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Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

Synthesis, structure and magnetic properties of a Pr(III) complex with chelating nitronyl nitroxide radicals

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To cite this Article Li, Dong-Jiao , Gao, Dong-Zhao , Liao, Dai-Zheng , Jiang, Zong-Hui and Yan, Shi-Ping(2004) 'Synthesis, structure and magnetic properties of a Pr(III) complex with chelating nitronyl nitroxide radicals', *Journal of Coordination Chemistry*, 57: 17, 1571 – 1576

To link to this Article: DOI: 10.1080/00958970412331302166

URL: <http://dx.doi.org/10.1080/00958970412331302166>

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SYNTHESIS, STRUCTURE AND MAGNETIC PROPERTIES OF A Pr(III) COMPLEX WITH CHELATING NITRONYL NITROXIDE RADICALS

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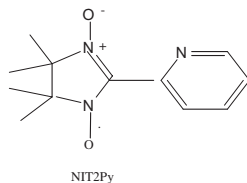
(Received 29 March 2004)

The synthesis and structure of Pr(III) complex with chelating nitronyl nitroxide radicals of formula [Pr(III)(NIT2Py)₂(NO₃)₃] (NIT2Py = 2-(2'-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide) is reported. Pr(III) is ten-coordinate with three bidentate nitrate anions and two radicals. The radical behaves as a bidentate chelating ligand through one oxygen atom of the nitronyl nitroxide group and one nitrogen atom of a pyridine ring. The electronic spectrum for the complex in THF and magnetic susceptibilities from 77–300 K are reported.

Keywords: Crystal structure; Nitronyl nitroxide radical; Ln(III) complexes; Magnetism

INTRODUCTION

In the last few years there has been growing interest in molecular coordination compounds of the lanthanides due to their luminescence [1,2], the use as contrast agents in magnetic resonance imaging [3–8] or as building blocks in molecule-based magnetic materials [9–14]. In the latter two fields of potential application, attention is more especially focussed on paramagnetic complexes. However, very few compounds in which a lanthanide ion (Ln) is bound to nitronyl nitroxide radicals have been reported [15]. We report the synthesis, X-ray structure and magnetic properties of a complex of formula [Pr(III)(NIT2Py)₂(NO₃)₃] consisting of a Pr(III) ion surrounded by two N,O-chelating nitronyl nitroxide radicals (NIT2Py = 2-(2'-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide) (scheme 1) and three nitrate groups.



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EXPERIMENTAL

Preparation of NIT2Py

2-(2'-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide was prepared by a literature method [16,17].

Preparation of [Pr(III)(NIT2Py)₂(NO₃)₃]

The complex was synthesized by the following procedure. Pr(NO₃)₃·6H₂O (0.044 g, 0.2 mmol) and NIT2Py (0.047 g, 0.2 mmol) were dissolved in 10 cm³ of anhydrous THF. The mixture was stirred at room temperature for 4 h and then filtered. The dark brown filtrate was allowed to stand in the dark for one week. Dark brown crystals were obtained. Anal. Calc. for C₂₄ H₃₂ N₉ O₁₃ Pr(%): C, 36.23; H, 4.03; N, 15.84. Found: C, 35.98; H, 4.31; N, 15.49. IR (KBr): $\nu_{\text{NO}_3} = 1520 \text{ cm}^{-1}$, 1360 cm^{-1} , $\nu_{\text{N-O}} = 1320 \text{ cm}^{-1}$.

Physical Measurements

Elemental analyses for carbon, hydrogen and nitrogen were carried out on a Model 240 Perkin-Elmer instrument. The infrared spectrum was measured on a Shimadzu 408 spectrophotometer in the range 4000–600 cm⁻¹ range, using KBr pellets. Variable temperature susceptibility measurements were carried out with an LDJ 9600 vibrating sample magnetometer in the temperature range 77–300 K at a magnetic field of 10 000 G.

X-ray Crystallography

A single crystal of the complex was mounted on a Bruker Smart 1000 CCD diffractometer equipped with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293(2) K. Data were collected at room temperature by the $Q-\omega$ scan mode. Unit-cell parameters were determined from $1.76^\circ \leq \theta \leq 26.44^\circ$ for the complex. Details of data collection, crystallographic data and structure refinement parameters for the complex are summarized in Table I.

