



Eclética Química

ISSN: 0100-4670

atadorno@iq.unesp.br

Universidade Estadual Paulista Júlio de  
Mesquita Filho  
Brasil

Ferenc, W.; Bernat, M.; Sarzynski, J.; Gluchowska, H.  
Complexes of 4-chlorophenoxyacetates of Nd(III), Gd(III) and Ho(III)  
Eclética Química, vol. 35, núm. 1, 2010, pp. 67-75  
Universidade Estadual Paulista Júlio de Mesquita Filho  
Araraquara, Brasil

Available in: <http://www.redalyc.org/articulo.oa?id=42913589008>

- How to cite
- Complete issue
- More information about this article
- Journal's homepage in redalyc.org

redalyc.org

Scientific Information System

Network of Scientific Journals from Latin America, the Caribbean, Spain and Portugal

Non-profit academic project, developed under the open access initiative

- [13] E. Dreassi, G.P. Corbini, M. Corti, Ulivelli, R. Rocchi, J. AOAC. Intl. 79: 6, ISSN 1060-3271 (1996) 1277.
- [14] N.F. Youssef, E.A. Taha, Chem. Pharm. Bull. 55 (2007) 4 541.
- [15] G-S. Elizabeth, S. Giannoutsos, D.R. Lower, M.A. Virji, M.D. Krasowski, J. Chromatogr. Sci. 45 (2007) 9 616.
- [16] Z.K. Shihabi, K.S. Oles, J. Chromatogr. B, Biomed Appl. 683 (1996) 119.
- [17] R. Theurillat, M. Kuhn, W. Thormann, J. Chromatogr. A. 979 (2002) 353.
- [18] R.A. Biddlecombe, K.L. Dean, C.D. Smith, S.C. Jeal, J. Pharm. Biomed. Anal. 8 (1990) 691.
- [19] J.M. Sailstad, J.W.A. Findlay, Ther. Drug. Monit., 13 (1991) 433.
- [20] R.S. Talekar, A.S.Dhake, D.B. Sonaje, V.K. Mourya, Ind. J. Pharm. Sci. 62 (2000) 51.
- [21] D-R. Olga, M.E Calvo, M. Acros-Martinez, J., Sensors. 8 (2008) 4201; DOI:10.3390/s8074201
- [22] N. Rahman, S.N. Hejaz-Azmi, J. Pharm. Biomed. Anal. 24 (2000) 33.
- [23] N. Silva, E.E.S. Schapoval, J. Pharm. Biomed. Anal. 29 (2002) 749.
- [24] T. Perez-Ruiz, C. Martinez-Lozano, V. Tomás, A. Sanz, E. Sauquillo, J. Pharm. Biomed. Anal. 26 (2001) 609.
- [25] K. Basavaiah, V.S. Charan, IL Farmaco. 57 (2002) 9.
- [26] H. Maghsoudi, A. Fawzi, J. Pharm. Sci. 67 (1978) 32.
- [27] H. Farsam, H.H. Yahya-saeb, A. Fawzy, Int. J. Pharm. 7 (1981) 343.
- [28] A.S. Douglas, M.W. Donald. "Principels of Instrumental Analysis," Holt, Rinhart. and Winston, New York, 1971.pp. 104.
- [29] N. Erk. Anal. Lett. 36 (2003) 1183.
- [30] H. Zavis, D. Ludvik, K. Milan, S. Ladislav, V. Frantisek, Handbook of Organic Reagents in Inorganic Analysis. Translated by Stanislav, K, Dr. Chalmers (The Series and Translation Editor: University of Aberdem, Ellis Horwood Limited, Chichester, A Division of John Wiley & Sons IC, New York, London, Sydney, Toronto.1976. pp.364.
- [31] International Conference on Harmonisation of Technical Requirements for Registration of Pharmaceuticals for Human Use, ICH Harmonised Tripartite Guideline, Validation of Analytical Procedures: Text and Methodology Q2(R 1),Complementary Guideline on Methodology dated 06 November 1996, incorporated in November 2005, London.
- [32] J. Inczedy, T. Lengyel, A.M. Ure, IUPAC Compendium of Analytical Nomenclature : 1998. Definitive Rules, Blackwell Science Inc., Boston.

