Polyhedron 28 (2009) 457-460

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Copper(II) and lanthanoid(III) complexes of a new β -diketonate ligand with an appended non-coordinating phenol group

Stefania Tanase^{a,*}, Marta Viciano-Chumillas^a, Jan M.M. Smits^b, René de Gelder^b, Jan Reedijk^a

^a Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA, Leiden, The Netherlands
^b Radboud University Nijmegen, Institute for Molecules and Materials, Heyendaalseweg 135, 6525 AJ, Nijmegen, The Netherlands

ARTICLE INFO

Article history: Received 10 October 2008 Accepted 16 November 2008 Available online 26 December 2008

Keywords: Copper(II) Lanthanoid(III) β-Diketone Crystal structure

ABSTRACT

New mononuclear compounds of the ligand 1-(2-hydroxyphenyl)-3-phenylpropane-1,3-dione (H₂L) with Cu(II) and several lanthanoid(III) ions, where Ln(III) = Pr, Nd, Eu, Gd, have been synthesized and characterized by spectroscopic methods and X-ray crystal structure determinations. In all compounds, the ligand coordinates in a bidentate chelating manner, using the diketone function. In the [Cu(HL)₂], the coordination geometry of Cu(II) ion is slightly distorted square-planar; two strong intramolecular (OH···O) hydrogen-bonding interactions are established between the phenolate group and the neighboring ketone function. The lanthanoid(III) compounds have the general formula [Ln(HL)₃(CH₃OH)₂] · CH₃OH · 2H₂O; the lanthanoid(III) ion (Ln) is eight-coordinated and the coordination geometry is based on a distorted square-antiprism. In addition to the intramolecular hydrogen bonding (OH··O), intermolecular hydrogen-bonding interactions are also present between the coordinated methanol molecule and the non-coordinated methanol molecule giving rise to a three-dimensional network.

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

The construction of molecular assemblies through the coordination of a metal ion with polydentate organic ligands has become a fascinating area of interest in inorganic chemistry. Particularly, coordination compounds of β -diketone ligands have attracted considerable attention due to their often supramolecular architectures and their peculiar optical or magnetic properties [1]. Transitionmetal complexes based on various analogues of acetylacetone have been largely studied and most of the examples reported so far belong to the category of cluster compounds [1]. Considerably fewer examples of compounds with extended networks have been isolated [1–5]. The coordination ability of β -diketone ligands towards lanthanoid(III) ions has been studied and representative examples of the formation of highly coordinated complexes are the lanthanoid(III) tris-(β-diketonates) containing several nitrogen ligands such as 2,2'-bipyridine, and 1,10-phenanthroline or their derivatives [6-8]. In this work, we report the synthesis, spectroscopic characterization and X-ray crystal structure determination of new Cu(II) and lanthanoid(III) complexes with the ligand 1-(2hydroxyphenyl)-3-phenylpropane-1,3-dione (H₂L). The ligand was selected because of its potential dual binding modes, namely coordination and hydrogen-bond donor, or bridging coordination.

Corresponding author.

E-mail address: s.grecea@chem.leidenuniv.nl (S. Tanase).

2. Experimental

2.1. General remarks

Starting materials were purchased from Aldrich and all manipulations were performed using materials as received. The ligand 1-(2-hydroxyphenyl)-3-phenylpropane-1,3-dione (H₂L) was synthesized according to the procedure reported previously for similar ligands [9].

