$ |
| Nb-Cl(2) | 2.6468(6) | Rb-Cl(3) | 3.5573(6) $3x$ |

five chlorine ligands. Each niobium atom is bonded to three different chlorine atoms, Cl1 and Cl3 which act as inner ligands and Cl2 which is at the terminal position.

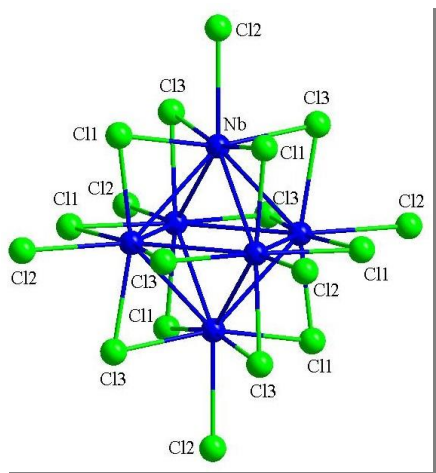


Figure 2. A view of $[Nb_6Cl_{12}Cl_6]^{4-}$ cluster unit in RbGdNb₆Cl₁₈

RbGdNb₆Cl₁₈ contains the Nb₆ cluster that is slightly distorted. The length of intracuster Nb-Nb bonds range from 2.9181 (3) Å to 2.9207 (3) Å with an average of 2.9194 Å. The length of the niobium-ligand bond is strongly influenced by the type of ligands (Nb-Clⁱ = 2.4534 Å and Nb-Cl^a = 2.6469 Å). This bond length is comparable to the values commonly found in various Nb₆ halide compounds (Perrin *et al.* 1995). The Nb-Cl^a distance is longer than the Nb-Clⁱ distance due to the electronic repulsion and steric effect of inner ligands, Clⁱ which build up the base of pyramidal sites inhabited by niobium atom.

In the network, the cluster units are linked with each other through Gd³⁺ and Rb⁺ cations as shown in Figure 3. Gadolinium atom is coordinated to six chlorine apical ligands from six neighboring cluster units that arranged in a slightly deformed octahedron of -3 symmetry with Gd-Cl distance of 2.6783(6) Å. This bond length is very close to the sum of Gd³⁺ radii (0.938 Å) and Cl⁻ radii (1.81 Å) (Shannon, 1976). The Gd-Cl bond in RbGdNb₆Cl₁₈ is longer than Lu-Cl one in KLuNb₆Cl₁₈. It corresponds to metal ionic radii, which is smaller for lutetium than for gadolinium.

Rubidium atom is surrounded tetrahedrally by four cluster units and bonded to twelve chlorine ligands. The bond length of Rb-Cl is about 3.4706(6) Å to 3.5573(6) Å with an average value of 3.5116 Å. There is no significant difference between this value and the sum of the ionic radii Rb⁺ (1.72 Å) and Cl⁻ (1.81 Å) (Shannon 1976).

In RbGdNb₆Cl₁₈, the alkaline site is only half occupied but it is fully occupied in Cs₂PbNb₆Cl₁₈ (Gulo *et al.* 2001). The substitution of divalent metal (Pb) with trivalent metal (Gd) is compensated by the

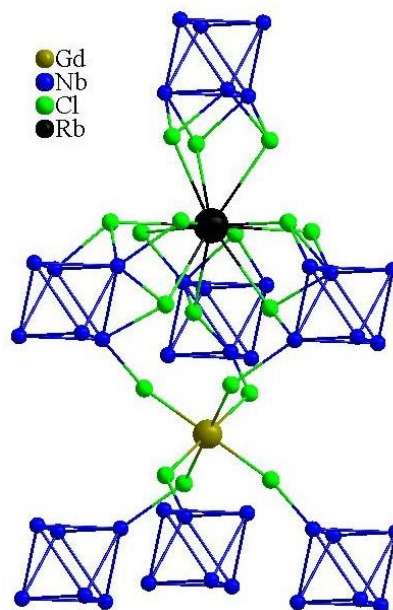


Figure 3. Rubidium and gadolinium environments. For clarity, Cl atoms coordinated to Rb and Gd are only represented

presence of only one rubidium atom per formula in RbGdNb₆Cl₁₈ instead of two cesium atoms in Cs₂PbNb₆Cl₁₈. Thus, the number of valence electrons as much as 16 per unit cluster can be maintained according to the magic number for valence electrons in the Nb₆Cl₁₈ unit.

