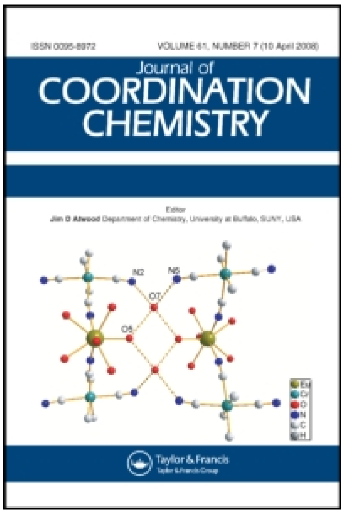

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SYNTHESIS AND CRYSTAL STRUCTURE OF TRIS(ACETYLACETONATO)-(1,10-PHENANTHROLINE-*N*-OXIDE)-YTTRIUM(III)

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The title complex, $C_{27}H_{29}N_2O_7Y$, was formed by the reaction of yttrium acetylacetonate with 1,10-phenanthroline-*N*-oxide in nonaqueous medium. The complex crystallizes in the monoclinic space group $P2_1/n$ with unit cell dimensions $a = 12.157(1)$, $b = 12.320(1)$, $c = 18.720(3)$ Å, $\beta = 104.43(1)°$ and $Z = 4$. The structure was refined by full-matrix least-squares procedures to a final $R = 0.0315$ for 3049 observed reflections with $I \geqslant 3\sigma(I)$. The yttrium atom is eight-coordinated by six acetylacetonate oxygen atoms and the oxgygen atom and nitrogen atom from the 1,10-phenanthroline-*N*-oxide, forming a distorted square antiprism.

Keywords: Yttrium acetylacetonate, 1,10-phenanthroline-*N*-oxide, complex, X-ray structure

INTRODUCTION

Aromatic amine *N*-oxides behave as strongly basic ligands towards many metal ions. In this class of ligand, 1,10-phenanthroline-*N*-oxide (PheNO) contains a relatively large conjugated π-bond system. Its complexes with 3d transition metal ions have been extensively studied.[1-6] However, there are few reports on complexes of this ligand with rare earth ions, and no complex of the ligand with yttrium has been reported. Previous work mainly concerns the synthesis and characterization of such complexes, while crystal structures of PheNO complexes with rare earth ions have not been reported. As an extension to our previous work with PheNO,[7] the present paper deals with the synthesis and crystal structure of the title complex $[Y(acac)_3(PheNO)]$ (acac = acetylacetonate anion).

EXPERIMENTAL

Preparation

To a stirred solution of $Y(acac)_3{\cdot}3H_2O$[8] (0.220 g, 0.50 mmol) in anhydrous ethanol ($15\,cm^3$) was added a solution of PheNO[1] (0.098 g, 0.50 mmol) in anhydrous ethanol ($5\,cm^3$). A pale yellow precipitate appeared. After 2 h stirring, the precipitate was filtered off, washed with ice-cold anhydrous ethanol and dried *in vacuo*. Yield: 80%. The solid complex was dissolved in acetonitrile and set aside in a closed beaker at

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room temperature. After about two weeks, pale yellow, needle-like crystals of the complex were formed in the solution. *Anal.*; Calcd.: C, 55.68; H, 5.02; N, 4.87; Y, 15.26%. Found: C, 55.64; H, 4.95; N, 4.81; Y, 15.65%.

Crystal Structure Analysis

Intensity data for a crystal 0.44 × 0.19 × 0.15 mm were measured on an Enraf-Nonius CAD4 diffractometer with the use of graphite monochromatized MoKα radiation and the $\omega:2\theta$ scan technique such that θ_{max} was 26°. The data were corrected for Lorentz and polarization effects and for absorption. Of the 5748 reflections measured, 3049 satisfied the $I \geqslant 3\sigma(I)$ criterion of observability. Crystal data and refinement details are given in Table I.

TABLE I
Crystal and refinement details for [Y(acac)$_3$(PhenNO)].