2.2. Synthesis

[Cu(HL)₂] (**1**). A solution of Cu(NO₃)₃ · 3H₂O (0.3 mmol) in 10 ml methanol was added to a solution of the ligand H₂L (0.6 mmol) and triethylamine (0.6 mmol) in 10 ml methanol. Slow evaporation of the resulting solution afforded green single crystals within one day. After filtration, the crystalline material was washed with diethyl ether and dried in air. C₃₀H₂₂CuO₆, **1** (*M* = 542.04 g/mol). Yield: 52% (85 mg). El. Anal. (%): calc. 66.48 C, 4.45 H; exp. 66.98 C, 4.41 H. IR (ν_{max}/cm^{-1}): 2992 (w), 1616 (m), 1584 (m), 1536 (s), 1517 (s), 1481 (s), 1455 (s), 1430 (m), 1389 (s), 1343 (m), 1309 (s), 1243 (m), 1201 (m), 1160 (w), 1137 (m), 1104 (w), 1056 (m), 1020 (m), 941 (m), 845 (m), 806 (w), 787(m), 764 (m), 749 (m), 728 (s), 702 (s), 686 (s), 580 (m), 563 (s), 526 (m) UV–Vis (λ /nm): 270, 365, 415, 620.

2.2.1. Synthesis of the compounds $[Ln(HL)_3(CH_3OH)_2] \cdot CH_3OH \cdot 2H_2O$

A solution of $Ln(NO_3)_3 \cdot 6H_2O$ (0.24 mmol) in 10 ml methanol was added to a solution of the ligand H_2L (0.72 mmol) and trieth-





^{0277-5387/\$ -} see front matter @ 2008 Elsevier Ltd. All rights reserved. doi:10.1016/j.poly.2008.11.025

ylamine (0.72 mmol) in 10 ml methanol. Slow evaporation of the resulting solution afforded yellow crystalline material in a few hours. After filtration, the crystalline material was washed with diethyl ether and dried in air.

 $C_{48}H_{49}O_{12}Pr$, **2** (*M* = 990.81 g/mol). Yield: 60% (137 mg). El. Anal. (%): calc. 58.19 C, 4.98 H; exp. 58.71 C, 4.57 H. IR ($v_{max}/$ cm⁻¹): 3344 (br), 2988 (m), 2858 (m), 1590 (m), 1544 (m), 1509 (s), 1461 (m), 1394 (m), 1343 (m), 1291 (s), 1199 (m), 1138 (m), 1069 (m), 1023 (m), 937 (m), 842 (m), 755 (m), 711 (m), 676 (w), 622 (s), 516 (m). UV–Vis (λ /nm): 270, 345, 410, 485, 608.

 $C_{48}H_{49}O_{12}Nd$, **3** (*M* = 994.32 g/mol). Yield: 61% (145 mg). El. Anal. (%): calc. 57.98 C, 4.97 H; exp. 58.06 C, 4.57 H. IR ($\nu_{max}/$ cm⁻¹): 3346 (br), 2988 (m), 2858 (m), 1590 (m), 1544 (m), 1506 (s), 1462 (m), 1397 (m), 1343 (m), 1291 (s), 1199 (m), 1138 (m), 1066 (m), 1023 (m), 937 (m), 842 (m), 754 (m), 711 (m), 676 (w), 623 (s), 516 (m). UV–Vis (λ /nm): 270, 346, 409, 520, 537, 586, 752, 810, 900.

 $C_{48}H_{49}O_{12}Eu,~\textbf{4}~(\textit{M}=1001.86~g/mol).$ Yield: 85% (210 mg). El. Anal. (%): calc. 57.55 C, 4.93 H; exp. 57.25 C, 4.17 H. IR ($\nu_{max}/$ cm $^{-1}$): 3360 (br), 2988 (m), 2858 (m), 1589 (m), 1542 (m), 1508 (s), 1457 (m), 1394 (m), 1339 (m), 1286 (s), 1198 (m), 1137 (m), 1066 (m), 1023 (m), 937 (m), 841 (m), 753 (m), 710 (m), 676 (w), 622 (s), 516 (m). UV–Vis (λ/nm): 270, 348, 408.

 $C_{48}H_{49}O_{12}Gd,~{\bf 5}~({\it M}$ = 1007.15 g/mol). Yield: 72% (175 mg). El. Anal. (%): calc. 57.24 C, 4.90 H; exp. 57.07 C, 4.51 H. IR ($\nu_{max}/$ cm $^{-1}$): 3360 (br), 2988 (m), 2858 (m), 1590 (m), 1547 (m), 1510 (s), 1461 (m), 1398 (m), 1334 (m), 1286 (s), 1198 (m), 1137 (m), 1066 (m), 1023 (m), 937 (m), 842 (m), 753 (m), 711 (m), 677 (w), 623 (s), 514 (m). UV–Vis (λ /nm): 270, 350, 405.

