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Synthesis of tripodal *tris*-phosphonate ligands and the structure of the dimeric complex $[Ce(NO_3)_3\{(EtO)_2P(O)CH_2)_3C_6Me_3]_2$

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Abstract

The *tris*-phosphonates 1,3,5 $[(RO)_2P(O)CH_2]_32,4,6\ Me_3C_6$ (= L–R) have been prepared from the corresponding tribromide and phosphites $(RO)_3P$ for R = Me, Et, ^{i}Pr and Bu). The phosphonates react with lanthanide nitrates to give dimeric complexes $Ln(NO_3)_3L_2Ln(NO_3)_3$. The X-ray crystal structure of the cerium(III) complex is reported. The behaviour of the complexes in solution has been examined by electrospray mass spectrometry and shows that the complex undergoes extensive ligand redistribution reactions in solution with no evidence for the presence of dimeric species. Molecular modelling calculations show that the *tris*-chelate monomer is unstable principally due to strain of the aromatic ring.

Keywords: Dimeric structures; Lanthanide nitrates; Ligand; Reaction

1. Introduction

Complexes of lanthanide nitrates continue to attract attention not only for their inherent structural interest [1,2] but also for their potential to act as selective extraction agents for the separation of lanthanides from short lived actinides in nuclear fuels reprocessing [3–5]. Phosphonate complexes appear attractive in this respect, as on ignition they would form poorly soluble phosphates as the only solid residue. The simple synthesis of 1,3,5-*tris*(bromomethyl)mesitylene [6] has provided a simple means to prepare tripodal ligands [7,8] and a simple extension to the corresponding *tris*(dialkylphosphonatomethyl)mesitylenes, L, where the organic group can be varied at will also seems feasible. The interesting molecular architecture of L allows several potential coordination modes to metals. Some of these are depicted in Fig. 1 and from the point of view of structural chemistry it is interesting to establish which, if any are formed in coordination complexes. We sought to prepare novel tripodal phosphonates whose preparation could be readily adapted to give ligands bearing hydrophobic groups that would facilitate solvent extraction and examine the solid state and solution structures of their lanthanide complexes.

2. Results and discussion

The *tris*-phosphonate ligands, L–Me, L–Et, L–Prop and L–Bu were readily synthesised as low melting colourless solids or oils by the standard Arbusov reaction between 1,3,5-*tris*(bromomethyl)mesitylene and the corresponding trialkylphosphite as indicated in the Scheme 1. The ^{13}C and ^{31}P NMR spectra are consistent with the formulation as 1,3,5-*tris*(dialkylphosphonatomethyl)mesitylenes.

The lanthanide complexes were prepared in good yield by the reaction of acetonitrile solutions of the metal nitrates and ligands. The isolated compounds are

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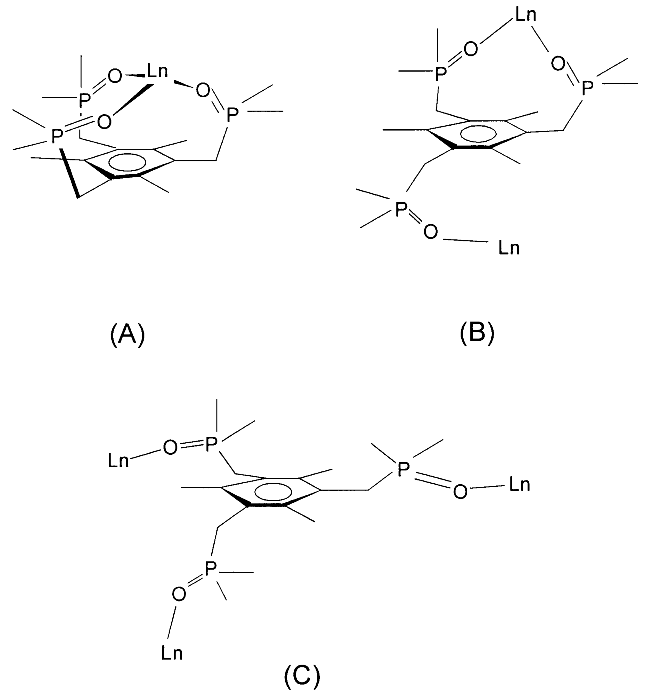
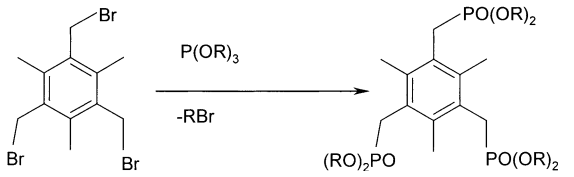


Fig. 1. Possible bonding modes of L to metal ions.