The site occupied by alkaline atoms in two latter compounds is vacant in LuNb₆Cl₁₈ (Ihmaïne *et al.* 1988). Alkaline site in RbGdNb₆Cl₁₈ is very different from that in CsLuNb₆Cl₁₈ (Ihmaïne *et al.* 1989). The cesium site is built from six ligands in the Clⁱ and six Cl^a ligands from six adjacent clusters. The cesium atom is linked to twelve chlorine ligands so that it occupies an octahedral void between the cluster units. In fact, for all ARENb₆Cl₁₈ compounds (A = monovalent cation, and RE = trivalent rare earth metal cation), rare earth metals always have octahedral environments built from six ligands belonging to six different clusters.

In RbGdNb₆Cl₁₈, arrangement of cluster units corresponds to an approximately close packed cubic stacking. The octahedral Nb₆Cl₁₈ cluster unit layers are arranged successively according to ... ABCA ... as presented in Figure 4. Rubidium and gadolinium atoms spread out between the layers. This is very different from what is observed in CsLuNb₆Cl₁₈. In this case, the Nb₆Cl₁₈ cluster units are organized according to stacking ... AA'A In this arrangement, the cluster units in plane A' experience a slope of about 20° to the cluster units in plane A [(Ihmaïne *et al.* 1989). The cohesion of cluster units in the compound ARENb₆Cl₁₈ is highly dependent on the size of the alkaline cation (A) and is less influenced by the size of the rare earth metal (RE) ions (Ihmaïne *et al.* 1988; Perrin *et al.* 1995). The R structure type

will be generated if $A = K$ and Rb while the **P** structure type will be obtained when $A = Cs$.

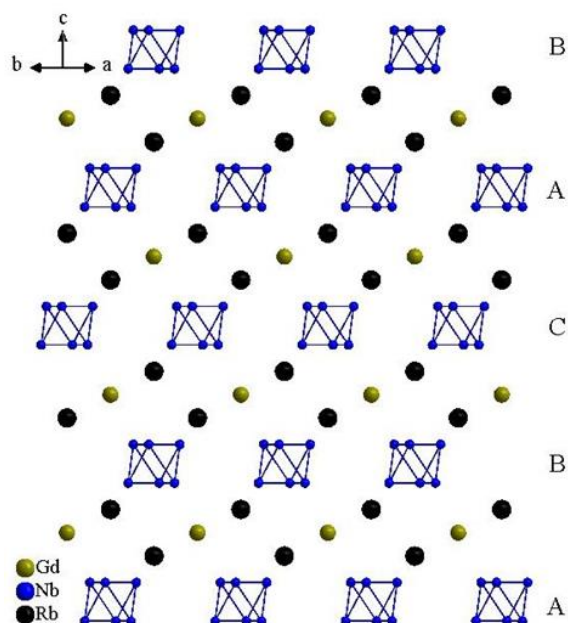


Figure 4. A view of the Nb_6 clusters, Gd^{3+} and Rb^+ in the hexagonal unit cell of $RbGdNb_6Cl_{18}$

The existence of discrete cluster units or the absence of intercluster connectivity in this compound $RbGdNb_6Cl_{18}$ is due to the equivalence of all niobium atoms. This has been observed in other halide compounds of the octahedral cluster of niobium. However, in the compounds Nb_6Cl_{14} (Simon *et al.* 1965) and $CsNb_6Cl_{12}O_2$ (Gulo & Perrin 2000), it appears that niobium atoms have unequal environments and ligands have different functions (bridging and non-bridging) leading to an anisotropic framework.

CONCLUSIONS

$RbGdNb_6Cl_{18}$ has been prepared by solid state routes. It crystallizes in a trigonal system with space group, $R-3$ in the **R** structure type. This compound contains the octahedral cluster of niobium atoms. The clusters are linked to each other via Rb^+ and Gd^{3+} cations.