2.3. Physical measurements

C, H, and N analyses were performed with a Perkin–Elmer 2400 series II analyzer. Infrared spectra (4000–300 cm⁻¹, resol. 4 cm⁻¹) were recorded on a Perkin–Elmer Paragon 1000 FTIR spectrometer equipped with a Golden Gate ATR device, using the reflectance technique. Diffuse reflectance spectra were obtained on a Perkin–Elmer Lambda 900 spectrophotometer using MgO as a reference. X-band powder EPR spectra were obtained on a Bruker-EMX*plus* electron spin resonance spectrometer (Field calibrated with DPPH (*g* = 2.0036)).

2.4. X-ray crystallography

Intensity data for a single crystal of **1** and **4a** were collected using Mo K α radiation ($\lambda = 0.71073$ Å) on a Nonius Kappa CCD diffractometer. Crystal data for **1** and **4a** are collected in Table 1. The intensity data were corrected for Lorentz and polarization effects, for absorption (multiscan absorption correction) and extinction. The structures were solved by Patterson methods. The programs SABABS [10], DIRDIF96 [11] and SHELXL-97 [12] were used for data reduction, structure solution and structure refinement, respectively. Refinement of F^2 was done against all reflections. The weighted *R* factor, *wR*, and goodness of fit S are based on F^2 . Conventional R factors are based on *F*, with *F* set to zero for negative F^2 . All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed at calculated positions and were refined riding on the parent atoms. Geometric calculations and molecular graphics were performed with the PLATON package [13].

3. Results and discussions

3.1. Synthesis and characterization of the complex [Cu(HL)₂]

Complex 1 is easily obtained by the reaction of hydrated Cu(II) nitrate with triethylamine and the β -diketone ligand H₂L (1:2:2

ratio) using methanol as solvent. The infrared spectrum of **1** shows the vibration characteristic of the organic ligand; the most important feature that indicates the coordination of the β -diketone ligand to the Cu(II) ion, is the shift of the $v_C=_0$ stretching vibration of the carbonyl group to lower energy, *ca.* 1616 cm⁻¹ as compared with the free ligand (at 1657 cm⁻¹). The ligand field spectrum, measured as a solid with the diffuse reflectance technique, shows a broad band at 620 nm which is ascribed to the d-d transitions of the Cu(II) ion and a Cu–O charge transfer band at 415 nm.

The molecular structure of **1** consists of a centrosymmetric mononuclear unit in which the Cu(II) ion is coordinated by two bidentate chelating HL⁻ ligands that use the diketonate function for coordination to the metal center (Fig. 1). Schematic geometric information is given in Table 2. The coordination geometry of Cu(II) ion is slightly distorted square–planar. The Cu–O bond lengths of 1.889(3) Å and 1.896(4) Å, respectively are normal and comparable with the similar distances in other Cu(II) complexes with β -diketonate ligands [14–18]. The in-plane O–Cu–O angle differs slightly from 90°, being 87.03(15)°. As shown in Fig. 1, the molecular structure is stabilized by two strong intramolecular hydrogen-bonding interactions established between the phenol group and the neighboring coordinating ketonate function (O5…O1 = 2.5038 Å; O5–H5…O1 = 144°). A view of the crystal packing of **1** is shown in Fig. 2; the shortest intermolecular Cu…Cu distance is 5.838 Å.

The X-band spectrum of the complex **1** as a powder, recorded at room temperature (Fig. 3), is slightly anisotropic with a *g* value of 2.05 and a g_{\parallel} value of 2.25. No hyperfine splitting is resolved. This might be due to some exchange interactions leading to exchange narrowing, in view of the rather short intermolecular Cu…Cu distance indicated by the X-ray crystal structure.

