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SYNTHESIS AND CRYSTAL STRUCTURE OF THE DINUCLEAR COMPLEX OF 1,5-BIS(1′-PHENYL-3′-METHYL-5′-PYRAZOLONE-4′)-1,5-PENTANEDIONE WITH SAMARIUM

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Abstract—The dinuclear complexes of 1,5-bis(1′-phenyl-3′-methyl-5′-pyrazolone-4′)-1,5-pentanedione (H_2L) with samarium, $Sm_2L_3 \cdot 7H_2O$ (**1**) and $Sm_2L_3 \cdot 5DMF$ (**2**), have been synthesized. The X-ray crystal structure of $Sm_2L_3 \cdot 5DMF$ has been determined. In complex **2**, each L bonds two samarium atoms with its two β-diketonate groups. The L acts as a bridging ligand. There are two DMF molecules bonded to each samarium atom. The coordination number of the two samarium atoms is eight (six oxygen atoms from three β-diketonates and the other two oxygen atoms from two DMF carbonyls). The eight atoms around the samarium make up a distorted square antiprism configuration. There are large differences between coordinated and uncoordinated DMF molecules.

The 1-phenyl-3-methyl-4-acetyl-pyrazolone derivative is well known as a β-diketone type chelating ligand coordinating to metal ions with oxygen atoms as "hard" Lewis base.[1] 4-Acetyl-bis-pyrazolones are a new type of chelating ligand which have two β-diketone donor sites in their molecules.[2] They are expected to form specific complexes. The coordination compounds of bis-pyrazolones with lanthanides have strong fluorescence[3,4] and high herbicidal activities.[5] To our knowledge, no crystal structures of bis-pyrazolone-containing complexes have been reported in the literature. Recently, we were successful in the synthesis and structural characterization of the complexes of the lanthanides with tetraketone ligands. In this paper we report the first crystal structure of a bis-pyrazolone-containing complex, the crystal structure of the dinuclear complex of samarium(III) with 1,5-bis(1′-phenyl-3′-methyl-5′-pyrazolone-4′)-1,5-pentanedione (H_2L).[6]

EXPERIMENTAL

Synthesis of $Sm_2L_3 \cdot 7H_2O$

Aqueous NaOH solution (2 mmol) was added slowly to a suitable ethanol solution containing 1 mmol H_2L with stirring giving a clear light yellow solution. $Sm(NO_3)_3$ aqueous solution (2 mmol, about 0.2 M) was added slowly to the above solution with magnetic stirring at room temperature. The mixture was continually stirred for about 10 h. The white precipitate obtained was collected and washed throughly with ethanol, water and ethanol respectively, then dried in air at room temperature. Found: C, 51.4; H, 4.3; N, 9.1. Calc. for $Sm_2L_3 \cdot 7H_2O$: C, 51.4; H, 4.6; N, 9.6%.

Synthesis of the single crystal of $Sm_2L_3 \cdot 5DMF$

A little $Sm_2L_3 \cdot 7H_2O$ was dissolved in *N*,*N*-dimethylformamide (DMF). The dilute solution

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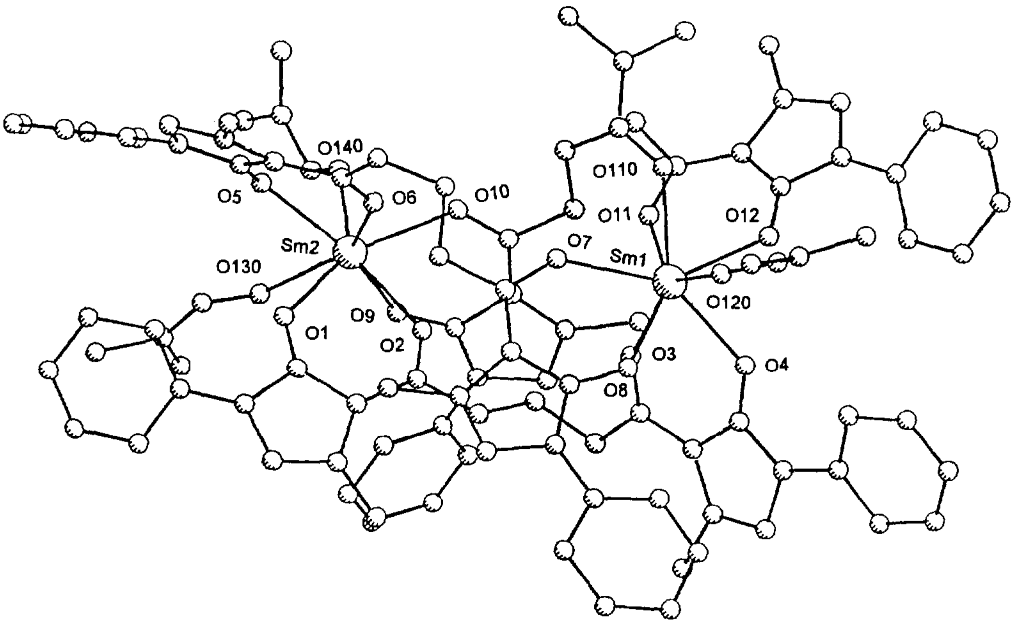

