



# Reaction of a tetranuclear *N,N*-di-*iso*-propylcarbamato complex of cerium(III) with dioxygen: synthesis and X-ray characterization of both the oxidation product and its precursor

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Dedicated to Professor Renato Ugo on the occasion of his 65th birthday anniversary, in recognition of his outstanding scientific contributions

## Abstract

The tetranuclear *N,N*-di-*iso*-propylcarbamato complex of cerium(III)  $\text{Ce}_4(\text{O}_2\text{CN}^i\text{Pr}_2)_{12}$ , **1**, has been synthesized and its crystal structure solved through X-ray diffraction methods. The oxidation of the cerium(III) complex by dioxygen produces the  $\mu_3$ -oxo tetranuclear cerium(IV) derivative  $\text{Ce}_4(\mu_3\text{-O})_2(\text{O}_2\text{CN}^i\text{Pr}_2)_{12}$ , **2**, which has been characterised by single crystal X-ray diffractometry. Structural rearrangements on going from the cerium(III) derivative to the corresponding cerium(IV) product have been established. This is the first case of a  $\mu$ -oxo-carbamato complex being obtained by oxygenation, whereby product and precursor maintain the basic structural features.

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**Keywords:** Cerium; Carbamate; Oxidation;  $\mu$ -Oxo

## 1. Introduction

Increasing interest has been directed to lanthanide complexes due to their relevance in several areas of fundamental and applied inorganic chemistry [1–7].

Earlier papers from these laboratories [8] have reported a series of isotypical *N,N*-dialkylcarbamato complexes of lanthanides(III), of formula  $\text{Ln}_4(\text{O}_2\text{CN}^i\text{Pr}_2)_{12}$  ( $\text{Ln} = \text{Nd, Gd, Ho, Yb}$ ). The observed

lanthanide contraction in this series of molecular complexes was suggested to correspond to an increasing bond strength along the lanthanide series. This paper deals with our efforts to extend this series of compounds to the elements with a lower atomic number, notably cerium, which is of importance as a catalyst for the oxidation reactions of organic substrates [9–11]. This paper reports the results of our studies on  $\text{Ce}_4(\text{O}_2\text{CN}^i\text{Pr}_2)_{12}$  and on its reaction with dioxygen to give the tetranuclear  $\text{Ce}_4(\mu_3\text{-O})_2(\text{O}_2\text{CN}^i\text{Pr}_2)_{12}$ . The  $\mu_n$ -oxo derivatives containing the dialkylcarbamato supporting ligand have normally been obtained by hydrolytic processes [12,13]. On the contrary, this paper sets a clear-cut example of two structurally defined systems in different oxidation states, obtained through an oxygenation process, in the absence of water. The

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readily obtained, well-defined molecular compounds reported in this paper are predicted to be useful in grafting reactions of cerium(III) and cerium(IV) on inorganic matrices. The grafting methodology pertaining to *N,N*-dialkylcarbamato complexes as precursors has been established earlier [14–16].

## 2. Experimental

### 2.1. General

All preparations were carried out in standard Schlenk tubes. All solvents were freshly distilled over conventional drying agents under dinitrogen and all reactions were carried out under dinitrogen, unless otherwise stated. Thionyl chloride and  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$  were C. Erba products used as received. Elemental analyses (C, H, N) were performed by Laboratorio di Microanalisi, Facoltà di Farmacia, Università di Pisa, with a C. Erba mod. 1106 elemental analyzer. IR spectra were measured with a Perkin-Elmer FT-IR mod. 1725X spectrophotometer.

### 2.2. Synthesis of $\text{CeCl}_3(\text{DME})$

Cerium(III) chloride  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$  (8.80 g, 23.6 mmol) was suspended in dimethoxyethane (DME) (250 cm<sup>3</sup>) and thionyl chloride (70 cm<sup>3</sup>, 962 mmol) was added dropwise at room temperature. After 3 days of stirring, the suspension was filtered under dinitrogen and the colourless solid thus obtained was dried in vacuo (ca. 10<sup>-2</sup> Torr) at room temperature for about 4 h (7.73 g, 97% yield). Anal. Calc. for  $\text{C}_4\text{H}_{10}\text{CeCl}_3\text{O}_2$ : Ce, 41.6; Cl, 31.6. Found: Ce, 41.8; Cl, 31.3. IR (Nujol mull, most significant bands in the 1300–1000 cm<sup>-1</sup> range): 1282(w), 1233(w), 1185(vw), 1107(m), 1082(m), 1038(s), 1001(w).