Scheme 1. Preparation of the 1,3,5-*tris*(dialkylphosphonatomethyl)mesitylenes.

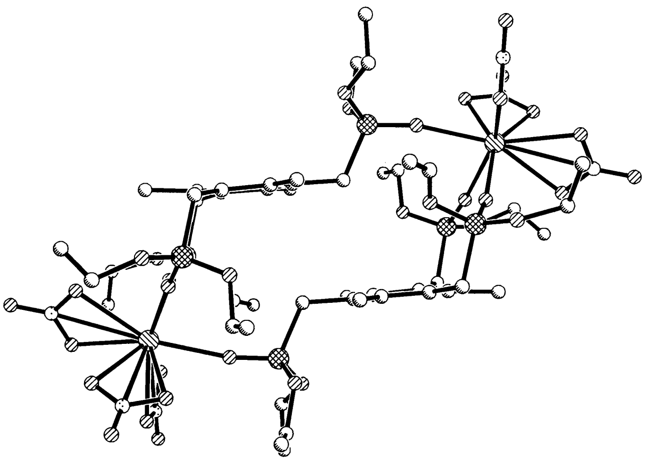


Fig. 2. A view of the dimeric unit of $[Ce(NO_3)_3L]_2$ showing the alignment of the mesityl rings.

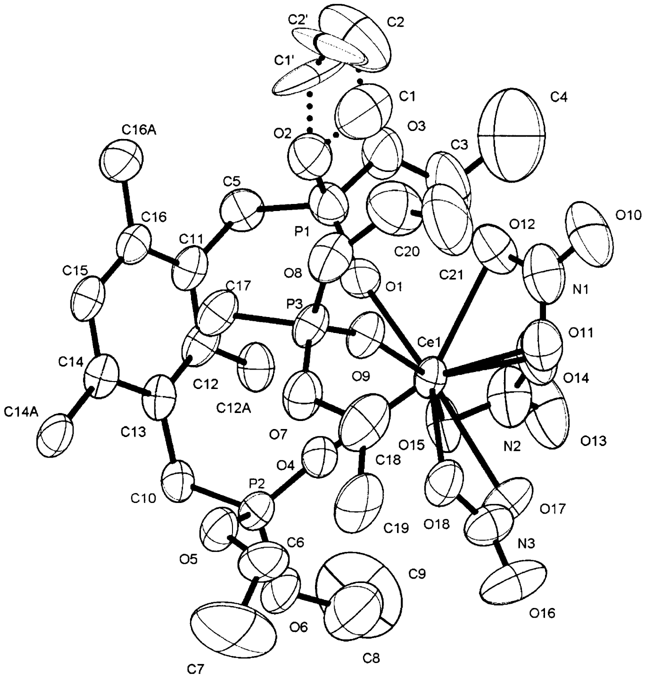


Fig. 3. The Asymmetric unit in $[Ce(NO_3)_3L]_2$, displacement ellipsoids are shown at the 30% level, dashed bonds indicate resolved disorder. H atoms are omitted for clarity.

insoluble in most common organic solvents for complexes of L–Me and L–Et, water being the only good solvent. The complexes of L–Pr and L–Bu show the reverse trend being soluble in chlorinated solvents but less so in water as a result of the increasing hydrophobic nature of the organic groups.

The complex $Ce(NO_3)_3$(L–Et) was chosen for single crystal X-ray study. It crystallises with the phosphonate bridging between two $Ce(NO_3)_3$ moieties as shown in Fig. 2. Two phosphoryl oxygens from the ligand chelate to one metal whilst the third bonds to the second metal giving a symmetrically bridged dimeric structure. The two aromatic rings are parallel but not eclipsed and thus there is no reinforcement of the bonding in the dimer by any π–π interaction. The structure of the asymmetric unit is shown in Fig. 3 with the atom labelling, selected bond lengths and angles in Table 1 and details of the data collection and refinement in Table 2. The Ce–O distances are slightly shorter (by about 0.05 Å) than might be expected from an analysis of the Ln–O distances in lanthanide nitrate *bis*-phosphonate complexes [9,10]. The geometry about the cerium ion can be considered to be a distorted octahedron, if the bidentate nitrate ligands are conceptualised as pseudomonodentate ligands. The ligands are disposed in a facial arrangement with N–Ce–N angles being slightly wider than 90° with an average of 96.4° whilst the O(phosphonate)–Ce–O(phosphonate) display a narrower angle of 85.2°. This would appear to be an electrostatic rather than steric effect, with the repulsions from two negatively charged oxygens per nitrate ligand dominating the increased steric repulsions from the bulky phosphonate groups. The angle at the phosphonate oxygens approaches linearity ranging from 162.73° to 173.24° and

