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SYNTHESIS AND X-RAY STRUCTURE OF THE DYSPROSIUM(III) COMPLEX DERIVED FROM THE LIGAND 5-CHLORO-1,3-DIFORMYL-2-HYDROXYBENZENE-BIS-(2-HYDROXYBENZOYLHYDRAZONE) $[Dy_2(C_{22}H_{16}ClN_4O_5)_3](SCN)_3.(H_2O).(CH_3OH)$

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ABSTRACT. The title compound $[Dy_2(C_{22}H_{16}ClN_4O_5)_3](SCN)_3(H_2O)(CH_3OH)$ has been synthesized and its crystal structure determined by single X-ray diffraction at room temperature. The two nine coordinated Dy(III) are bound to three macromolecules ligand through the phenolic oxygens of the *p*-chlorophenol moieties, the nitrogen atoms and the carbonyl functions of the hydrazonic moieties. The phenolic oxygen atoms of the 2-hydroxybenzoyl groups are not bonded to the metal ions. In the bases of the coordination polyhedra the six Dy-N bonds are in the range 2.563(13)-2.656(13) Å and the twelve Dy-O bonds are in the range 2.281(10)-2.406(10) Å.

KEY WORDS: Dysprosium(III) complex, 5-Chloro-1,3-diformyl-2-hydroxybenzene-bis-(2-hydroxybenzoylhydrazone), Crystal structure

INTRODUCTION

Schiff's base compounds find applications in many fields. Particularly they show excellent potential for preparation of new optical and magnetic materials [1].

This work forms a part of a study of lanthanide complexes with hydrazone ligands which present donors atoms suitable for coordinating two or more lanthanide(III) ions linked together through an atom of oxygen acting as a bridge. In this case the O atom influences the magnetic exchange interaction between the two lanthanide ions. The 5-chloro-1,3-diformyl-2-hydroxybenzene-bis-(2-hydroxybenzoylhydrazone) possesses potential nitrogen and oxygen donors. The abundance of the potential donor atoms present in the ligand suggested that it could act as an aggressive coordinator on lanthanide ions to yield stable complexes of different types. Further, the two hydroxy groups lying at the ortho-position of the benzoylhydrazone moieties may affect stoichiometry and nature of the complexes. In view of these facts, reaction of dysprosium thiocyanate has been carried out and the structure of the resulting complex was investigated using spectroscopic techniques and X-ray diffraction. The results of these studies are described in the present paper.

EXPERIMENTAL

General. The compounds $Ln(NO_3)_3.mH_2O$ were obtained from Aldrich and were used without purification. The salicylaldehydehydrazide, ethanol and methanol were obtained from Jansen and were used without further purification. The 2,6-diformyl-4-chlorophenol was synthesized by the method described in the literature and recrystallized from n-hexane/chloroform [2]. The

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magnetic measurement was carried out at room temperature with a Gouy balance and $CuSO_4$ was used as a calibrant. The molar conductance measurement was made using a WTW LF-330 conductivity meter with a WTW conductivity cell on a 1 mmol dm^{-3} DMF solution at room temperature. The IR spectra of the compounds were recorded from Nujol mulls on a Perkin Elmer 580 B FTIR spectrophotometer using CsF windows or KBr pellets in the range 4000-400 cm^{-1}. ^1H and ^{13}C NMR spectra were recorded on a Bruker AM 300 spectrometer operated at 300 and 75 MHz, respectively, with Me_4Si as internal standard in DMSO-d_6 solution. The ^{13}C NMR assignments were made by polarization transfer using DEPT sequences. The mass spectra were obtained on a VG Micromass 16 F spectrometer. Elemental analyses were obtained from the Microanalytical Service of the University of Padova (Italy).

Synthesis of 5-chloro-1,3-diformyl-2-hydroxybenzene-bis-(2-hydroxybenzoylhydrazone) (H_5L). 2,6-Diformyl-4-chlorophenol (10.8 mmol) and salicylaldehydehydrazide (21.7 mmol) were dissolved in 30 mL of ethanol and two drops of glacial acetic acid were added. The mixture was then refluxed for two hours. Upon cooling, a yellowish precipitate was obtained. The product was isolated by filtration, washed with 2 x 10 mL of ether and dried at room temperature over P_4O_{10}. The compound crystallized with two molecule of water. Yield 4.38 g; 83%. Anal. calc. for $C_{22}H_{21}ClN_4O_7$: C, 54.05; H, 4.33; N, 11.46%. Found: C, 54.36; H, 4.58; N, 11.25%.