Ni(II) ions were synthesized and their properties were studied [10,16,17].

As a continuation of our studies on chlorophenoxyacetates and also on carboxylates [10,18-30] we decided to synthesized 4-chlorophenoxyacetates with Nd(III), Gd(III) and Ho(III) and to study some of those of their properties not to have been investigated so far, such as magnetic properties in the range of 76-303K, thermal stability in air at 293-1173K, solubility in water at 293K and to record their FTIR spectra.

Thermal stability investigations give informations about the process of dehydration about the ways of decompositions, and the magnetic susceptibility measurements let study the kinds of the manner of central ion coordination. The determination of the solubility is valuable because it informs about the practical use of acid for separation of transition metal ions by extraction or ion-exchange chromatographic methods.

**Table 1.** Elemental analysis data of Nd(III), Gd(III) and Ho(III) 4-chlorophenoxyacetates and their solubility in water at 293K.

Complex L- = C <sub>8</sub> H <sub>6</sub> ClO <sub>3</sub>	H/%		C/%		Cl/%		M/%		Solubility mol·dm <sup>-3</sup>
	calcd	found	calcd	found	calcd	found	calcd	found	
NdL <sub>3</sub> ·2H <sub>2</sub> O	3.00	2.77	39.10	38.96	14.50	14.48	19.60	22.70	5,3 · 10 <sup>-4</sup>
GdL <sub>3</sub> ·2H <sub>2</sub> O	2.90	2.79	38.40	38.94	14.20	14.18	20.90	19.50	7,6 · 10 <sup>-4</sup>
HoL <sub>3</sub> ·3H <sub>2</sub> O	3.10	2.88	37.10	37.16	14.10	14.08	21.80	21.20	8,5 · 10 <sup>-4</sup>

The contents of M<sup>3+</sup> were established gravimetrically and by XRF method using spectrometer of X-ray fluorescence with energy dispersion EDXRF-1510 (CANBERRA firm).

The IR and FIR spectra of complexes were recorded over the ranges 4000-400cm<sup>-1</sup> and 600-100cm<sup>-1</sup>, respectively, using M-80 and Perkin-Elmer 180 spectrometers. Samples for IR spectra measurements were prepared as KBr discs. FIR spectra were obtained in Nujol mulls sandwiched between polyethylene plates (Table 2).

The FTIR spectra of the intermediate and final products obtained from the complex thermal decompositions were also registered.

## Experimental details

The 4-chlorophenoxyacetates of Nd(III), Gd(III) and Ho(III) were prepared by the addition of the equivalent quantities of 0,1mol·dm<sup>-3</sup> ammonium 4-chlorophenoxyacetate (pH ≈ 5) to a hot solutions containing the 0,1 mol·dm<sup>-3</sup> Nd(III), Gd(III) and Ho(III) nitrates (V) and crystallizing at 293K (1h). The solids formed were filtered off, washed with hot water and methanol to remove ammonium ions and dried at 303K to a constant mass.