Table 1
Selected bond lengths (Å) and angles (°) for $[Ce(NO_3)_3]_2L_2$

Bond lenghts			
Ce(1)–O(1)	2.409(8)	Ce(1)–O(9)	2.420(7)
Ce(1)–O(4)	2.454(7)	Ce(1)–O(11)	2.556(9)
Ce(1)–O(14)	2.570(8)	Ce(1)–O(15)	2.571(8)
Ce(1)–O(17)	2.581(8)	Ce(1)–O(18)	2.587(8)
Ce(1)–O(12)	2.601(9)	P(1)–O(1)	1.476(8)
P(2)–O(4)	1.475(8)	P(3)–O(9)	1.461(7)
Bond angles			
O(1)–Ce(1)–O(9)	84.0(3)	O(1)–Ce(1)–O(4)	85.8(3)
O(9)–Ce(1)–O(4)	85.7(3)	O(1)–Ce(1)–O(11)	120.3(3)
O(9)–Ce(1)–O(11)	79.7(3)	O(4)–Ce(1)–O(11)	148.1(3)
O(1)–Ce(1)–O(14)	89.0(3)	O(9)–Ce(1)–O(14)	148.3(3)
O(4)–Ce(1)–O(14)	124.6(3)	O(11)–Ce(1)–O(14)	77.3(3)
O(1)–Ce(1)–O(15)	81.6(3)	O(9)–Ce(1)–O(15)	156.5(3)
O(4)–Ce(1)–O(15)	74.9(3)	O(11)–Ce(1)–O(15)	123.6(3)
O(14)–Ce(1)–O(15)	49.8(3)	O(1)–Ce(1)–O(17)	152.7(3)
O(9)–Ce(1)–O(17)	121.5(3)	O(4)–Ce(1)–O(17)	86.4(3)
O(11)–Ce(1)–O(17)	77.5(3)	O(14)–Ce(1)–O(17)	74.1(3)
O(15)–Ce(1)–O(17)	71.1(3)	O(1)–Ce(1)–O(18)	151.9(3)
O(9)–Ce(1)–O(18)	72.9(3)	O(4)–Ce(1)–O(18)	76.9(3)
O(11)–Ce(1)–O(18)	71.7(3)	O(14)–Ce(1)–O(18)	119.1(3)
O(15)–Ce(1)–O(18)	114.2(3)	O(17)–Ce(1)–O(18)	48.9(3)
O(1)–Ce(1)–O(12)	71.6(3)	O(9)–Ce(1)–O(12)	76.7(3)
O(4)–Ce(1)–O(12)	152.5(3)	O(11)–Ce(1)–O(12)	48.7(3)
O(14)–Ce(1)–O(12)	71.8(3)	O(15)–Ce(1)–O(12)	115.6(3)
O(17)–Ce(1)–O(12)	120.7(3)	O(18)–Ce(1)–O(12)	116.6(3)

implying a strong ionic component to the P–O bond as seen in many other phosphonate complexes [9,10].

The infrared spectra confirm the bidentate nature of the nitrate bonding with two strong bands at around 1500, 1290cm^{-1}.

Electrospray mass spectra were obtained on the Nd and Eu complexes in order to examine the solution speciation. The results shown in Table 3 indicate that the dimeric structure is not present in solution and that extensive ligand redistribution reactions and ionisation of nitrate occur. Simple ions derived from the dimeric structure are absent, and whilst the low intensity feature at m/z 838.0 in the spectrum of $Nd(NO_3)_3(L{-}Et)$ (and analogous peaks in the other spectra) could be assigned as $[(L{-}Et)Nd(NO_3)2]^+$ or $[(L{-}Et)Nd(NO_3)_2]_2^{2+}$ on the basis of the mass to charge ratio, the comparison of the theoretical and observed isotope profiles allows unambiguous assignment as the monometallic ion as shown in Fig. 4.

The negative ion spectra show an intense signals due to $[NO_3]^-$, $[NO_3{+}H2O]^-$, $[NO_3{+}n\,MeOH]^-$ with lanthanide containing ions $[Ln(NO_3)_4]^-$ and $[Ln(NO_3)_4L]^-$ observable as very low intensity (< 1%).