Synthesis of $[Dy_2(C_{22}H_{16}ClN_4O_5)_3](SCN)_3(H_2O)(CH_3OH)$. Dysprosium(III) thiocyanate (1 mmol) in 95% ethanol (20 mL) and 5-chloro-1,3-diformyl-2-hydroxybenzene, bis(2-hydroxybenzoylhydrazone) (1.5 mmol) in 95% ethanol (80 mL) were refluxed for 2 h. The resulting yellow solution was filtered and the filtrate kept at 298 K. Yellow crystals began to appear after one day and were collected by filtration. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a methanolic solution of the complex. Yield 413 mg; 43.4%. Anal. calc. for $C_{70}H_{54}Cl_3N_{15}O_{17}S_3Dy_2$: C, 44.49; H, 2.83; N, 10.38%. Found: C, 43.83; H, 2.77; N, 11.11%.

Structure determination. The crystal data and details of collection are given in Table 1. Data from yellow needle (0.15 x 0.18 x 0.25 mm) were collected on a CAD4 diffractometer, using graphite crystal-monochromated Mo-Kα radiation and were corrected for Lorenz, polarization and absorption effects. The structure was solved by the heavy atom method by use of the SHELXS-86 program [3] and refined by full-matrix least squares with the SHELXL-97 program [4]. All the H-atoms are located from the difference Fourier map and refined.

Table 1. Crystal and structure refinement data of the complex.

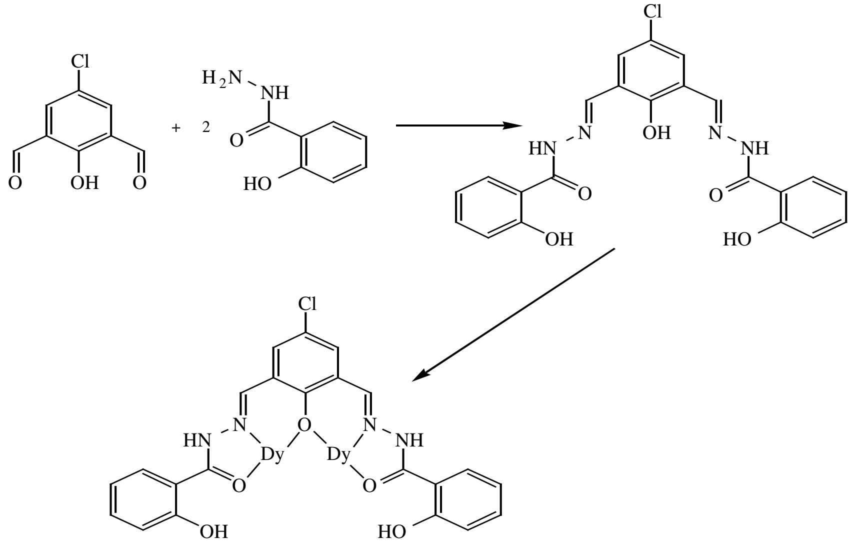
Chemical formula	$C_{70}H_{54}Cl_3N_{15}O_{17}S_3Dy_2$		
Formula weight	1904.8	ρ (calc.) (g cm^{-3})	1.613
Crystal system	Monoclinic	μ (mm^{-1})	1.037
Space group	$P2_1/n$	$2\theta_{max}$ (°)	40
a (Å)	13.501(3)	No. of reflexions	7447
b (Å)	22.777(5)	No. of parameters	989
c (Å)	24.729(4)	Crystal dimension (mm)	0.15 x 0.18 x 0.25
β (°)	93.71(2)	h; k; l range	0→12; 0 →21; -23→ 23
V ($Å^3$)	7589(3)	Unique reflexions, R_{int}	7053; 0.036
Z	4	R^a_1, wR^b_2	0.072; 0.182
Temperature	293(2)	Goof	1.263
λ Mo Kα (Å)	0.71073	CCDC	210087

$^aR_1 = \sum\|F_0| - |F_c\|/\sum|F_0|$; $^bR_w = [\sum w(|F_0^2| - |F_c^2|)^2/\sum w(|F_0^2|^2]^{1/2}$; $w = 1/[\sigma^2(F_0^2) + (0.0890\ P)^2 + 47.11P]$, where $P = \{Max(F_0^2, 0)+2F_c^2\}/3$.