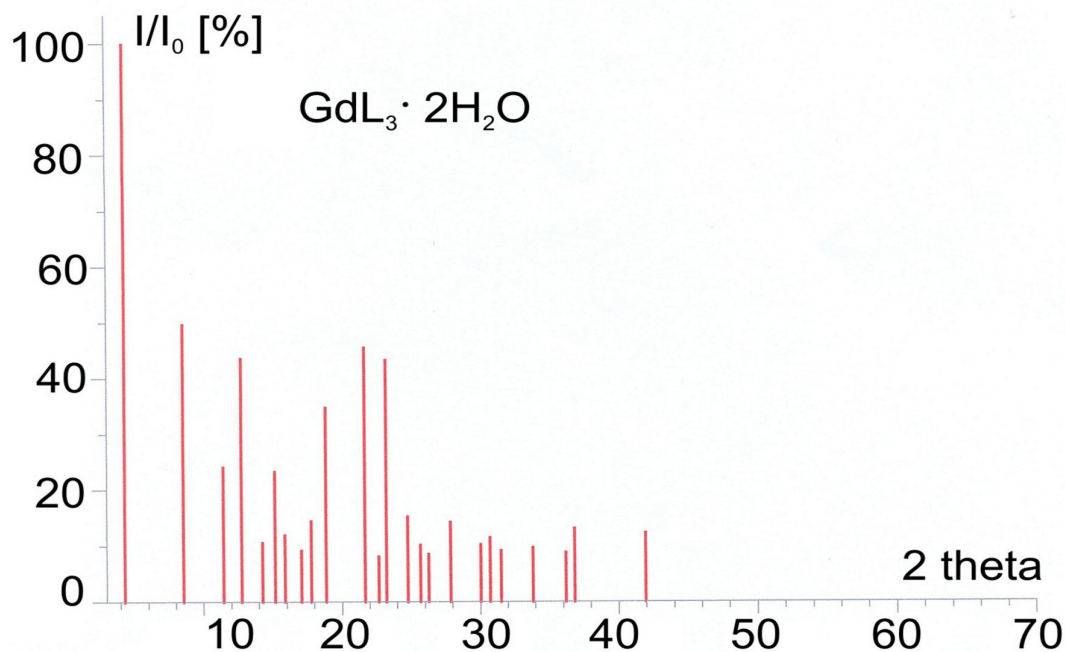
The contents of carbon and hydrogen in the complexes and in the intermediate and final products obtained from their thermal decompositions were determined by elemental analysis using a CHN 2500 Perkin-Elmer analyzer and the content of chlorine by the Schöniger method (Table 1).

were calculated from TG curves and verified by the diffraction pattern registration and IR spectra. The thermogravimetric analysis of DSC/TG was performed at temperature 323-723K using a differential thermoanalyzer Netzsch STA 409C 3F. The measurements were carried out under nitrogen flow (99,995% purity) and temperature increase rates of 1-12K min<sup>-1</sup>.

**Table 3.** Temperature ranges of thermal stability of Nd(III), Gd(III) and Ho(III) 4-chlorophenoxyacetates in air.

Complex L = C <sub>8</sub> H <sub>6</sub> ClO <sub>3</sub>	$\Delta T_1/K$	Mass loss/%		n H <sub>2</sub> O	$\Delta T_2/K$	Mass loss/%		Intermediate product	$\Delta H/kJ \cdot mol^{-1}$	$\Delta H_{1H_2O}/kJ \cdot mol^{-1}$	TK/K	Mass of residue/%		Final product of decomposition
		calcd.	found			calcd.	found					calcd.	found	
NdL <sub>3</sub> ·2H <sub>2</sub> O	338-416	4,34	4,88	2	553- 873	73,45	72,14	NdOCl	90,8	45,4	1273	22,80	~23,3	Nd <sub>2</sub> O <sub>3</sub>
GdL <sub>3</sub> ·2H <sub>2</sub> O	316-412	4,27	4,81	2	573- 923	72,18	71,42	GdOCl	136,5	68,3	1270	24,30	~24,0	Gd <sub>2</sub> O <sub>3</sub>
HoL <sub>3</sub> ·3H <sub>2</sub> O	312-425	6,96	6,68	3	573- 912	70,20	68,22	HoOCl	156,8	52,3	1223	24,27	24,3	Ho <sub>2</sub> O <sub>3</sub>

$\Delta T_1$  – temperature range of dehydration process,  $\Delta T_2$  – temperature range of anhydrous complex decomposition, n – number of water molecules lost in the one step of dehydration process,  $\Delta H$  – enthalpy value of dehydration process,  $T_K$  – final temperature of decomposition process,  $\Delta H_{1H_2O}$  – enthalpy value for one molecule of water,  $T_K$  – final temperature of decomposition process



**Fig. 2.** TG,DTG and DTA curves for Ho(III) 4-chlorophenoxyacetate in air

white for Gd(III) complexes. In these compounds the  $f \rightarrow f$  electron transitions of the central ions are those of the lowest energy and absorption occurs at relatively high wave lengths that depends on the nature of the metal ion [33,34].