3. Molecular modelling

In order to further examine the observed preference for the dimeric bridging phosphonate structure molecular modelling studies were carried out. The bonding mode A, a *tris*-chelate, seems feasible and simple geometric calculations indicate that reasonable Ln–O distances might be obtained for such a structure. As a result molecular mechanics geometry optimisation calculations were carried out using a tricapped trigonal prismatic Gd ion as a representative lanthanide ion, with the nitrates constrained as bidentate ligands. These

Table 2
Crystal data and structure refinement for $[Ce(NO_3)_3]_2L_2$

Empirical formula	$C_{48}H_{90}Ce_2\cdot N_6O_{36}P_6$
Formula weight	1793.32
Temperature (K)	190(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	11.986(5)
b (Å)	15.036(3)
c (Å)	21.154(7)
α (°)	90
β (°)	95.01(3)
γ (°)	90
V (Å^3)	3798(2)
Z	2
D_{calc} (Mg m^{-3})	1.568
Absorption coefficient (mm^{-1})	1.398
$F(0\,0\,0)$	1828
Crystal size (mm)	0.37 × 0.22 × 0.16
θ-range for data collection (°)	1.89–26.02
Index ranges	$-1 \leqslant h \leqslant 14$, $-18 \leqslant k \leqslant 1$, $-26 \leqslant l \leqslant 25$
Reflections collected	8797
Independent reflections	7463 [$R_{int} = 0.0664$]
Completeness to $\theta = 26.00°$	99.7%
Absorption correction	psi-scan
Max. and min. transmission	0.695 and 0.538
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	7463/0/460
Goodness-of-fit on F^2	1.012
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0827$, $wR_2 = 0.1666$
R indices (all data)	$R_1 = 0.1750$, $wR_2 = 0.2099$
Largest difference peak and hole (e Å^{-3})	1.444 and −1.600

Table 3
Electrospray mass spectral data for $[Ln(NO_3)_3]_2L_2$

Ion	L–Me, Ln=Eu	L–Et, Ln=Nd	Ln=Eu
$[L_2Ln]^{3+}$	375.1(100)	427.8(100)	431.2(100)
$[L_3Ln]^{3+}$	537.2(25)	618.1(30)	621.2(35)
$[L_4Ln]^{3+}$	699.1(5)	808.2(10)	811.3(5)
$[LLn(NO_3)]^{2+}$	350.1(40)	387.7(40)	392.2(30)
$[L_2Ln(NO_3)]^{2+}$	593.7(30)	672.9(40)	677.8(30)
$[LLn(NO_3)_2]^+$	763.1(< 5)	838.0(10)	847.2(< 5)

In aqueous solution. Values of m/z are quoted for the most intense peak in the isotope profile and are within ±1 Da of the theoretical values. The relative intensities of the signals are given in parentheses.