RESULTS AND DISCUSSIONS

Formation of the complex

The dysprosium complex was readily made by reaction of $Dy(SCN)_3$ with the macroacyclic 5-chloro-1,3-diformyl-2-hydroxybenzene-bis-(2-hydroxybenzoyl hydrazone) in a 2:3 ratio in ethanol at reflux. The color change upon addition of the ethanolic solution of the $Dy(SCN)_3$ indicated the coordination of the Dy(III) to the N_2O_3 metal-binding sites of the macroacyclic ligand (Scheme 1). No precipitation of the product was observed during reflux. After filtration, the product was isolated by slow evaporation of a methanolic solution.



Scheme 1. Two molecules of the ligand are removed in the structure of the complex for clarity.

Characterization and spectroscopic studies

The hydrazone exhibits signals at δ 7.6-8 (H_{Ar}, 10H), 8.6 (HC=N-, 2H), 9.30 (-NH-, 2H), 12.2 (HO-, 2H) and 12.6 (HO-, 1H) in the ^1H NMR spectrum and at δ 164.3 (C=O), 155.5 (C=N), 145.9 (C_{Ar}), 133 (C_{Ar}), 132.1 (C_{Ar}), 129 (C_{Ar}), 127 (C_{Ar}), 124.1 (C_{Ar}), 122.3 (C_{Ar}) in the ^{13}C NMR spectrum. The signals at δ 8.6 and the signals at δ 164.3 and 155.5 indicate the formation of the Schiff base. The FAB mass spectrum of the ligand gave a parent peak at *m/z* 453 corresponding to $[C_{22}H_{17}ClN_4O_5]^+$.

Possible coordination sites are phenol-oxygens (three), azomethine nitrogens (two) and amido nitrogens (two). The infrared spectra of the ligand and the complex suggest, however, that the ligand is pentadentate with two carbonyl-oxygen, one 4-chlorophenol oxygen and two azomethine coordination sites.

The infrared spectrum of the ligand was devoid of absorptions characteristic of the NH_2 function. A strong band *ca.* 1635 cm^{-1} is assigned to the ν(C=O) vibration. The strong band due to the ν(C=N) vibration is at 1614 cm^{-1}. The N-H stretching bands occur at 3290 and 3220 cm^{-1}. The broad band of medium intensity occurring in the range 3500-3400 cm^{-1} is due to the O-H stretching vibration of the phenolic OH groups.

Upon coordination, the band due to N-H stretching in the free ligand remains unaffected precluding the possibility of coordination through the amido oxygen in its amide form. A considerable lowering of the ν(C=O) frequency is observed in the spectrum of the complex, indicating a decrease in the stretching force constant of the C=O bond as a consequence of the coordination of the oxygen atom to the metal ion. This band appears at *ca*. 1615 cm^{-1}. The important band at 1614 cm^{-1} in the free ligand attributed to ν(C=N) is shifted to lower frequencies and appears at 1595 cm^{-1} in the spectrum of the complex. This fact assumes the involvement of the nitrogen atom of the azomethine moiety in the coordination [5].

The bands at 3500-3400 cm^{-1} are slightly affected upon coordination. The assignment of these bands as phenolic ν(OH) is frustrated by the presence of three phenolic groups in the ligand. In the region 410-480 cm^{-1} there is an intensive band characteristic of the ν(Dy-O) vibration of the phenolic oxygen. In the far infrared spectra of the complex bands in the region 280-240 cm^{-1} can be assigned to ν(Dy-N) vibrations.

The room temperature magnetic moment (21.9 μ_B) of the new dinuclear complex $[Dy_2(H_4L)_3](SCN)_3(H_2O)(CH_3OH)$ shows little deviation from the Van Vleck [6] value, indicating the non participation of the 4f electrons in bonding.