The compounds were characterized by elemental analysis (Table 1), FTIR and FIR spectra (Table 2).

The 4-chlorophenoxyacetates of Nd(III), Gd(III) and Ho(III) exhibit similar solid state IR spectra. The band at  $1708\text{ cm}^{-1}$  originating from the RCOOH group, presented in the acid spectrum, is replaced in the spectra of complexes by two bands at  $1572\text{--}1567\text{ cm}^{-1}$  and  $1346\text{--}1328\text{ cm}^{-1}$ , which can be ascribed to the asymmetric and symmetric vibrations of  $\text{COO}^-$  group, respectively [35-38].

The bands with the maxima at  $3429\text{--}3410\text{ cm}^{-1}$  characteristic for  $\nu_{\text{OH}}$  vibrations [35-40] confirm the presence of crystallization water molecules in the complexes.

The bands of C-H vibrations are observed at  $2929\text{--}2918\text{ cm}^{-1}$ . The bands of  $\nu(\text{C}=\text{C})$  ring vibrations appear at  $1624\text{--}1622\text{ cm}^{-1}$ ,  $1494\text{ cm}^{-1}$ ,  $1177\text{--}1174\text{ cm}^{-1}$ ,  $1111\text{--}1104\text{ cm}^{-1}$  and  $1068\text{--}1066\text{ cm}^{-1}$ . The valency  $\nu(\text{C-Cl})$  vibration bands occur at  $734\text{--}730\text{ cm}^{-1}$  and those of the asymmetric and symmetric  $\nu(\text{C-O-C})$  at  $1082\text{--}1068\text{ cm}^{-1}$  and  $1060\text{--}1058\text{ cm}^{-1}$ , respectively. The bands at  $451\text{--}449\text{ cm}^{-1}$  confirm the ionic metal-oxygen bond [41-50]. These bands change insignificantly their positions which may suggest the different stability of these complexes.

The bands in the range of  $118\text{--}106\text{ cm}^{-1}$  are connected with the O-H...O stretching vibrations and they change their shapes according to the rise of atomic number of elements and the degree of hydration in 4-chlorophenoxyacetates. The bands at  $138\text{--}122\text{ cm}^{-1}$  confirm the internal C-C torsion vibrations and the bands at  $283\text{--}267\text{ cm}^{-1}$  arising from the aromatic ring vibrations also change their shapes.

Table 2 presents the values of the two band frequencies of asymmetrical and symmetrical vibrations for carboxylate group of analysed complexes.

The separations of the  $\nu_{\text{as}}(\text{COO}^-)$ , and  $\nu_{\text{s}}(\text{COO}^-)$  modes in the compounds,  $\Delta\nu(\text{COO}^-)$ , are smaller than that of the sodium salt ( $\Delta\nu_{\text{COO}^-} =$

$271\text{ cm}^{-1}$ ) indicating a smaller degree of M-O ionic bonds in 4-chlorophenoxyacetates compared to that of the sodium salt. For the complexes the shifts of the frequencies of bands of  $\nu_{\text{as}}(\text{COO}^-)$ , and  $\nu_{\text{s}}(\text{COO}^-)$  are lower, and lower or the same, respectively, than those for sodium 4-chlorophenoxyacetate. Accordingly, taking into account the spectroscopic criteria [36-38,49,51] the carboxylate ions appear to be bidentate groups.