Formula	$C_{27}H_{29}N_2O_7Y$
M_r	582.45
System	monoclinic
Space group	$P2_1/n$
a, Å	12.157(1)
b Å	12.320(1)
c Å	18.720(3)
β(°)	104.43(1)
Vol. (A^3)	2715.3
Z	4
Dc (g cm^{-3})	1.425
μ, cm^{-1}	22.03
$F(000)$	1200
Transmission factors (max./min.)	0.9424; 0.8585
θ limits (°)	1.0–26.0
Total reflections	5748
No. $I \geqslant 3\sigma(I)$	3049
R	0.0315
R_w	0.0341
$(\Delta/\sigma)_{max.}$	0.15
ρ(e A^{-3})	< 0.338

The structure was solved by the Patterson method and subsequent difference Fourier techniques and refined by full-matrix least-squares procedures based on F. Non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were located in a difference Fourier map. The hydrogen atoms were not refined but included in the calculation of structure factors. Final $R = 0.032$, $R_w = 0.034$ and S = 1.572 for 3049 observed reflections, with weight $w = 1$ for observed reflections.

Fractional atomic coordinates are listed in Table II and the numbering scheme employed is shown in Figure 1. All calculations were carried out on a PDP11/44 computer using the SDP/PDP software package (ENRAF-NONIUS, 1985). Listings of thermal parameters, hydrogen atom parameters, all bond distances and angles, dimensions of the coordination polyhedron about the yttrium ion and observed and calculated structure factors are available from T.M.

TABLE II
Fractional atomic coordinates ($\times 10^5$ for Y; $\times 10^4$ for others) for the complex.

Atom	*x/a*	*y/b*	*z/c*
Y	75926(3)	24432(3)	98330(2)
O(1)	7795(2)	648(2)	9520(1)
N(1)	7941(3)	244(3)	8892(2)
N(2)	5984(3)	1708(3)	8695(2)
C(1)	8869(4)	−383(4)	8947(3)
C(2)	9075(4)	−918(4)	8353(3)
C(3)	8348(4)	−788(4)	7672(3)
C(4)	7404(4)	−105(4)	7598(2)
C(5)	6635(4)	35(4)	6885(2)
C(6)	5706(4)	646(4)	6806(2)
C(7)	5451(4)	1188(4)	7412(2)
C(8)	4465(4)	1819(4)	7313(2)
C(9)	4228(3)	2325(4)	7904(2)
C(10)	5027(3)	2262(4)	8586(2)
C(11)	6196(3)	1124(3)	8129(2)
C(12)	7182(3)	434(3)	8215(2)
O(1a)	8244(2)	2557(3)	8758(1)
O(2a)	9543(2)	2699(3)	10200(2)
C(1a)	9211(4)	2365(5)	7816(3)
C(2a)	9196(3)	2502(4)	8613(2)
C(3a)	10228(3)	2558(5)	9125(2)
C(4a)	10351(3)	2698(4)	9889(3)
C(5a)	11529(4)	2859(5)	10388(3)
O(1b)	6678(2)	3942(2)	9222(2)
O(2b)	7837(2)	3861(3)	10693(2)
C(1b)	5515(4)	5471(4)	8809(3)
C(2b)	6282(3)	4810(4)	9418(2)
C(3b)	6534(4)	5214(4)	10133(2)
C(4b)	7338(4)	4743(4)	10718(2)
C(5b)	7666(5)	5324(5)	11445(3)
O(1c)	8088(2)	1415(3)	10908(1)
O(2c)	5945(2)	2206(2)	10225(2)
C(1c)	8213(5)	−124(5)	11667(3)
C(2c)	7526(4)	749(4)	11179(2)
C(3c)	6348(4)	750(4)	11058(3)
C(4c)	5633(4)	1488(4)	10607(3)
C(5c)	4375(4)	1426(5)	10585(4)

RESULTS AND DISCUSSION

The crystal structure is composed of discrete molecular units linked by weak van der Waals forces. A diagram of the molecular structure is shown in Figure 1 and selected interatomic parameters are given in Table III.

The yttrium atom is eight-coordinated by six acetylacetonate oxygen atoms and the oxygen atom and nitrogen atom from the 1,10-phenanthroline-*N*-oxide, forming a distorted square antiprism (Figure 2). The Y–O (PheNO) distance of 2.317 Å is roughly the same as the average Y–O (acac) distance of 2.324 Å, which is not