3.2. Synthesis and characterization of the compounds of formula

3.2.1. [Ln(HL)₃(CH₃OH)₂] · CH₃OH · 2H₂O

The reaction of the hydrated lanthanoid(III) nitrates with the ligand H_2L in the presence of triethylamine as base (1:3:3 molar ratio) and using methanol as solvent afforded yellow crystalline materials. The analytical studies have shown that these compounds have the general formula $[Ln(HL)_3(CH_3OH)_2] \cdot CH_3OH$. An X-ray crystallographic study has been performed for the complex $[Ln(HL)_3(CH_3OH)_2] \cdot CH_3OH$ (**4a**) and its crystal structure is described below. The crystallinity of the complexes

Fig. 1. View of the molecular structure of **1** showing the intramolecular hydrogen bonds. Hydrogen atoms not involved in hydrogen bonding were omitted for clarity.





Fig. 2. View of the crystal packing of **1** in the *ac* plane. Hydrogen atoms were omitted for clarity. Cu···Cu contacts are 5.838 Å.

Table 1Crystallographic data for compounds 1 and 4a.

	1	4a
Formula	C ₃₀ H ₂₂ CuO ₆	C48H45O12Eu
Formula weight	542.02	965.80
Crystal system	Monoclinic	Triclinic
Space group	C2/c	ΡĪ
a (Å)	26.511(3)	12.5036(19)
b (Å)	5.8379(3)	13.9203(15)
c (Å)	16.475(2)	14.406(2)
α (°)	90	67.418(12)
β (°)	114.997(10)	85.335(16)
γ (°)	90	67.022(9)
$V(Å^3)$	2311.1(4)	2124.5(6)
Ζ	4	2
$D_{\text{calc}} (\text{mg m}^{-3})$	1.564	1.510
μ (Mo- α) (mm ⁻¹)	0.992	1.541
T (K)	208	208
Data collected	15011	46359
Unique data	2006	9667
R _{int}	0.0317	0.0424
$R(F) \left[I > 2\sigma(I) \right]$	0.0686	0.0450
$R_w(F^2)$	0.1877	0.0934
S	1.101	1.120
$\Delta ho_{ m min}$, $\Delta ho_{ m max}$ (e Å ⁻³)	-0.43; 2.33	-0.53, 1.76



Fig. 3. Room temperature EPR spectrum of complex 1.

Table	2			
	_			

Selected bond lengths (Å) and angles (°) for compounds ${\bf 1}$ and ${\bf 4a}.$

Complex 1			
Cu1-01	1.889(3)	01-Cu1-O3	92.97(15)
Cu1-03	1.896(4)		
Cu⊷Cu	5.838		
Complex 4a			
Eu1–O1a	2.334(3)	O1a-Eu1-O1b	76.17(10)
Eu1–O1b	2.335(3)	O1a-Eu1-O1c	139.98(10)
Eu1–O1c	2.319(3)	01a-Eu1-03a	71.90(9)
Eu1–O3a	2.396(3)	O1a-Eu1-O3b	106.77(10)
Eu1–O3b	2.359(3)	01a-Eu1-03c	146.77(10)
Eu1–O3c	2.347(3)	01a-Eu1-021	76.15(11)
Eu1-021	2.477(3)	01a-Eu1-023	81.96(12)
Eu1-023	2.447(3)	01c-Eu1-01c	143.49(10)
		O1b-Eu1-O3a	138.49(10)
		O1b-Eu1-O3b	70.76(9)
		O1b-Eu1-O3c	76.80(10)
		01b-Eu1-021	121.30(9)

 $[Ln(HL)_3(CH_3OH)_2] \cdot CH_3OH$ is partly lost upon removing the crystals from the mother liquid and the elemental analysis and spectroscopic studies suggest that these compounds all have the general formula $[Ln(HL)_3(CH_3OH)_2] \cdot CH_3OH \cdot 2H_2O$ (Ln = Pr **2**, Nd **3**, Eu **4**, Gd **5**).