In order to estimate the crystalline forms of the 4-chlorophenoxyacetates the X-ray powder diffraction measurements were done. The diffractogram values suggest them to be polycrystalline compounds with various degree of crystallinity [52] (Fig.1)

The thermal stability of Nd(III), Gd(III) and Ho(III) 4-chlorophenoxyacetates was studied in air at  $293\text{--}1273\text{ K}$  (Table 3, Fig.2).

When heated to  $1273\text{ K}$  the Nd(III) complex is dehydrated in one step. In the temperature range of  $338\text{--}416\text{ K}$  it losses two water molecules and forms anhydrous salt. The loss of mass calculated from TG curve is equal to  $4,88\%$  (theoretical value is  $4,34\%$ ). The anhydrous salt at  $553\text{--}1273\text{ K}$  is gradually decomposed to  $\text{Nd}_2\text{O}_3$  that is the final product of complex decomposition. The intermediate compound formed in this range of  $553\text{--}873\text{ K}$  is  $\text{NdOCl}$ . The found mass loss is equal to  $72,14\%$  and the calculated value  $73,45\%$ . The residue mass estimated from TG curve is equal to  $23,27\%$  while that theoretically calculated  $22,80\%$ . The dehydration process is connected with endothermic effect whereas the combustion of the organic ligand is accompanied by exothermic one. The final product of complex decomposition was confirmed by IR spectra and X-ray powder diffractogram.

The dihydrate of Gd(III) 4-chlorophenoxyacetate during heating in air losses the water molecules in one stage in the range of  $316\text{--}412\text{ K}$  and forms anhydrous salt. The final product of complex decomposition was identified by elemental analysis and X-ray powder diffractogram as  $\text{Gd}_2\text{O}_3$ . The intermediate product of complex decomposition is  $\text{GdOCl}$  formed at  $573\text{--}923\text{ K}$ . The found weight loss is equal to  $71,42$  and calculated one  $72,18\%$ . The residue mass estimated from TG curve is  $24,0\%$  and theoretically determined  $24,30\%$ . The dehydration process is connected

following: 3,74  $\mu_B$  for Nd; 7,23  $\mu_B$  for Gd and 10,60  $\mu_B$  for Ho [63].

From the values of magnetic moments determined for the complexes it appears that energies of 4f electrons in the central ions are not changed compared to those in the free lanthanide ions. Thus, the colours of the complexes stay the same as those in the free lanthanide ions. The electron density in the molecules makes the f-f electronic transitions of the central ions to be those of the lowest energy and the absorption occurs at relatively high wavelengths. The 4f orbitals of lanthanide ions effectively shielded by the 5s<sup>2</sup>5p<sup>6</sup> octet. Therefore the metal ligand bonding in lanthanide complexes is mainly electrostatic in nature [64,65].

## Conclusions

On the basis of the results obtained it appears that 4-chlorophenoxyacetates of Nd (III), Gd(III), and Ho(III) were synthesized as hydrated complexes. Their colours are typical for the particular Ln(III) ion, i.e. violet for Nd, white for Gd, and cream for Ho, having their origin in the lowest energy of f-f electronic transitions of the central ions. Their energies are not radically changed in comparison with the free lanthanide ions, therefore the colours of the complexes are the same as those for the free lanthanide ions. The Ln-O band is mainly electrostatic in nature. The complexes are crystalline compounds that on heating in air to 1173K decompose in three steps. In the first step they dehydrate to form anhydrous complexes that next decompose to the oxides of appropriate metals with intermediate formation of LnOCl. The values of  $\mu_{\text{eff}}$  calculated for the compounds are close to those obtained for Ln<sup>3+</sup> by Hund and Van Vleck. There is no influence of the ligand field of 4f electrons on lanthanide ions.

The solubilities of Nd(III), Gd(III) and Ho(III) 4-chlorophenoxyacetates in water at 293K are of the order of 10<sup>-4</sup>mol·dm<sup>-3</sup>.