The molar conductance of this complex was measured 216.9 $ohm^{-1}cm^2mol^{-1}$ at room temperature. The recorded value is comparable with those usually found for 1:3 electrolytes [7] indicating that the three SCN^- anions are not coordinated to the dysprosium(III) ion in solution. The above information together with the analytical data led to the formulation of the complex as $[Dy_2(C_{22}H_{16}ClN_4O_5)_3](SCN)_3.(H_2O).(CH_3OH)$.

Crystal structure of $[Dy_2(C_{22}H_{16}ClN_4O_5)_3](SCN)_3 .(H_2O).(CH_3OH)$

The acyclic nature of the dinuclear complex $[Dy_2(C_{22}H_{16}ClN_4O_5)_3](SCN)_3.(H_2O).(CH_3OH)$ is confirmed by X-ray structure analysis. The molecular structure is presented in the Figure 1 with bonds and angle presented in Table 2. The monodeprotonated ligand/metal stoichiometry of the complex formed is 3:2 and the three counter ions SCN^- are non-bonding. The ligand is pentadentate with one of the phenolato oxygen atom acting as a bridge between the two Dy(III) ions. Each molecule of the ligand is linked to one Dy(III) atom via one N atom and two O atoms. Thus each metal ion is nine coordinate, the bonding being provided by three N atoms and six O atoms from the ligand. The two phenolic oxygens in each ligand molecule are not coordinated. The triple bridge of phenolate oxygens holding the two dysprosium atoms defines closed loops which are far from planar, as visualized by the dihedral angles between the least-squares planes defined by O1-Dy1-O6 and O1-Dy2-O6, 49.06(4)°; O1-Dy1-O11 and O1-Dy2-O11, 46.22(4)°; O6-Dy1-O11 and O6-Dy2-O11, 44.97(4)°. These phenoxo bridges lead a Dy·····Dy distances of 3.539(2) Å. All the Dy-O bond lengths are in the range 2.281(10)-2.406(10) Å. The Dy-O bonds to the phenolic O atoms, which act as bridge, are significantly shorter than the other bond from the metal to the O atom of the hydrazonic moieties. All the Dy-N bond lengths are in the range 2.563(13)-2.656(13) Å. Structurally characterized nine coordinate dysprosium complexes are well known. In the structure of $[Dy(C_{23}H_{29}N_3O_5)(H_2O)_4]Cl_3.(H_2O)$ [8] the Dy-O distances are in the range 2.250(1)-2.640(1) Å and are comparable to those found for the title complex. In the $[Dy_2(H_4L)_3](SCN)_3(H_2O)(CH_3OH)$ complex the bond lengths of $Dy\text{-}O_{carbonyl}$ are longer (2.357 Å) than those for $Dy\text{-}O_{phenolic}$ for which the average value is 2.333 Å. The coordination polyhedron around each Dy atom can be described as a distorted tricapped trigonal prism in which (e.g. for Dy2) O1, O6 and O11 are the caps as shown in Figure 2. Distortions from idealized geometry arise from geometrical constraints due to the rigid structure induced by the three bridges between the two Dy atoms.