Fig. 1. Perspective view of the $Sm_2L_3(DMF)_4 \cdot DMF$.

Table 1. Selected bond distances (Å)[a]

Sm(1)—O(3)	2.395(6)	Sm(1)—O(11)	2.392(7)
Sm(1)—O(4)	2.334(9)	Sm(1)—O(12)	2.355(9)
Sm(1)—O(7)	2.222(9)	Sm(1)—O(110)	2.461(7)
Sm(1)—O(8)	2.317(7)	Sm(1)—(120)	2.406(7)
Sm(2)—O(1)	2.360(8)	Sm(2)—O(9)	2.318(7)
Sm(2)—O(2)	2.428(7)	Sm(2)—O(10)	2.308(8)
Sm(2)—O(5)	2.365(7)	Sm(2)—O(130)	2.545(8)
Sm(2)—O(6)	2.417(7)	Sm(2)—O(140)	2.421(8)
O(1)—C(17)	1.34(1)	C(17)—C(18)	1.33(2)
O(2)—C(21)	1.25(2)	C(18)—C(21)	1.36(1)
O(3)—C(25)	1.27(1)	C(25)—C(38)	1.31(1)
O(4)—C(37)	1.26(1)	C(37)—C(38)	1.46(1)
C(21)—C(22)	1.5(2)	C(24)—C(25)	1.61(2)
O(5)—C(47)	1.39(1)	C(47)—C(48)	1.43(2)
O(6)—C(51)	1.28(1)	C(48)—C(51)	1.41(2)
O(7)—C(55)	1.28(1)	C(55)—C(68)	1.58(2)
O(8)—C(67)	1.61(1)	C(67)—C(68)	1.51(2)
O(9)—C(77)	1.22(1)	C(77)—C(78)	1.46(1)
O(10)—C(81)	1.32(1)	C(78)—C(81)	1.61(2)
O(11)—C(85)	1.26(1)	C(85)—C(98)	1.39(1)
O(12)—C(97)	1.24(1)	C(97)—C(98)	1.40(1)
O(110)—C(111)	1.19(1)	N(112)—C(113)	1.49(3)
C(111)—N(112)	1.39(2)		
O(120)—C(121)	1.20(1)	C(122)—C(123)	1.54(2)
O(121)—N(122)	1.49(3)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits

evaporated very slowly in room temperature for several months, until single crystals suitable for X-ray data collection were obtained.

X-ray data collection, structure determination and refinement for the complex $Sm_2L_3 \cdot 5DMF$

A transparent colourless crystal of $C_{90}H_{101}N_{17}O_{17}Sm_2$, $[PhCH_3C_3N_2(O)C(O)(CH_2)_3C(O)C_3N_2(O)CH_3Ph]_3Sm_2 \cdot 5DMF$, having approximate dimensions $0.2 \times 0.2 \times 0.3$ mm was mounted on a glass fibre in a random orientation. The determination of the unit cell and the data collection were performed with Mo-K_α radiation ($\lambda = 0.71073$ Å) on an Enraf–Nonius CAD4 diffractometer equipped with a graphite crystal monochromator. A total of 9920 independent reflections were collected in the range $2° \leqslant \theta \leqslant 21°$ by the ω–2θ scan technique at room temperature (23 ± 1°C) in which 3205 reflections with $[I \geqslant 3\sigma(I)]$ were considered to be observed and used in the succeeding refinement. A correction for Lorentz-polarization effects was applied to the data.