## References

- [1] S.C. Mojumdar, D. Hudecova, and M. Melnik, *Pol. J. Chem.*, 73 (1999)759
- [2] M. McCann, J.F. Cronin, and M. Devereux, *Polyhedron*, 17(1955)2379
- [3] C.N. Rao, and S. Natarajan, *Angew. Chem. Int. Ed.*, 43(2004)1446
- [4] E.V. Dikarev, R.G. Gray, and B.Li, *Angew. Chem. Int. Ed.*, 44(2005) 1721
- [5] L.Lewellyn, Jim – Ho Lee, Jong-San Chang, and G. Ferey, *Angew. Chem. Int. Ed.*, 45 (2006) 8227
- [6] C.J. Kepert, T.J. Prior, and M.J. Rosseinsky, *J. Sol. State Chem.*, 152 (2000) 261
- [7] Y. Kim, and D.Y. Yung, *Inorg. Chim. Acta*, 338(2002)229
- [8] Y. Bao-Hui, T. Ming-Liang, and Xiao-Ming Chem., *Kord. Chem. Rev.*, 249(2005)545
- [9] E.G. Palacios, and A.J. Monchemius, *Hydrometallurgy*, 62(2001)135
- [10] W.Ferenc, M.Bernat, J. Sarzyński, and B. Paszkowska, *Ecl.Quim.*, São Paulo, 33(1): 7-14, 2008
- [11] Beilstein Handbuch der Organischen Chemie, Bd. VI/2, Springer Verlag, Berlin 1942
- [12] Franklin and Jones, American Chemical Paint Co, U.S. 2.390, 941, Dec. 11.1945
- [13] K.N. Goswami, Z. Krist., 121(5), (1965), 400
- [14] Kennard, Colin H.L., Smith, Graham, and White Allan.H., *Acta Crystallogr.*, Sect.B 1981, B37(6), 1317-19
- [15] S.Kumar, Vijay, and Rao Leela M., *Acta Crystallogr.*, Sect. B. 1982 B 38(7), 2062
- [16] Denis, Janes C. Ramband Jerome, and Ger Offen. 1.906,199, 11 Sept. 1969, Fr. Appl. 16 Feb. 1968
- [17] G. Plesch, M. Blahova, J. Kratsmar-Smogrovic, and S. Surka, *Z. Naturforsch.*, B, 28, 1973, 521
- [18] W.Ferenc, A.Walków-Dziewulska, and S. Kuberski, *Chem. Pap.*, 57(5) (2003) 321-330
- [19] W.Ferenc, and B. Bocian, *J. Them. Anal. Cal.*, 74(2003) 521
- [20] W.Ferenc, A.Walków-Dziewulska, and J. Sarzyński, *J.Serb.Chem.Soc.*, 70(2005) 1075
- [21] W.Ferenc, B. Cristóvão, and J. Sarzyński, *J. Them. Anal. Cal.*, 86(2006) 783
- [22] W.Ferenc, A.Walków-Dziewulska, and J. Sarzyński, *Ecl. Quim.*, São Paulo, 31(2) (2006) 17
- [23] W.Ferenc, A.Walków-Dziewulska, J. Sarzyński, and B. Paszkowska, *Ecl. Quim.*, São Paulo, 31(3) (2006) 7
- [24] W.Ferenc, A.Walków-Dziewulska, J. Sarzyński, B. Paszkowska, *Ecl.Quim.*, São Paulo, 31(4) (2006) 53
- [25] K. Stepniak, W.Ferenc, B. Bocian, and T. Lis, *Ecl. Quim.*, São Paulo, 32(3) (2007) 23
- [26] W.Ferenc, A.Walków-Dziewulska, J. Sarzyński, and B. Paszkowska, *J. Therm. Anal. Cal.*, 91 (2008) 285
- [27] W.Ferenc, B. Cristóvão, J. Sarzyński, and B. Paszkowska, *Ecl. Quim.*, São Paulo, 31(4) (2006) 7