The IR spectra of compounds **2–5** are nearly identical, in agreement with the fact that these compounds are isostructural. The binding of the β -diketone ligand to the lanthanoid(III) ions is indicated by the shift of the $v_{C=0}$ stretching vibration of the carbonyl group to lower energy, *ca.* 1590 cm⁻¹ as compared with the free ligand at 1657 cm⁻¹. The broad band in the range 3200–3400 cm⁻¹ is characteristic to the v_{O-H} stretching vibrations of the lattice water molecules.

The UV–Vis absorption spectrum of the ligand shows characteristic bands at 267, 345 and 425 nm. In the UV range, the spectral features observed for compounds **2–5** are similar to those observed for the corresponding ligand. In the visible range, compounds **2** and **3** display the characteristic bands due to the f–f transitions. Roomtemperature excitation in the UV absorption bands ($\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$) of the free ligand does not result in lanthanoid emission in these complexes. This result points to the presence of efficient non-radiative deactivation pathways in all compounds, which is due to the presence of lattice water molecules. Nevertheless, a weak ligand emission was observed at $\lambda_{em} = 545$ nm ($\lambda_{exc} =$ 275 nm).

The crystal structure of 4a consists of a mononuclear Eu(III)containing molecule, [Eu(HL)₃(CH₃OH)₂] and a lattice methanol molecule. As shown in Fig. 4, the Eu(III) ion is eight-coordinated by three monodeprotonated ligands (HL⁻) and two methanol molecules. The coordination geometry of Eu(III) is based on distorted square-antiprism; the two bases are identical and they are formed by two oxygen atoms of the same bidentate ligand, an oxygen atom of a second HL⁻ ligand and an oxygen atom from a methanol molecule. Selected bond lengths and angles are listed in Table 2. The Eu–O bond lengths are in the range 2.320(4)–2.479(3) Å, with the Eu-O bond lengths involving the methanol molecules being the longest. The average of the C–O bond length of the β -diketone group is ca. 1.269 Å, much shorter than the corresponding bond in other lanthanoid(III) complexes with β -diketone ligands. This short distance suggests a lower π -electron delocalization of the C=O bond [19].

The molecular structure is stabilized by multiple intra- and intermolecular $O-H\cdots O$ hydrogen-bonding interactions (Fig. 5, Table 3). Three intramolecular hydrogen bonds are established between the phenolic group and the neighboring oxygen of the diketonate function. Additionally, the phenolic group of the ligand is also involved in a hydrogen bond with one of the coordinated



4. Conclusions

The reaction of a new β -diketonate ligand, 1-(2-hydroxyphenyl)-3-phenylpropane-1,3-dione, with Cu(II) and Ln(III) ions does result in the formation of mononuclear complexes. In all compounds, the ligand is coordinated in a bidentate chelating manner, using the diketone function for coordination to the metal center, and stabilization of the chromophore by strong intramolecular hydrogen bonding (OH···O). The preparation of the compounds reported in this paper offers promising prospects in the direction of heterobimetallic polynuclear compounds. We are currently exploring the coordination chemistry of the 1-(2-hydroxyphenyl)-3-phenylpropane-1,3-dione ligand with other metals.

Supplementary data

CCDC 705139 - 705140 contains the supplementary crystallographic data for the compounds **1** and **4a**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgments

This research was financially supported by a Veni grant from the Netherlands Organization for Scientific Research (NWO) to S. T. and the ECNetwork of Excellence "MAGMANet" (No. 515767-2).