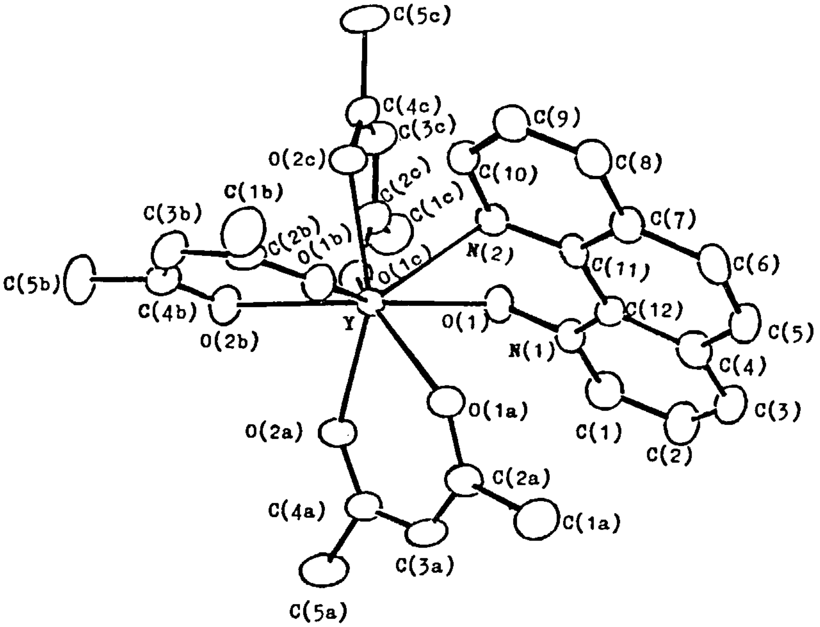

FIGURE 1 Molecular structure and numbering scheme for the complex molecule.

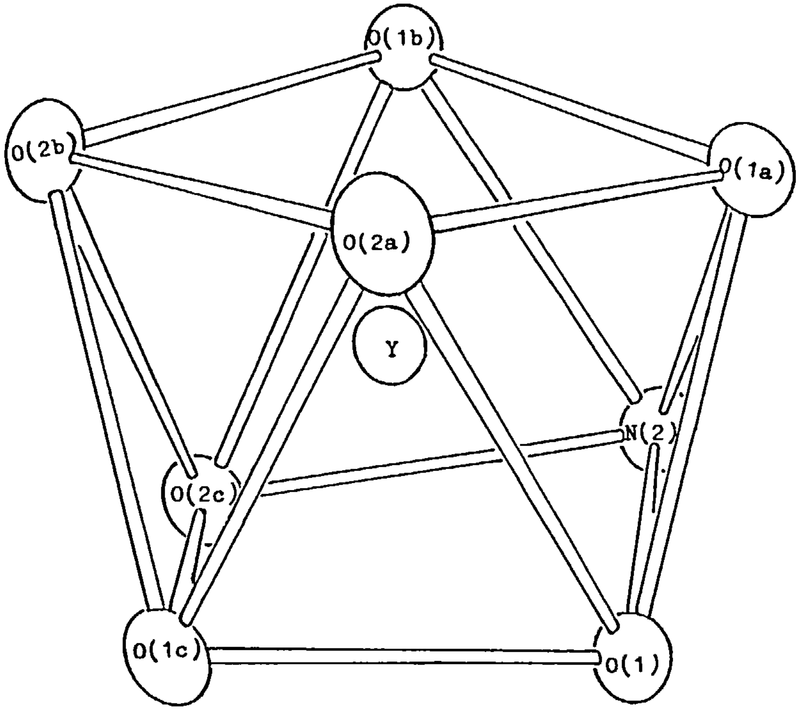

FIGURE 2 The coordination polyhedron about the yttrium atom in the complex molecule. Coordination bonds are unfilled.

significantly shorter than the distance of 2.366 Å in $[Y(acac)_3(H_2O)_2]\cdot H_2O$.[9] The Y–N(2) distance of 2.666 Å is longer than the Y–O bond lengths. Because of unequal Y–N and Y–O bond lengths, the coordination polyhedron has a larger distortion from a square antiprism than that of $[Y(acac)_3(H_2O)_2]\cdot H_2O$. The angles of the upper quadrilateral O(1a)–O(2a)–O(2b)–O(1b) range from 85.5 to 93.8°, as compared with from 87.6 to 90.0° in $[Y(acac)_3(H_2O)_2]\cdot H_2O$. These angles of the bottom face range from 75.6 to 105.9°, as compared with from 74.8 to 100.6° in $[Y(acac)_3(H_2O)_2]\cdot H_2O$.

TABLE III
Selected bond lengths (Å) and bond angles (°) for the complex.