### 2.3. Preparation of compound 1

By operating under a dinitrogen atmosphere in a 250 cm<sup>3</sup> flask, di-*iso*-propylamine (11.6 cm<sup>3</sup>, 82.1 mmol) and 70 cm<sup>3</sup> of toluene were stirred under a carbondioxide atmosphere until the CO<sub>2</sub> uptake was over. The chloride  $\text{CeCl}_3(\text{DME})$  (2.765 g, 8.2 mmol) was then added and the mixture stirred under CO<sub>2</sub> at 40 °C for 1 h. When the absorption of carbondioxide

had ceased, the mixture was filtered at room temperature under dinitrogen. The little soluble colourless solid  $[\text{NH}_2^i\text{Pr}_2]\text{Cl}$  was discarded, while the solvent and the excess of amine were removed from the filtrate in vacuo (ca. 10<sup>-2</sup> Torr of residual pressure at the end of the process). The pale yellow residue was transferred into sealed ampoules under dinitrogen (1.53 g, 32% yield). Anal. Calc. for  $\text{C}_{84}\text{H}_{168}\text{Ce}_4\text{N}_{12}\text{O}_{24}$ : Ce, 24.5. Found: Ce, 24.7. Colourless crystals of the product were obtained by recrystallization from heptane. IR (Nujol mull, most significant bands in the 1600–1000 cm<sup>-1</sup> range): 1576(m), 1558(m), 1507(s), 1354(vs), 1260(w), 1211(w), 1162(m), 1135(m), 1063(m), 1031(m), 900(w), 869(w), 797(s), 695(w), 615(m), 604(m), 507(m).

### 2.4. Preparation of compound 2

A suspension of  $\text{Ce}_4(\text{O}_2\text{CN}^i\text{Pr}_2)_{12}$  (2.19 g, 3.82 mmol of cerium) in 20 cm<sup>3</sup> of heptane, maintained at 22.5 °C, was exposed to dry dioxygen for about 15 h. The yellow oxidation product, well soluble even in heptane at -30 °C, was recovered by completely removing the volatiles in vacuo (1.60 g, 72.2% yield). The product was recrystallized from hot heptane. IR (Nujol mull, most significant bands in the 1600–1000 cm<sup>-1</sup> range): 1562(m), 1538(m), 1506(vs), 1350(vs), 1261(m), 1209(m), 1162(m), 1134(w), 1097(m), 1064(m), 1033(m), 899(w), 871(w), 799(s), 637(m), 615(w), 604(m). Colourless crystals of **1**, exposed to dioxygen at room temperature changed their colour to yellow, apparently maintaining their morphology. However, an X-ray diffraction experiment showed the oxidized product to be amorphous.

### 2.5. X-ray crystallographic studies

The X-ray diffraction experiments were carried out at room temperature ( $T = 293\text{ K}$ ) by means of a Bruker P4 diffractometer operating with a graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ). Samples were sealed in glass capillaries under an atmosphere of dinitrogen saturated with the crystallization solvent. The intensity data collection was carried out with the  $\omega/2\theta$  scan mode, collecting a redundant set of data. Three standard reflections were measured every 97 measurements to check sample

Table 1  
Crystal data and structure refinement

Empirical formula	C <sub>84</sub> H <sub>168</sub> Ce <sub>4</sub> N <sub>12</sub> O <sub>24</sub> ( <b>1</b> )-0.5C <sub>7</sub> H <sub>16</sub>	C <sub>84</sub> H <sub>168</sub> Ce <sub>4</sub> N <sub>12</sub> O <sub>26</sub> ( <b>2</b> )
Crystal size (mm <sup>3</sup> )	0.07 × 0.30 × 0.50	0.13 × 0.28 × 0.50
Formula weight	2340.88	2322.78
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
a (Å)	15.931(2)	14.835(1)
b (Å)	17.942(4)	15.444(1)
c (Å)	22.494(3)	15.502(2)
α (°)	101.28(1)	60.335(7)
β (°)	95.73(1)	83.977(8)
γ (°)	94.04(1)	68.421(6)
Volume (Å <sup>3</sup> )	6247(2)	2856.8(5)
Z	2	1
D <sub>calc</sub> (g cm <sup>-3</sup> )	1.244	1.350
μ (mm <sup>-1</sup> )	1.490	1.629
F(000)	2418	1196
θ range (°); compl. (%)	2.14–22.00, 99.2	2.02–22.50, 94.0
Reflections collected	17272	8010
Independent reflections	15195 [R <sub>int</sub> = 0.0345]	7019 [R <sub>int</sub> = 0.0123]
Data/restraints/parameters	15195/0/1153	7019/0/568
Goodness-of-fit <sup>a</sup> on F <sup>2</sup>	1.013	1.018
Final R indices <sup>a</sup> [I > 2σ(I)]	R <sub>1</sub> = 0.050, wR <sub>2</sub> = 0.128	R <sub>1</sub> = 0.025, wR <sub>2</sub> = 0.053
R indices <sup>a</sup> (all data)	R <sub>1</sub> = 0.086, wR <sub>2</sub> = 0.150	R <sub>1</sub> = 0.035, wR <sub>2</sub> = 0.057
Δρ, max–min (e Å <sup>-3</sup> )	0.839, –0.895	0.378, –0.271