The crystals are triclinic, space group $P\bar{1}$, with $a = 16.92(2)$, $b = 17.953(6)$, $c = 18.248(5)$ Å, $\alpha = 110.38(2)$, $\beta = 101.19(5)$, $\lambda = 111.25(6)°$, $V = 4505(9)$ Å^3, $M_r = 1993.61$, $Z = 2$, $D_x = 1.47$ g cm^{-3}, $\mu = 13.67$ cm^{-1}, $F(000) = 2040$.

The structure was solved by the Direct Method

Table 2. Bond angles (°)

O(3)—Sm(1)—O(4)	74.9(3)	O(7)—Sm(1)—O(11)	83.1(3)
O(3)—Sm(1)—O(7)	84.7(3)	O(7)—Sm(1)—O(12)	145.0(3)
O(3)—Sm(1)—O(8)	78.3(3)	O(7)—Sm(1)—O(110)	71.6(3)
O(3)—Sm(1)—O(11)	74.5(2)	O(7)—Sm(1)—O(120)	104.7(3)
O(3)—Sm(1)—O(12)	112.8(3)	O(8)—Sm(1)—O(11)	145.2(3)
O(3)—Sm(1)—O(110)	139.0(2)	O(8)—Sm(1)—O(12)	138.1(3)
O(3)—Sm(1)—O(120)	145.0(2)	O(8)—Sm(1)—O(110)	123.1(3)
O(4)—Sm(1)—O(7)	144.6(4)	O(8)—Sm(1)—O(120)	72.8(4)
O(4)—Sm(1)—O(8)	74.5(4)	O(11)—Sm(1)—O(12)	73.8(3)
O(4)—Sm(1)—O(11)	117.6(3)	O(11)—Sm(1)—O(110)	70.0(2)
O(4)—Sm(1)—O(12)	70.3(3)	O(11)—Sm(1)—O(120)	139.4(2)
O(4)—Sm(1)—O(110)	140.6(3)	O(12)—Sm(1)—O(110)	76.1(3)
O(4)—Sm(1)—O(120)	78.8(2)	O(12)—Sm(1)—O(120)	78.6(3)
O(7)—Sm(1)—O(8)	73.3(4)	O(110)—Sm(1)—O(120)	74.9(2)
O(1)—Sm(2)—O(2)	72.6(3)	O(5)—Sm(2)—O(9)	140.1(3)
O(1)—Sm(2)—O(5)	75.3(3)	O(5)—Sm(2)—O(10)	124.2(3)
O(1)—Sm(2)—O(6)	82.2(3)	O(5)—Sm(2)—O(130)	74.3(3)
O(1)—Sm(2)—O(9)	108.0(3)	O(5)—Sm(2)—O(140)	70.1(3)
O(1)—Sm(2)—O(10)	145.2(3)	O(6)—Sm(2)—O(9)	144.2(3)
O(1)—Sm(2)—O(130)	70.4(3)	O(6)—Sm(2)—O(10)	76.8(3)
O(1)—Sm(2)—O(140)	137.1(3)	O(6)—Sm(2)—O(130)	143.1(3)
O(2)—Sm(2)—O(5)	137.6(2)	O(6)—Sm(2)—O(140)	111.9(3)
O(2)—Sm(2)—O(6)	73.6(3)	O(9)—Sm(2)—O(10)	76.1(3)
O(2)—Sm(2)—O(9)	77.0(2)	O(9)—Sm(2)—O(130)	70.1(3)
O(2)—Sm(2)—O(10)	75.0(3)	O(9)—Sm(2)—O(140)	84.3(3)
O(2)—Sm(2)—O(130)	118.4(2)	O(10)—Sm(2)—O(130)	138.6(3)
O(2)—Sm(2)—O(140)	149.5(3)	O(10)—Sm(2)—O(140)	77.2(3)
O(5)—Sm(2)—O(6)	75.3(3)	O(130)—Sm(2)—O(140)	76.2(2)
Sm(1)—O(110)—C(111)	134.5(9)	C(111)—N(112)—C(114)	113(1)
O(110)—C(111)—N(112)	119(1)	C(111)—N(112)—C(113)	124(1)
Sm(1)—O(120)—C(121)	125.1(8)	O(120)—C(121)—N(122)	123(1)

(MULTAN 82). The positions of the two samarium atoms were located on an E-map. All the other non-hydrogen atoms were determined from successive difference Fourier syntheses.