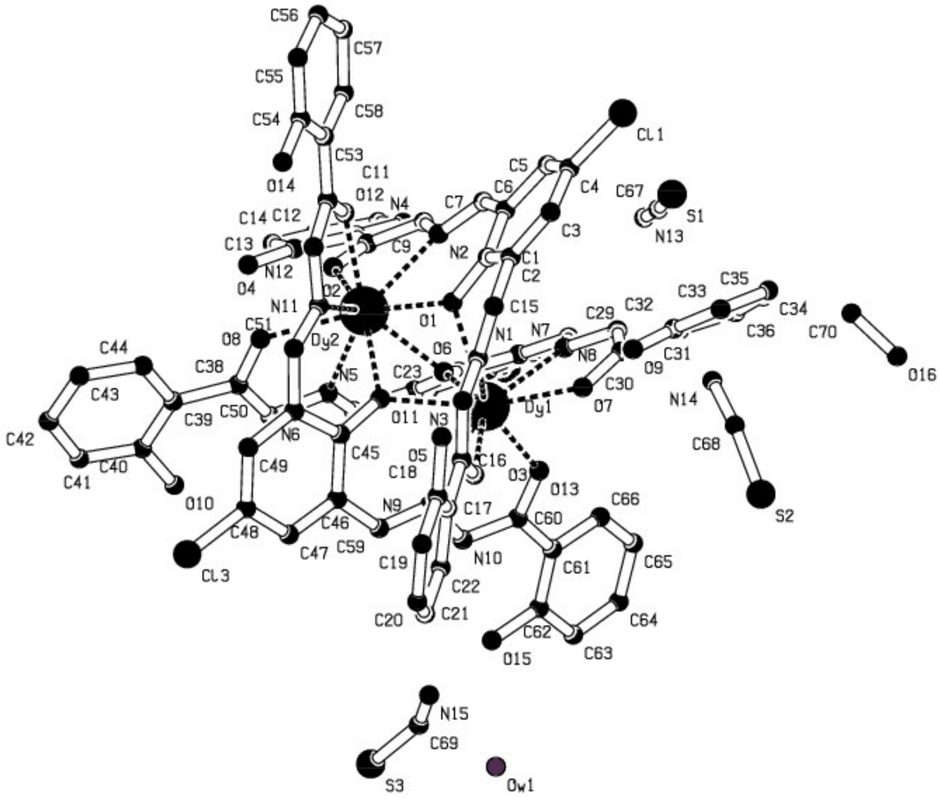
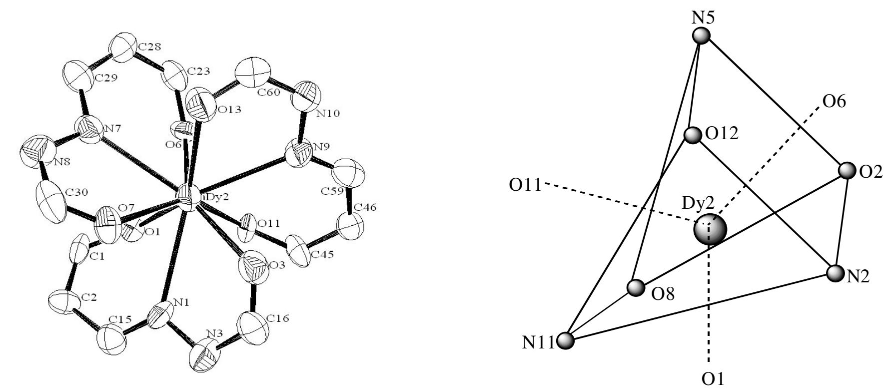


Figure 1. The crystal structure of $[Dy_2(C_{22}H_{16}ClN_4O_5)_3](SCN)_3.(H_2O).(CH_3OH)$.



(a) (b)

Figure 2. (a) Coordination polyhedron around each Dy center; (b) coordination polyhedron around Dy described as a distorted tricapped trigonal prism.

Table 2. Selected geometric parameters (Å, °).