References

- [1] G. Aromi, P. Gamez, J. Reedijk, Coord. Chem. Rev. 252 (2008) 964.
- [2] J.K. Clegg, K. Gloe, M.J. Hayter, O. Kataeva, L.F. Lindoy, B. Moubaraki, J.C. McMurtrie, K.S. Murray, D. Schilter, Dalton Trans. (2006) 3977.
- [3] J.K. Clegg, L.F. Lindoy, J.C. McMurtrie, D. Schilter, Dalton Trans. (2005) 857.
 [4] D.V. Soldatov, A.S. Zanina, G.D. Enright, C.I. Ratcliffe, J.A. Ripmeester, Cryst. Growth Des. 3 (2003) 1005.
- [5] Y.S. Zhang, S.R. Breeze, S.N. Wang, J.E. Greedan, N.P. Raju, LJ. Li, Can. J. Chem. 77 (1999) 1424.
- [6] A. Bellusci, G. Barberio, A. Crispini, M. Ghedini, M. La Deda, D. Pucci, Inorg. Chem. 44 (2005) 1818.
- [7] P.N. Remya, S. Biju, M.L.P. Reddy, A.H. Cowley, M. Findlater, Inorg. Chem. 47 (2008) 7396.
- [8] A.P. Vigato, V. Peruzzo, T. Tamburini, Coord. Chem. Rev., in press, doi:10.1016/ j.ccr.2008.07.013.
- [9] T.S. Wheeler, Org. Synth. 32 (1952) 72.
- [10] G.M. Sheldrick, SADABS, Program for Empirical Absorption Correction, University of Göttingen, Germany, 1996.
- [11] P.T. Beurskens, G. Beurskens, R. de Gelder, S. García-Granda, R.O. Gould, R. Israël, J.M.M. Smits, The DIRDIF Programme, Report on the Crystallography Laboratory, University of Nijmegen, Nijmegen, The Netherlands, 1996.
- [12] G.M. Sheldrick, SHELXL97. Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.
- [13] A.L. Spek, PLATON, a Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 2003.
- [14] A.M. Madalan, M. Noltemeyer, M. Neculai, H.W. Roesky, M. Schmidtmann, A. Muller, Y. Journaux, M. Andruh, Inorg. Chim. Acta 359 (2006) 459.
- [15] G. Aromi, C. Boldron, P. Gamez, O. Roubeau, H. Kooijman, A.L. Spek, H. Stoeckli-Evans, J. Ribas, J. Reedijk, Dalton Trans. (2004) 3586.
- [16] G. Aromi, J. Ribas, P. Gamez, O. Roubeau, H. Kooijman, A.L. Spek, S. Teat, E. MacLean, H. Stoeckli-Evans, J. Reedijk, Chem. Eur. J. 10 (2004) 6476.
- [17] A.M. Madalan, V.C. Kravtsov, D. Pajic, K. Zadro, Y.A. Simonov, N. Stanica, L. Ouahab, J. Lipkowski, M. Andruh, Inorg. Chim. Acta 357 (2004) 4151.
- [18] G. Aromi, P. Gamez, O. Roubeau, H. Kooijman, A.L. Spek, W.L. Driessen, J. Reedijk, Angew. Chem., Int. Ed. 41 (2002) 1168.
- [19] A. Mech, Polyhedron 27 (2008) 393.

Fig. 4. View of the molecular structure of 2. The non-coordinated methanol molecule and hydrogen atoms were omitted for clarity.

Eu1

O5h

O3c

O5c

023

010

03:

O5a

Fig. 5. View of the hydrogen bonding interactions in 2.

Details of the hydrogen bonding interactions in 4a.

D–H	H···A	D···A	D−H···A
0.83	1.76	2.489(5)	146.1
0.83	1.75	2.489(4)	146.9
0.83	1.76	2.495(4)	146.5
0.94	1.89	2.711(4)	144.4
0.94	1.83	2.673(6)	147.3
0.83	1.98	2.789(6)	163.3
	D-H 0.83 0.83 0.83 0.94 0.94 0.83	D−H H…A 0.83 1.76 0.83 1.75 0.83 1.76 0.94 1.89 0.94 1.83 0.83 1.98	D-H H···A D···A 0.83 1.76 2.489(5) 0.83 1.75 2.489(4) 0.83 1.76 2.495(4) 0.94 1.89 2.711(4) 0.94 1.83 2.673(6) 0.83 1.98 2.789(6)