The structure was solved by direct methods using SHELXS-97 [18]. H atoms were assigned common isotropic displacement factors and included in the final refinement by use of geometrical restraints. A full-matrix least-squares refinement on F^2 was carried out using SHELXL-97 [18]. Reliability factors were defined as $R_1 = \sum(|F_0| - |F_c|) / \sum|F_0|$ and the function minimized was $wR_2 = (\sum w(|F_0|^2 - |F_c|^2)^2 / \sum w|F_0|^2)^2$, where in the least-squares calculation unit weights were used. All non-hydrogen atoms were refined isotropically. Final atomic coordinates for all non-hydrogen atoms and equivalent thermal parameters are listed in Table II.

RESULTS AND DISCUSSION

Description of the Structure of [Pr(III)(NIT2Py)₂(NO₃)₃]

An ORTEP drawing of [Pr(III)(NIT2Py)₂(NO₃)₃] is shown in Fig. 1. Selected bond lengths and angles for the complex are given in Table III. In the complex, the metal ion is ten-coordinated by two radicals and three nitrate anions. The radical behaves

TABLE I Crystallographic data and structure refinement parameters for the complex

Empirical formula	C ₂₄ H ₃₂ N ₉ O ₁₃ Pr
Formula weight	795.50
Temperature (K)	293(2) K
Wavelength (Å)	0.71073
Crystal system, space group	Monoclinic, <i>P</i> ₂ ₁ / <i>n</i>
Unit cell dimensions (Å)	<i>a</i> = 12.422(3) <i>b</i> = 11.135(3) <i>β</i> = 98.317(6)° <i>c</i> = 23.389(7)
Volume	3201.3(15) (Å ⁻³)
<i>Z</i>	4
Absorption coefficient (mm ⁻¹)	1.599
<i>F</i> (000)	1608
Crystal size (mm)	0.24 × 0.18 × 0.14
<i>θ</i> range for data collection (°)	1.76 to 26.44
Limiting indices	-15 ≤ <i>h</i> ≤ 10, -13 ≤ <i>k</i> ≤ 13, -22 ≤ <i>l</i> ≤ 29
Reflections collected/unique	17970/6540 [<i>R</i> (int) = 0.1218]
Completeness to <i>θ</i> = 26.44	99.2%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000000 and 0.751110
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	6540/0/432
Goodness-of-fit on <i>F</i> ²	0.958
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0625, <i>wR</i> 2 = 0.1059
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1481, <i>wR</i> 2 = 0.1273
Largest diff. peak and hole	0.829 and -0.620 e Å ⁻³

as a bidentate chelating ligand through one oxygen of a nitronyl nitroxide and one nitrogen of a pyridyl group, while the other oxygen of the nitronyl nitroxide remains uncoordinated. The coordination sphere of the Pr atom is completed by η²-coordination of three NO₃⁻ anions. The N2–O1 and N5–O3 (coordinated to Pr(III) ion) bond lengths (1.297(7) Å and 1.313(7) Å) are longer than N3–O2 and N6–O4 (uncoordinated to Pr(III) ion) bond lengths (1.260(8) Å and 1.284(8) Å). This is in agreement with the observation that the N–O stretching vibration at 1360 cm⁻¹ for the free radical is shifted to lower frequencies (1320 cm⁻¹) for the complex. The O(1)N(2)C(6)N(3)O(2) moiety is almost planar; maximum and minimum deviation of the atoms from this plane are 0.0211 Å for N(2) and 0.0015 Å for O(2), indicating the delocalization of the free electron. Dihedral angles between the nitronyl nitroxide moieties and the pyridyl substituents are 38.2° and 35.2° for two radicals in the complex, respectively. The Pr–N(pyridyl) bond lengths are 2.736(6) Å and 2.799(6) Å. The Pr–O(NO₃) bond lengths can be classified into two groups: (a) those with Pr–O bond lengths (Pr–O6, Pr–O12, Pr–O5 and Pr–O8) ranging from 2.540(6) Å to 2.551(5) Å and (b) those with bond lengths of 2.605(6) Å (Pr–O9) and 2.609(5) Å (Pr–O11). The bond lengths in the second group are longer. The nitronyl nitroxide groups are well separated with the closest O(2)⋯O(2), O(4)⋯O(4), and O(2)⋯O(4) distances being, respectively, 6.158, 7.766, and 5.635 Å.