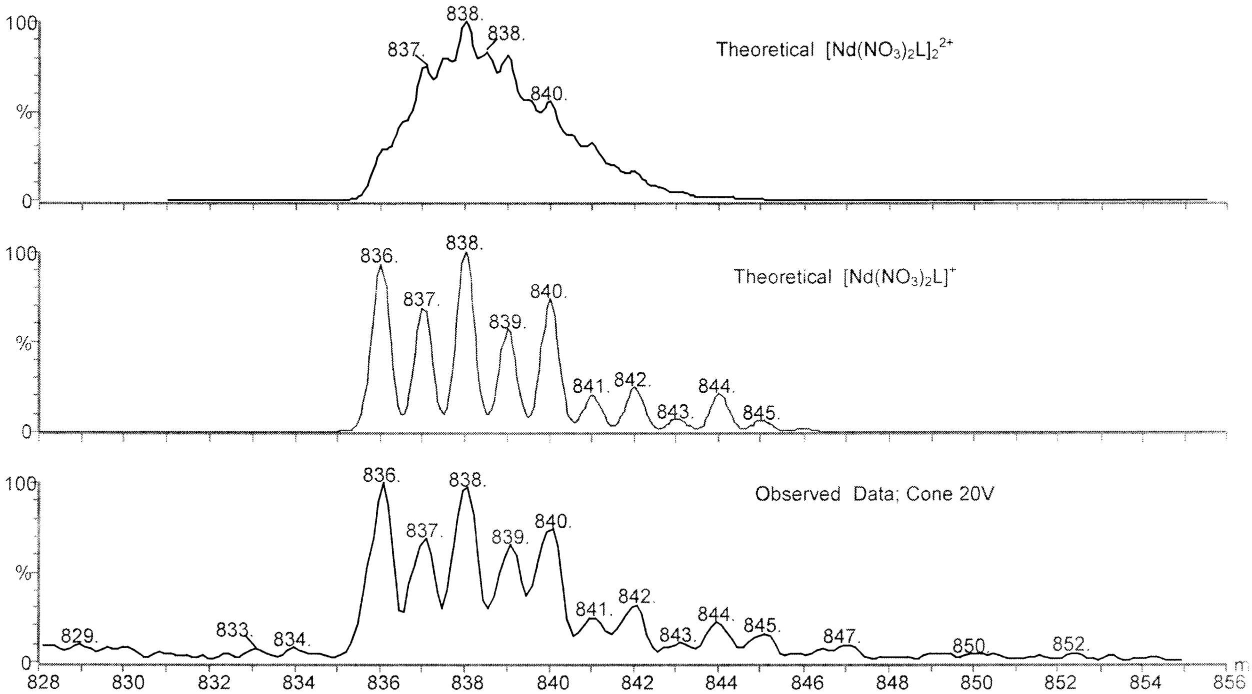


Fig. 4. Comparison of the isotope profiles for $m/z = 838$ in the positive ion electrospray mass spectrum of $[Nd(NO_3)_3L]_2$ in methanol.

calculations indicate that such a structure could indeed have a reasonable geometry about the metal with bond distances and angles which are within the normal range for lanthanides. There is, however, considerable strain imposed on the aromatic ring, with substituents forced out of the plane by as much as 26°, and in view of this it is unlikely that a simple monomer would represent the most stable structure.

4. Experimental

4.1. Preparative work

Tris(bromomethyl)mesitylene was prepared by the reaction of mesitylene, formaldehyde and hydrogen bromide in glacial acetic acid according to the literature method [6].

4.1.1. 1,3,5-(Tris(dimethylphosphonato)methyl)-mesitylene (L–Me)

Trimethylphosphite (10 ml) was added dropwise to a solution of the tribromide (5 g) in 50 ml xylene at 100 °C under a gentle stream of nitrogen. Vigorous reaction occurred on each addition. Removal of the solvent under reduced pressure left a pale brown viscous oil which solidified on standing to give a white solid. NMR data (H_2O) $\delta^{31}P$ 32.6, ^{13}C 18.6 (s) ($-CH_3$ aromatic), 28.4 (d) $^{1}J_{pc} = 136$ Hz, (PCH_2), 54.3 (d) $^{2}J_{pc} = 5$ Hz, (OCH_3) 128.1 (m), 137.5 (m) (aromatics).

4.1.2. 1,3,5-(Tris(diethylphosphonato)methyl)-mesitylene (L–Et)

Triethylphosphite (15 ml) was added dropwise to a solution the tribromide (5 g) in xylene at 120 °C under a gentle flow of nitrogen. The mixture was heated until evolution of ethyl bromide ceased and the volatiles removed under reduced pressure to leave a viscous oil which crystallised on standing. NMR data (H_2O) $\delta^{31}P$ 28.2, ^{13}C 17.0 (d) ($-OCH_2CH_3$) $^{3}J_{pc} = 3$ Hz, 18.8 (s) (CH_3 aromatic) 29.6 (d) $^{1}J_{pc} = 140$ Hz, ($-CH_2P$) 64.2 (s) ($-OCH_2CH_3$), 128.6 (m), 137.1 (m) (aromatics).

4.1.3. 1,3,5-(Tris(diisopropylphosphonato)methyl)-mesitylene (L–Prop)

Triisopropylphosphite (35 ml) were added to a solution of the tribromide (5 g) in xylene at 120 °C. After an hour the volatiles were removed under reduced pressure to leave a pale brown viscous oil. NMR data (H_2O) $\delta^{31}P$ 25.4, ^{13}C 18.7 (s) (CH_3 aromatic), 20.5 (d) $^{3}J_{pc} = 3$ Hz (CH_3 (^{i}Pr)), 31.1 (d) $^{1}J_{pc} = 140$ Hz, 70.7 (s) (CH), 128.2 (m), 136.3 (m) (aromatics).