CRYSTALLOGRAPHIC DETAILS

Crystal data collection and processing parameters of $RbGdNb_6Cl_{18}$ (CSD-2269483) are provided free of charge by The Cambridge Crystallographic Data Centre.

ACKNOWLEDGMENT

The authors wish to thank the Research Institute of Sriwijaya University for research fund and Dr. T. Roisnel, Centre de Diffractométrie de l'Université de Rennes 1, France for the data collection on the X-ray diffractometer.

REFERENCES

- Broll, A. & Schäfer, H. Dr. (1970). $Ba_2[Nb_6Cl_{12}]Cl_6$. *Journal of The Less Common Metals*. **22**: 367–368.
- Corbett, J. D. (2000). Exploratory synthesis in the solid state. Endless wonders. *Inorganic Chemistry*. **39**(23): 5178–5191.
- Cordier, S., Perrin, C. & Sergent, M. (1993). Crystallochemistry of some new niobium bromides with (Nb_6Br_{18}) units: Structures of $CsErNb_6Br_{18}$ and $Cs_2EuNb_6Br_{18}$. *Zeitschrift für anorganische und allgemeine Chemie*. **619**(4): 621–627.
- Duraisamy, T. & Lachgar, A. (2002). $K_2SrNb_6Cl_{18}$, dipotassium strontium hexaniobium octadecachloride. *Acta Crystallographica Section C: Crystal Structure Communications*. **58**(6): i85–i86.
- Duraisamy, T. & Lachgar, A. (2003). Potassium yttrium hexaniobium octadecachloride, $KYNb_6Cl_{18}$. *Acta Crystallographica Section C: Crystal Structure Communications*. **59**(4): i27–i28.
- Gulo, F., & Perrin, C. (2000). The crystal structure of $CsNb_6Cl_{12}O_2$, a novel niobium cluster oxychloride with interconnected $Nb_6Cl_{14}O_4$ units. *Journal of Materials Chemistry*. **10**(7): 1721–1724.
- Gulo, F., Cordier, S., & Perrin, C. (2001). Crystal structure of dicesium lead hexaniobium octadecachloride, $Cs_2PbNb_6Cl_{18}$. *Zeitschrift für Kristallographie-New Crystal Structures*. **216**(1-4): 197–198.
- Hiramatsu, T., Yoshida, Y., Saito, G., Otsuka, A., Yamochi, H., Shimizu, Y., Hattori, Y., Nakamura, Y., Kishida, H., Ito, H., Kirakci, K., Cordier, S. & Perrin, C. (2015). Spin frustration in antiperovskite systems: $(TTF^+ \text{ or } TSF^+)_3[(Mo_6X_{14})^{2-}Y^-]$. *Journal of Materials Chemistry C*. **3**(42): 11046–11054.
- Ihmaïne, S., Perrin, C. & Sergent, M. (1989). Structure of a new quaternary niobium chloride with Nb_6 clusters: $CsLuNb_6Cl_{18}$. *Acta Crystallographica Section C Crystal Structure Communications*. **45**(5): 705–707.
- Ihmaïne, S., Perrin, C., Peña, O. & Sergent, M. (1988). Structure and magnetic properties of two niobium chlorides with $[Nb_6Cl_{12}]^{n+}$ ($n = 2, 3$) units: $KLuNb_6Cl_{18}$ and $LuNb_6Cl_{18}$. *Journal of the Less Common Metals*. **137**(1-2): 323–332.
- Imoto, H., Corbett, J. D., & Cisar, A. (1981). Synthesis by hydrogen-driven disproportionation reactions. Synthesis and structure of the hexazirconium dodecahalide clusters Zr_6Cl_{12} and Zr_6Br_{12} and the double salt $Zr_6Cl_{12} \cdot M_2ZrCl_6$ ($M = \text{sodium, potassium, cesium}$). *Inorganic Chemistry*. **20**(1): 145–151.
- K. Brandenburg. (2014). DIAMOND: Structure and Molecular Structure Visualization (No. 3). CRYSTAL IMPACT GbR, Bonn, Germany.