Dy1—O1	2.406(10)	O13—Dy1—O1	139.0(3)	O1—Dy2—O8	148.0(4)
Dy1—O6	2.281(10)	O3—Dy1—O1	121.5(3)	O11—Dy2—O8	86.0(4)
Dy1—O11	2.313(10)	O7—Dy1—O1	94.0(3)	O2—Dy2—O8	79.5(5)
Dy1—O13	2.359(10)	O6—Dy1—N9	80.0(4)	O12—Dy2—O8	93.5(4)
Dy1—O3	2.359(11)	O11—Dy1—N9	68.0(4)	O1—Dy2—O6	68.0(3)
Dy1—O7	2.375(10)	O13—Dy1—N9	63.0(4)	O11—Dy2—O6	68.5(3)
Dy1—N9	2.578(12)	O3—Dy1—N9	70.0(4)	O2—Dy2—O6	96.0(4)
Dy1—N7	2.625(13)	O7—Dy1—N9	133.0(4)	O12—Dy2—O6	142.0(3)
Dy1—N1	2.656(13)	O1—Dy1—N9	132.0(4)	O8—Dy2—O6	123.5(4)
Dy2—O1	2.281(10)	O6—Dy1—N7	67.5(4)	O1—Dy2—N11	81.0(4)
Dy2—O6	2.391(9)	O11—Dy1—N7	133.0(4)	O11—Dy2—N11	66.0(4)
Dy2—O11	2.328(10)	O13—Dy1—N7	66.5(4)	O2—Dy2—N11	131.0(5)
Dy2—O12	2.344(11)	O3—Dy1—N7	143.0(4)	O12—Dy2—N11	63.0(4)
Dy2—O2	2.344(15)	O7—Dy1—N7	62.0(4)	O8—Dy2—N11	69.0(4)
Dy2—O8	2.359(11)	O1—Dy1—N7	76.0(3)	O6—Dy2—N11	131.0(4)
Dy2—N11	2.563(13)	N9—Dy1—N7	123.0(4)	O1—Dy2—N2	68.0(4)
Dy2—N2	2.578(14)	O6—Dy1—N1	129.0(4)	O11—Dy2—N2	132.0(4)
Dy2—N5	2.625(13)	O11—Dy1—N1	79.5(4)	O2—Dy2—N2	62.75(50)
O6—Dy1—O11	71.0(3)	O13—Dy1—N1	146.0(4)	O12—Dy2—N2	71.0(4)
O6—Dy1—O13	81.5(3)	O3—Dy1—N1	62.5(4)	O8—Dy2—N2	140.0(4)
O11—Dy1—O13	127.0(4)	O7—Dy1—N1	67.0(4)	O6—Dy2—N2	75.0(4)
O6—Dy1—O3	145.0(3)	O1—Dy1—N1	63.25(40)	N11—Dy2—N2	127.0(4)
O11—Dy1—O3	82.0(4)	N9—Dy1—N1	125.0(4)	O1—Dy2—N5	131.0(4)
O13—Dy1—O3	98.5(4)	N7—Dy1—N1	111.0(4)	O11—Dy2—N5	80.0(4)
O6—Dy1—O7	129.0(4)	O1—Dy2—O11	70.0(3)	O2—Dy2—N5	68.0(4)
O11—Dy1—O7	147.0(3)	O1—Dy2—O2	131.0(4)	O12—Dy2—N5	144.0(4)
O13—Dy1—O7	84.0(4)	O11—Dy2—O2	148.0(4)	O8—Dy2—N5	61.5(4)
O3—Dy1—O7	84.0(4)	O1—Dy2—O12	83.5(4)	O6—Dy2—N5	65.0(4)
O6—Dy1—O1	67.5(3)	O11—Dy2—O12	125.5(4)	N11—Dy2—N5	121.5(4)
O11—Dy1—O1	68.0(3)	O2—Dy2—O12	83.5(4)	N2—Dy2—N5	110.5(4)
Dy1—O1—Dy2	98.0(5)	Dy1—O6—Dy2	98.2(5)	Dy1—O11—Dy2	98.7(5)

REFERENCES

1. Guerriero, P.; Vigato, P.A.; Bünzli, J.C.G.; Moret, E. *J. Chem. Soc. Dalton Trans.* **1990**, 647.
2. Gaye, M.; Sall, A.S.; Sarr, O.; Russo, U.; Vidali, M. *Polyhedron* **1995**, 4, 655.
3. Sheldrick, G.M.; Kruger, C.; Goddard, R. *SHELXS-86*, *A direct methods program for crystal structure determination*, in *Crystallographic Computing*, Vol. 3, Oxford University Press: Oxford; pp; 175-189.
4. Sheldrick, G.M. *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen: Germany; **1997**.
5. Singh, B.; Sahai, P.; Singh, P.K. *Synth. Teact. Inorg. Met.-Org. Chem.* **1998**, 28, 685.
6. Van Vleck, J.H.; Frank, A. *Phys. Rev.* **1929**, 34,1625.
7. Geary, W.J. *Coord. Chem. Rev.* **1971**, 7, 81.
8. Casellato, U.; Tamburini, S.; Tomasin, P.; Vigato, P.A.; Aime, S.; Botta, M. *Inorg. Chem.* **1999**, 38, 2906.