<sup>a</sup> Goodness-of-fit =  $[\sum[w(F_o^2 - F_c^2)^2]/(N - P)]^{1/2}$ , where *N*, *P* are the numbers of observations and parameters, respectively,  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $wR_2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}$ ;  $w = 1/[\sigma^2(F_o^2) + (AQ)^2 + BQ]$ , where  $Q = [\text{MAX}(F_o^2, 0) + 2F_c^2]/3$ .

decay. The intensities were corrected for Lorentz and polarisation effects and for absorption by means of a  $\psi$ -scan method [17] for compound **1** and by an integration method based on the crystal shape for compound **2** [18]. The structure solutions, obtained by means of the automatic direct methods, and the refinements, based on full-matrix least-squares on  $F^2$ , were done by means of the SHELX97 programme [18]. Data reduction of measured intensities was done by the XSCANS package [19]. Some other utilities contained in the WINGX suite [20] were also used.

As far as molecule **1** is concerned, residual electron density (about  $1.3 e \text{ \AA}^{-3}$ ) peaks were present in the difference Fourier map around the inversion centre. They were assigned to disordered heptane, whose carbon atoms were refined with an occupancy factor of 0.5, while isotropic thermal factors were introduced without constraints. The final refinement cycle was carried out by using anisotropic thermal parameters for all the ordered heavy atoms. The hydrogens of the

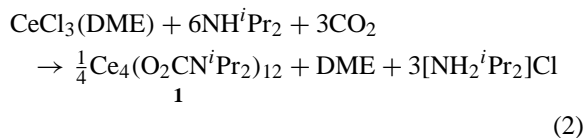
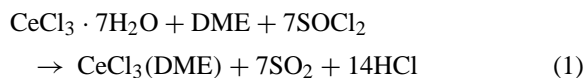
disordered solvent molecules were not introduced in calculations.

The crystal data and final reliability factors for both the structure determinations are listed in Table 1.

### 3. Results and discussion

Metal *N,N*-dialkylcarbamato complexes have been extensively studied in these laboratories [21–25] and elsewhere [26–30]. A well-established synthetic route to these complexes starts from the anhydrous metal halide to be reacted with the dialkylamine/carbondioxide system. The dimethoxyethane adduct of CeCl<sub>3</sub>, CeCl<sub>3</sub>(DME), was found to be the most appropriate starting material for the preparation of the carbamato derivative. Prior to describing the final products, it is therefore worthwhile to comment on the preparation of the precursor. The synthesis of CeCl<sub>3</sub>(DME) was carried out by treating the

commercial hydrated chloride with  $\text{SOCl}_2/\text{DME}$ . As for the stoichiometry of Eq. (1), thionyl chloride takes care of the chemical elimination of water, while DME gives the corresponding adduct. In view of the earlier results on the conversion of lanthanide oxides with the  $\text{SOCl}_2/\text{DME}$  mixture, it is believed that any possible trace of oxide or oxy-chloride being present in the commercial product could also be converted to the trichloride [31]. The final cerium-containing product of reaction (1) is little soluble in DME, see Section 2; it is therefore believed to be a polynuclear compound. In this connection, it is interesting to notice that the DME adducts of some lanthanide trichlorides with a smaller ionic radius than cerium(III), e.g.  $\text{Eu(III)}$ , were found [31,32] to be mononuclear with two DME groups per metal atom, i.e.  $\text{EuCl}_3(\text{DME})_2$ . The central metal atom is therefore seven-coordinated.



The crude product of reaction (2) was pale yellow and presumably contaminated by a small amount of an unknown impurity, which could easily be removed by recrystallization from heptane.

The molecular structure of **1** is shown in Fig. 1. The cerium(III) centres form a tetranuclear carbamate complex, similar to other lanthanides [5], but the molecular structure is less symmetrical and slightly more complex than in the previously encountered cases. While from Nd to Lu the four metal atoms are disposed at the apexes of a distorted tetrahedron (ditrion) possessing a twofold axis, in the cerium compound the tetrahedron is flattened in a sort of bent lozenge, where the maximum deviation of the cerium atoms from the mean plane is 0.326 Å.