Spectroscopic and Magnetic Properties

In the IR spectrum of the complex, two characteristic strong bands in the 1520–1360 cm⁻¹ region, can be attributed to the ν_{as}(NO₃) (1520 cm⁻¹) and ν_s(NO₃) (1360 cm⁻¹) vibrations of the coordinated NO₃⁻ groups. These two bands are separated

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for the complex

	x/a	y/b	z/c	$U(eq)$
Pr(1)	8184(1)	1615(1)	8971(1)	29(1)
N(1)	9543(5)	1136(5)	8143(3)	28(2)
N(2)	10874(4)	2369(5)	9112(3)	26(2)
N(3)	12022(5)	2822(6)	8507(3)	32(2)
N(4)	8464(5)	-804(5)	8851(3)	30(2)
N(5)	6171(5)	-294(6)	8496(3)	31(2)
N(6)	5802(5)	-2157(6)	8633(3)	43(2)
N(7)	6961(7)	3461(8)	9526(4)	74(3)
N(8)	8268(5)	3626(7)	8117(3)	43(2)
N(9)	7871(5)	491(6)	10099(3)	39(2)
O(1)	10117(4)	1836(4)	9346(2)	28(1)
O(2)	12480(4)	2848(5)	8061(2)	51(2)
O(3)	6669(4)	697(5)	8380(2)	36(1)
O(4)	5940(5)	-3291(7)	8712(3)	82(2)
O(5)	7903(5)	3119(6)	9756(3)	63(2)
O(6)	6600(5)	3022(5)	9045(3)	61(2)
O(7)	6440(7)	4136(8)	9786(4)	134(4)
O(8)	8855(4)	3609(5)	8617(2)	46(2)
O(9)	7622(4)	2749(5)	7999(2)	47(2)
O(10)	8342(5)	4436(6)	7775(3)	67(2)
O(11)	7068(4)	591(5)	9699(2)	45(2)
O(12)	8788(4)	723(5)	9968(2)	50(2)
O(13)	7753(5)	214(6)	10596(3)	62(2)
C(1)	056(6)	402(7)	7730(3)	40(2)
C(2)	9614(7)	-300(8)	7386(3)	45(2)
C(3)	10718(7)	-209(9)	7456(4)	58(3)
C(4)	11239(6)	593(7)	7836(4)	44(2)
C(5)	10635(6)	1246(7)	8177(3)	31(2)
C(6)	11161(6)	2131(7)	8598(3)	27(2)
C(7)	11621(5)	3250(7)	9458(3)	33(2)
C(8)	12281(6)	3742(7)	8992(4)	36(2)
C(9)	12301(7)	2544(8)	9936(4)	61(3)
C(10)	10921(7)	4156(8)	9718(4)	58(3)
C(11)	13514(6)	3833(8)	9156(4)	54(3)
C(12)	11842(7)	4940(8)	8723(4)	61(3)
C(13)	9522(6)	-1130(8)	8948(4)	41(2)
C(14)	9912(7)	-2233(8)	8812(4)	53(3)
C(15)	9185(8)	-3039(8)	8539(4)	60(3)
C(16)	8108(7)	-2768(7)	8444(4)	47(2)
C(17)	7771(5)	-1673(7)	8608(3)	30(2)
C(18)	6605(6)	-1369(7)	8566(3)	34(2)
C(19)	4954(6)	-305(8)	8459(4)	40(2)
C(20)	4787(6)	-1552(9)	8739(4)	48(2)
C(21)	4565(6)	770(8)	8763(4)	56(3)
C(22)	4498(7)	-267(9)	7810(4)	61(3)
C(23)	4841(7)	-1493(9)	9394(4)	65(3)
C(24)	3796(7)	-2253(9)	8473(5)	71(3)

by 160 cm^{-1} , suggesting a bidentate coordination mode. In addition, the N-O stretch at 1360 cm^{-1} for free NIT2Py is shifted to lower frequencies (1320 cm^{-1}) in the complex. This indicates the coordinated N-O group.

The electronic spectrum of the complex in THF shows a strong, broad absorption centred around 570 nm attributed to a $n \rightarrow \pi^*$ transition [19], and a band around 370 nm can be attributed to $\pi \rightarrow \pi^*$ of the ONCNO group of the radical. The Absorption around 290 nm can be attributed to the $\pi \rightarrow \pi^*$ transition involving the 2-pyridyl group.

