ICL 2020

# A new series of luminescent tetrakis $Ln^{3+}$-complexes with α-substituted β-diketonate ligands and $Na^{+}$ as countercation

Assunção, I.P.,[1,2*] Brito, H.F.,[1] Felinto, M.C.F.C.,[3]Teotônio, E.E.S.[4] and Malta, O.L.[5]

[1]*Department of Fundamental Chemistry, University of São Paulo, São Paulo, 05508-000, Brazil,* [2]*Education, Science and Technology Federal Institute of São Paulo, São Paulo, 01109-010, Brazil* [3]*Nuclear and Energy Research Institute-IPEN/CNEN, São Paulo, 05508-000, Brazil,* [4]*Department of Chemistry, Federal University of Paraíba, João Pessoa, 58051-970, Brazil,* [5]*Department of Fundamental Chemistry, Federal University of Pernambuco, Recife, 50670-901, Brazil*

**E-mail: ipassunc@iq.usp.br*

The $Ln^{3+}$ β-diketonate coordination compounds have received growing attention in the past few years, mainly due to their inherent huge variety of applications. The *tris* and *tetrakis* species have also been widely used as an emitting layer in organic light-emitting diodes (OLEDs) due to their high intensity and monochromatic emission. The *tetrakis* complexes usually present improved properties such as thermal and chemical stabilities, besides higher luminescence lifetimes than its correspondent *tris* complexes. Moreover, the commonly hydrated *tris* $Ln^{3+}$-complexes show a luminescence quenching due to vibronic coupling between $H_2O$ molecules and the $Ln^{3+}$ principal emitting levels (*e.g.*, $^4G_{5/2}$, $^5D_0$, $^5D_4$, $^4F_{9/2}$ and $^1G_4$ of the $Sm^{3+}$, $Eu^{3+}$, $Tb^{3+}$, $Dy^{3+}$ and $Tm^{3+}$ ions, respectively) [1]. The acetylacetone (2,4-pentanedione) ligand, Hacac, is one of the most extensively used and studied β-diketonate ligands, especially for the $Tb^{3+}$ ion. Nevertheless, the α-substituted $Ln^{3+}$ β-diketonate complexes are relatively scarce in the literature [2]. Hence, this work reports the synthesis, characterization, and photoluminescent study of a new series of *tetrakis* coordination compounds containing the α-substituted β-diketonates 3-chloro acetylacetone (Cl-acac), presenting the general formula $Na[Ln(Cl\text{-}acac)_4]$, where Ln: $Sm^{3+}$, $Eu^{3+}$, $Tb^{3+}$, $Dy^{3+}$, and $Tm^{3+}$.

All complexes were characterized by elemental analysis, complexometric titration, thermal analysis, infrared absorption spectroscopy (FTIR), and X-ray powder diffraction (XPD). The $Ln^{3+}$ complex photoluminescent properties (Figure 1) as well as the experimental intensity parameters ($\Omega_{2,4}$) of the $Eu^{3+}$ were determined.

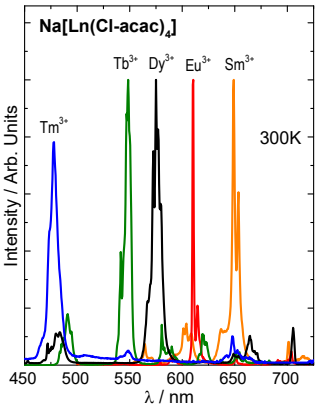


**Figure 1**. Emission spectra of the $Na[Ln(Cl\text{-}acac)_4]$ complexes, where Ln: $Sm^{3+}$ ($^4G_{5/2} \rightarrow {}^6H_{9/2}$), $Eu^{3+}$ ($^5D_0 \rightarrow {}^7F_2$), $Tb^{3+}$ ($^5D_4 \rightarrow {}^7F_5$), $Dy^{3+}$ ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) and $Tm^{3+}$ ($^1G_4 \rightarrow {}^3H_6$) recorded at 300 K.

## References

[1] Guedes, M.A., Paolini, T.B., Felinto, M.C.F.C., Kai, J., et al., *J. Lumin.* **131**, 99–103 (2011).
[2] Nolasco, M.M., Vaz, P.M., Vaz, P.D., Ferreira, R.A.S., et al. *J. Coord. Chem.* **67**, 4076–4089 (2014).