- Naumov, N. G., Cordier, S. & Perrin, C. (2003). Synthesis and structures of new cyanide and thiocyanate complexes based on Nb₆Cl₁₂ cluster core: Cs₄[Nb₆Cl₁₂(CN)₆].H₂O, Cs₄[Nb₆Cl₁₂(NCS)₆] and the double salt (Me₄N)₄[Nb₆Cl₁₂(CN)₆]₂Me₄NCl.H₂O. *Solid State Sciences*. **5(10)**: 1359-1367.
- Nguyen, N. T. K., Lebastard, C., Wilmet, M., Dumait, N., Renaud, A., Cordier, S., Ohashi, N., Uchikoshi, T. & Grasset, F. (2022). A review on functional nanoarchitectonics nanocomposites based on octahedral metal atom clusters (Nb₆, Mo₆, Ta₆, W₆, Re₆): inorganic 0D and 2D powders and films. *Science and Technology of Advanced Materials*. **23(1)**: 547–578.
- Perrin, C., Cordier, S., Gulo, F. & Perrin, A. (2001). The octahedral cluster compounds of early transition metals: An original class of dielectric materials. *Ferroelectrics*. **254(1)**: 83-90.
- Perrin, C., Cordier, S., Ihmaine, S. & Sergent, M. (1995). Recent investigations on the (Me₆L₁₈)_n unit based halides and oxyhalides (Me = Nb, Ta and L = Cl, Br, O) with rare earths as counterions: Electronic and steric effects. *Journal of Alloys and Compounds*. **229(1)**: 123–133.
- Sägebarth, M. E., Simon, A., Imoto, H., Weppner, W. & Kliche, G. (1995). NaNb₆Cl₁₅ - Preparation, Structure, Ionic Conduction. *Zeitschrift für Anorganische und Allgemeine Chemie*. **621(9)**: 1589–1596.
- Shannon, R. D. (1976). Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica Section A*. **32(5)**: 751–767.
- Sheldrick, G. M. (2018a). SHELXL-2018/3: Program for Refinement of Crystal Structures. University of Göttingen, Germany.
- Sheldrick, G. M. (2018b). SHELXS-2018/3: Program for Solution of Crystal Structures. University of Göttingen, Germany.
- Simon, A., Georg Schnering, H., Wöhrle, H. & Schäfer, H. (1965). Beiträge zur Chemie der elemente niob und tantal. 44. Nb₆Cl₁₄ synthese, eigenschaften, struktur. *Zeitschrift für Anorganische und Allgemeine Chemie*. **339(3-4)**: 155-170.
- Simon, A., von Schnering, H. G. & Schäfer, H. (1968). Beiträge zur Chemie der Elemente Niob und Tantal. LXIX K₄Nb₆Cl₁₈ Darstellung, Eigenschaften und Struktur. *Zeitschrift für Anorganische und Allgemeine Chemie*, **361(5-6)**: 235-248.
- Zhang, J. & Corbett, J. D. (1993). Two families of centered zirconium cluster phases with M₁, 2M'Cl₆. Zr₆Cl₁₂Z compositions. *Inorganic Chemistry*. **32(9)**: 1566-1572.
- Zhang, J. J., Day, C. S. & Lachgar, A. (2011). Self-assembly and solvent-mediated structural transformation of one-dimensional cluster-based coordination polymer. *CrystEngComm*. **13(1)**: 133-137.
- Zhou, H., & Lachgar, A. (2007). Octahedral metal clusters [Nb₆Cl₁₂(CN)₆]⁴⁺ as molecular building blocks: from supramolecular assemblies to coordination polymers. *European Journal of Inorganic Chemistry*. **2007(8)**: 1053–1066.
- Zhou, H., Zhang, J. J. & Lachgar, A. (2011). Self-assembly of a new 1D coordination polymer built of [Nb₆Cl₁₂(CN)₆]⁴⁺ and Mn(III) complexes. *Journal of Chemical Crystallography*. **41(1)**: 73–76.