4.1.4. 1,3,5-(Tris(dibutylphosphonato)methyl)-mesitylene (L–Bu)

Tributylphosphite (30 ml) was added in small portions to a solution of the tribromide (5 g) in boiling xylene. After 30 min the volatiles were removed under reduced pressure to leave a viscous colourless oil. NMR data ($CDCl_3$) $\delta^{31}P$ 26.7, ^{13}C 13.8 (s) (CH_3(Bu)), 183 (s) (CH_2(Bu)), 19.0 (s) (CH_3 aromatic) 29.6 (d) $^{1}J_{pc} = 139$ Hz (PCH_2), 32.9 (CH_2(Bu)), 65.9 (s) (OCH_2(Bu)).

The complexes were prepared by reaction of hydrated lanthanide nitrates with an excess of the ligands in boiling acetonitrile. On mixing the solutions the products crystallised as solids (L–Me, L–Et) in 60–80% and 60–95% yields, respectively. With L–Prop and L–Bu viscous oils were obtained which were not investigated further.

In a typical preparation $Pr(NO_3)_3 \cdot 6H_2O$ (0.20 g 0.46 mmol) was dissolved in 10 ml warm acetonitrile. This solution was added to a refluxing solution of L–Et (0.26 g 0.46 mmol) in 15-ml acetonitrile. Crystallisation occurred during the addition and the solution was allowed to cool to room temperature. The product was filtered, washed with acetonitrile and dried at the pump to give 0.24 g (58%). Analysis (%) Required (found) C 32.12(31.44), H 5.05(5.10), N 4.68(4.54). Infrared (KBr disc)/cm^{-1} 1504 (s), 1290 (s) (NO), 1176 (s) (P=O), 1045 (s) (P–O).

5. Mass spectrometry

Electrospray mass spectra were obtained by the EPSRC National Mass Spectrometry Service Centre at the University of Wales, Swansea as described previously [11]. Assignments are based on the *m/z* ratio and the comparison between observed and calculated isotope distribution patterns which are particularly characteristic for some of the lanthanides.

6. X-ray crystallography

All data were collected on a Bruker P4 diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). Data were corrected for Lorentz and polarisation effects and an empirical absorption correction was applied. The structure was solved by Patterson methods and refined by full-matrix least-squares on F^2 using SHELXTL [12]. All carbon bonded hydrogen atoms were included in calculated positions (C–H = 0.96 Å) with isotropic displacement parameters set to I.5 $U_{eq}(C)$ for methyl H atoms and I.2 $U_{eq}(C)$ for all other H atoms.

7. Molecular modelling

Calculations were carried out using the SPARTAN V (version 4.1) package on a dedicated Silicon Graphics work station.

8. Supplementary material

Crystallographic data may be obtained from the Cambridge Crystallographic Data Centre, No. 197633 for CIF files. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

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References

[1] E.M. Bond, X. Gan, J.R. Fitzpatrick, R.T. Paine, J. Alloys Compd. 271–273 (1998) 172.

[2] X. Gan, E.N. Duesler, R.T. Paine, P.H. Smith, Inorg. Chim. Acta 247 (1996) 29.

[3] K.-W. Kim, S.-H. Kim, K.-C. Song, E.-H. Lee, J.-H. Yoo, J.Radioanal. Nucl. Chem. 253 (2002) 3.

[4] Y.M. Kulyako, D.A. Malikov, M.K. Chmutova, M.N. Litvina, B.F. Myasoedov, J. Alloys Compd. 271–273 (1998) 760.

[5] C. Hill, C. Madic, P. Baron, M. Ozawa, Y. Tanaka, J. Alloy Compd. 271–273 (1998) 159.

[6] J. Avada, M. Pankova, P. Holy, M. Tichy, Synthesis–Stuttgart (1994) 1132.

[7] W.M. Pankou, K. Vershst, G. von Kiederawski, J.C.S. Chem. Commun. (2001) 519.

[8] Y. Yuan, R. Xiao, X.Y. Su, H. Yu, J.S. You, R.G. Xie, J. Chem. Res. (2002) 267.

[9] J. Fawcett, A.W.G. Platt, D. Simpson, D.R. Russell, Inorg. Chim. Acta 223 (1994) 43.

[10] A.M.J. Lees, J.M. Charnock, R.A. Kresinski, A.W.G. Platt, Inorg. Chim. Acta 312 (2001) 170.

[11] J. Fawcett, A.W.G. Platt, D.R. Russell, Polyhedron 21 (2002) 287.

[12] SHELXTL, an integrated system for solving, refining and displaying crystal structures. Version 5.10, Bruker Analytical X-ray Systems, Madison, WI, USA, 1997.