The final refinement by full-matrix least-squares with isotropic thermal parameters for all of the carbon atoms and anisotropic thermal parameters for other non-hydrogen atoms converged with agreement factors of $R = \Sigma|\Delta F|/\Sigma|F_o| = 0.078$ and $R_w = [\Sigma w|\Delta F|^2/\Sigma|F_o|^2]^{1/2} = 0.087$ (unit weights for all observed reflections). The highest peak on the final difference Fourier map had a height of 0.70 e Å^{-3}.

All calculations were performed on a PDP 11/44 computer using the SDP-PLUS program system.

Tables of final atomic positional and thermal parameters, full lists of bond lengths and angles, and equations of least-squares plane have been deposited as supplementary material with the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

The molecular structure of the complex $Sm_2L_3 \cdot 5DMF$ is shown in Fig. 1. Some bond lengths and angles are given in Tables 1 and 2, respectively.

In the complex $Sm_2L_3 \cdot 5DMF$, L is a tetradentate ligand. Each L bonds two samarium atoms and acts as a bridging ligand. The O(1) and O(2), O(5) and O(6), O(9) and O(10) atoms (from three Ls) bond to Sm(2). The other six oxygen atoms of three Ls bonded to Sm(1) are O(3) and O(4), O(7) and O(8), O(11) and O(12). The seventh and eighth coordinated atoms for each samarium come from the carbonyl oxygen atom of two coordinated DMF

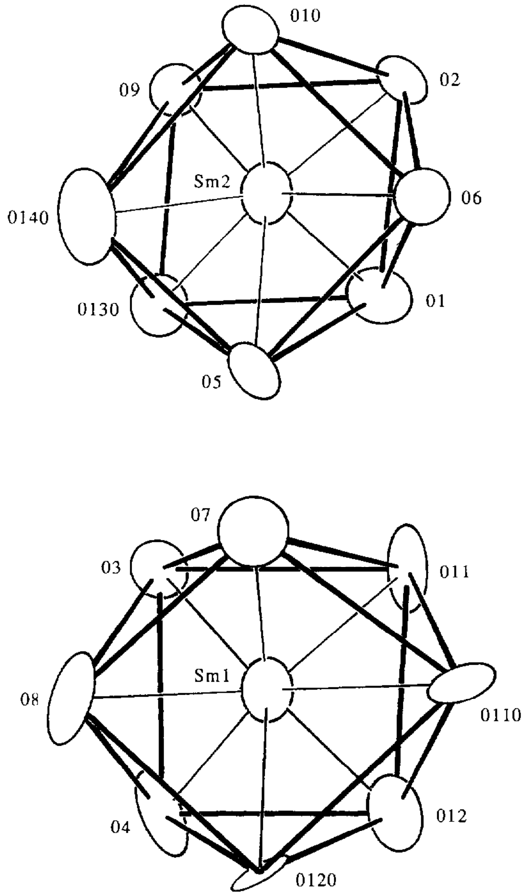

Fig. 2. The coordination polyhedron of samarium(III) ions.

molecules. The Sm—O distances range from 2.222(9) to 2.461(7) Å (mean 2.359 Å) for Sm(1)—O and 2.398(7)–2.545(8) Å (mean 2.395 Å) for Sm(2)—O. The longest is Sm(1)—O(110)(DMF) and Sm(2)—O(130)(DMF).

The samarium is eight-coordinated in a distorted square antiprism configuration (Fig. 2). The O(3), O(4), O(11) and O(12) atoms lie approximately in a plane (Plane 14). The O(7), O(8), O(110) and O(120) atoms make up Plane 13. The distances between Sm(1) and the two planes are −1.2729 and 1.2682 Å for Planes 13 and 14, respectively. The dihedral angle between these two planes is 1.46°. Plane 15 consists of O(5), O(6), O(10) and O(140) atoms, and Plane 16 O(1), O(2), O(9) and O(130) atoms. The distances between Sm(2) and the two planes are −1.2206 and 1.3199 Å, respectively. The dihedral angle between Planes 15 and 16 is 3.30°. The two coordination polyhedra show little difference.

The dihedral angles between phenyl planes and their connected pyrazoline planes range from 10.54 to 34.58°. The smallest dihedral angle is between Plane 7 [C(61)—C(66)] and Plane 8 [C(67)—C(69), N(7), N(8)]. The largest is between Plane 11 [C(91)—C(96)] and Plane 12 [C(97)—C(99), N(11), N(12)].

Each samarium atom bonds two DMF molecules.

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