Distances			
Y–O(1)	2.317(2)	C(4)–C(5)	1.436(5)
Y–O(1a)	2.343(2)	C(4)–C(12)	1.416(5)
Y–O(2a)	2.320(2)	C(5)–C(6)	1.334(5)
Y–O(1b)	2.306(2)	C(6)–C(7)	1.417(5)
Y–O(2b)	2.332(2)	C(7)–C(8)	1.401(5)
Y–O(1c)	2.327(2)	C(7)–C(11)	1.421(4)
Y–O(2c)	2.315(2)	C(8)–C(9)	1.361(5)
Y–N(2)	2.666(3)	C(9)–C(10)	1.401(5)
O(1)–N(1)	1.328(3)	C(10)–N(2)	1.320(4)
N(1)–C(1)	1.350(4)	N(2)–C(11)	1.358(4)
C(1)–C(2)	1.369(5)	C(11)–C(12)	1.445(4)
C(2)–C(3)	1.366(5)	C(12)–N(1)	1.389(4)
C(3)–C(4)	1.402(5)		
Angles			
O(1)–Y–O(1a)	76.08(9)	O(2b)–Y–N(2)	138.02(8)
O(1)–Y–O(2a)	92.27(9)	O(1c)–Y–O(2c)	73.46(8)
O(1)–Y–O(1b)	134.98(8)	O(1c)–Y–N(2)	119.10(9)
O(1)–Y–O(2b)	152.18(8)	O(2c)–Y–N(2)	71.95(8)
O(1)–Y–O(1c)	71.23(8)	O(1)–N(1)–C(1)	116.1(3)
O(1)–Y–O(2c)	96.56(9)	O(1)–N(1)–C(12)	122.6(3)
O(1)–Y–N(2)	64.96(8)	C(1)–N(1)–C(12)	121.2(3)
O(1a)–Y–O(2a)	72.96(8)	N(1)–C(1)–C(2)	122.2(4)
O(1a)–Y–O(1b)	75.56(9)	C(1)–C(2)–C(3)	119.6(4)
O(1a)–Y–O(2b)	121.91(9)	C(2)–C(3)–C(4)	119.1(4)
O(1a)–Y–O(1c)	134.84(9)	C(3)–C(4)–C(12)	121.2(4)
O(1a)–Y–O(2c)	141.56(8)	C(5)–C(4)–C(12)	119.3(4)
O(1a)–Y–N(2)	70.82(8)	C(4)–C(5)–C(6)	120.6(4)
O(2a)–Y–O(1b)	111.65(9)	C(5)–C(6)–C(7)	121.6(3)
O(2a)–Y–O(2b)	75.46(9)	C(6)–C(7)–C(11)	121.0(3)
O(2a)–Y–O(1c)	78.04(9)	C(8)–C(7)–C(11)	118.6(3)
O(2a)–Y–O(2c)	145.48(8)	C(7)–C(8)–C(9)	119.5(3)
O(2a)–Y–N(2)	140.80(9)	C(8)–C(9)–C(10)	118.5(3)
O(1b)–Y–O(2b)	72.71(8)	N(2)–C(10)–C(9)	123.6(3)
O(1b)–Y–O(1c)	148.64(9)	C(10)–N(2)–C(11)	119.0(3)
O(1b)–Y–O(2c)	84.85(9)	N(2)–C(11)–C(7)	120.5(3)
O(1b)–Y–N(2)	73.05(8)	C(7)–C(11)–C(12)	117.0(3)
O(2b)–Y–O(1c)	81.74(9)	C(4)–C(12)–C(11)	120.4(3)
O(2b)–Y–O(2c)	81.49(9)	N(1)–C(12)–C(4)	116.5(3)

The acetylacetonate groups are nearly planar; the average deviation of the carbon and oxygen atoms from the least-squares planes are 0.037, 0.045 and 0.038 Å for the groups containing O(1a)–O(2a), O(1b)–O(2b) and O(1c)–O(2c), respectively. The distances of the Y atom from these planes are 0.260, 0.041 and 0.643 Å, respectively. Thus, each of the metal-acetylacetonate rings is folded about the O–O vector. A similar geometry has also been found in $[Y(acac)_3(H_2O)_2]\cdot H_2O$.

Two coordinating atoms, N(2) and O(1), of 1,10-phenanthroline-*N*-oxide are situated on both sides of the least-squares plane of 1,10-phenanthroline-*N*-oxide molecule. The deviations from the plane are 0.123 and 0.092 Å, respectively. This indicated that 1,10-phenanthroline-*N*-oxide undergoes a slight distortion upon coordination.

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