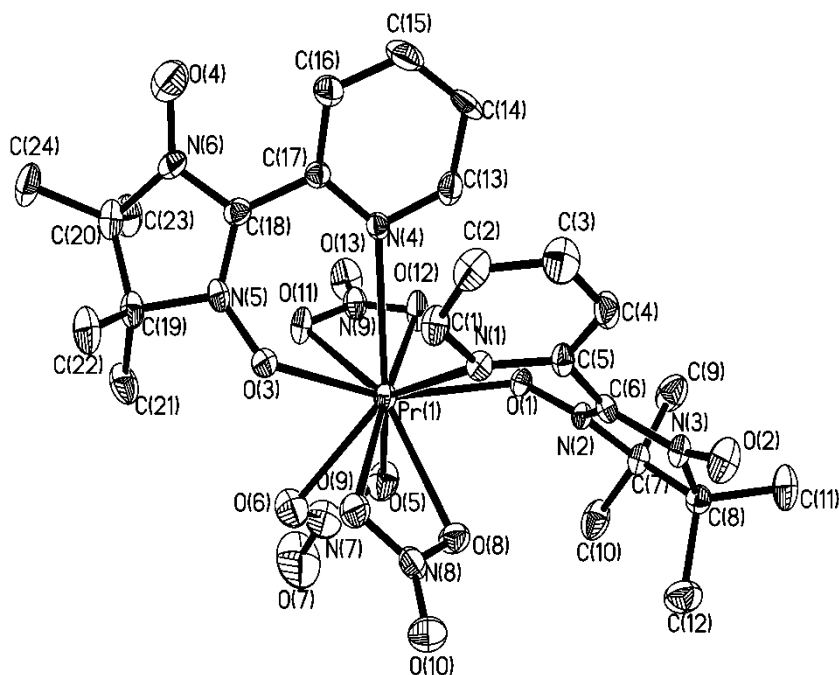

 FIGURE 1 ORTEP drawing of $[\text{Pr}(\text{III})(\text{NIT2Py})_2(\text{NO}_3)_3]$ showing the atom labelling scheme.

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

Bond	Lengths	Bond	Angles
Pr(1)–O(3)	2.397(5)	O(3)–Pr(1)–O(1)	153.83(16)
Pr(1)–O(1)	2.447(4)	O(3)–Pr(1)–O(6)	75.58(19)
Pr(1)–O(6)	2.540(6)	O(1)–Pr(1)–O(6)	130.05(18)
Pr(1)–O(12)	2.546(5)	O(3)–Pr(1)–O(12)	117.66(18)
Pr(1)–O(5)	2.547(6)	O(1)–Pr(1)–O(12)	64.33(16)
Pr(1)–O(8)	2.551(5)	O(3)–Pr(1)–O(5)	121.20(19)
Pr(1)–O(9)	2.605(6)	O(1)–Pr(1)–O(5)	84.58(18)
Pr(1)–O(11)	2.609(5)	O(3)–Pr(1)–O(8)	116.76(17)
Pr(1)–N(4)	2.736(6)	O(1)–Pr(1)–O(8)	71.30(16)
Pr(1)–N(1)	2.799(6)	O(3)–Pr(1)–O(9)	67.33(18)
N(1)–C(1)	1.340(9)	O(1)–Pr(1)–O(9)	112.94(17)
N(1)–C(5)	1.352(8)	O(3)–Pr(1)–O(11)	75.07(17)
N(2)–O(1)	1.297(7)	O(1)–Pr(1)–O(11)	113.37(16)
N(2)–C(6)	1.330(9)	O(3)–Pr(1)–N(4)	67.75(17)
N(2)–C(7)	1.503(9)	O(1)–Pr(1)–N(4)	90.18(16)
N(3)–O(2)	1.260(8)	O(3)–Pr(1)–N(1)	91.23(17)
N(3)–C(6)	1.359(9)	O(1)–Pr(1)–N(1)	66.94(16)
N(3)–C(8)	1.528(9)	C(1)–N(1)–Pr(1)	111.1(5)
N(4)–C(13)	1.352(9)	C(5)–N(1)–Pr(1)	129.9(5)
N(5)–O(3)	1.313(7)	N(5)–O(3)–Pr(1)	126.5(4)
N(6)–O(4)	1.284(8)	N(2)–O(1)–Pr(1)	128.9(4)

Magnetic susceptibilities, χ_M , for the complex were measured in the 77–300 K region. The $\chi_M T$ value at room temperature is $1.99 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, lower than the theoretical value of $2.36 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ expected for two radicals and one Pr ion in the $^3\text{H}_4$ ground state ($g = 4/5$) [20]. When the system is cooled to 77 K, the $\chi_M T$ values decrease slowly.

Magnetic data alone do not provide much information on coupling between the radical and the Pr(III) ion, because the observed decrease of $\chi_M T$ at low temperature may be due to large anisotropy effects observed for the Pr(III) ion [21].

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 20331010 and No. 20171025) and the Tianjin National Natural Science Foundation (No. 033602011).

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