In agreement with the greater ionic radius of  $\text{Ce}^{3+}$ , the Ce–O distances are longer than those observed in  $\text{Nd}_4(\text{O}_2\text{CN}^i\text{Pr})_{12}$  and the coordination number, which in the neodymium compound is seven for all metal atoms, is seven for three of the cerium atoms and eight for Ce(4). Table 2, which lists the Ce–O bond distances, shows that from Ce(1) to Ce(3) the

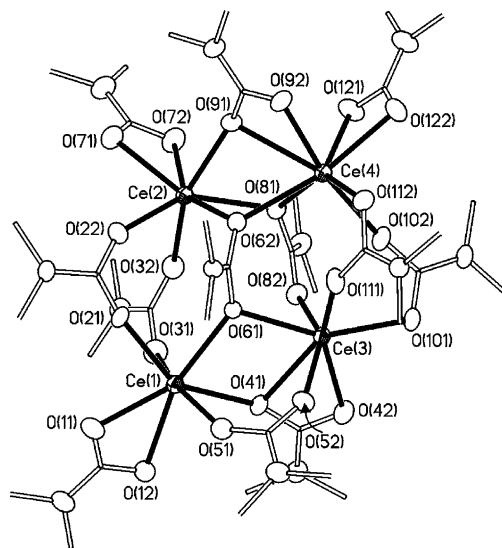


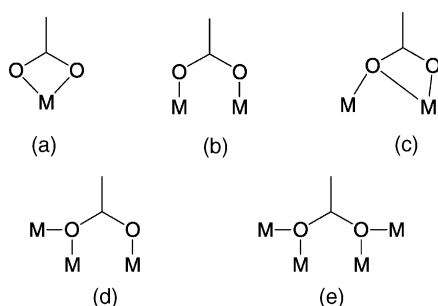
Fig. 1. View of the molecular structure of  $\text{Ce}_4(\text{O}_2\text{CN}^i\text{Pr}_2)_{12}$ . Methyl groups and carbon atoms have been omitted for clarity. Thermal ellipsoids of Ce, N and O atoms are at 30% probability.

lengths of Ce–O bonds range from 2.322 [Ce(2)] to 2.690 Å [Ce(3)], while the eight-coordinated Ce(4) shows Ce–O distances ranging between 2.405 and 2.746 Å, the shortest Ce...O nonbonding contact being 2.864 Å [O(82)].

The seven-coordinated cerium atoms, as for other lanthanide carbamates [5], have a distorted pentagonal bipyramidal geometry, while the eight-coordinated one is a distorted square antiprism. The carbamate ligands show the five ligation types sketched in

Table 2  
Ce–O bond distances (Å) in the structure of **1**

Ce(1)–O(31)	2.349(8)	Ce(3)–O(111)	2.365(7)
Ce(1)–O(21)	2.357(7)	Ce(3)–O(82)	2.368(7)
Ce(1)–O(51)	2.384(7)	Ce(3)–O(42)	2.399(7)
Ce(1)–O(11)	2.464(8)	Ce(3)–O(101)	2.408(7)
Ce(1)–O(41)	2.472(7)	Ce(3)–O(52)	2.416(7)
Ce(1)–O(12)	2.492(7)	Ce(3)–O(61)	2.507(6)
Ce(1)–O(61)	2.594(6)	Ce(3)–O(41)	2.690(7)
Ce(2)–O(32)	2.322(7)	Ce(4)–O(102)	2.405(7)
Ce(2)–O(22)	2.338(7)	Ce(4)–O(112)	2.412(7)
Ce(2)–O(91)	2.409(7)	Ce(4)–O(121)	2.429(7)
Ce(2)–O(71)	2.450(7)	Ce(4)–O(92)	2.468(7)
Ce(2)–O(81)	2.482(7)	Ce(4)–O(122)	2.490(7)
Ce(2)–O(72)	2.482(7)	Ce(4)–O(81)	2.542(7)
Ce(2)–O(62)	2.590(6)	Ce(4)–O(62)	2.653(7)
		Ce(4)–O(91)	2.746(7)



Scheme 1.

**Scheme 1.** While types a, b and d have been found earlier [5] in other lanthanide carbamates, types c and e are less usual and have been observed only in the U(IV), Cr(III) and Mg(II) derivatives [28,33,34] for type c and in a Fe(II) derivative [35] for type e.

The carbamato derivative of cerium(III), **1**, gave a yellow product of irreversible oxidation to cerium(IV). The oxidation product maintained the CO<sub>2</sub>/Ce molar ratio of 3, as in the starting material. The product of the oxidation by dioxygen was demonstrated to be the  $\mu$ -oxo derivative of cerium(IV), of formula Ce<sub>4</sub>( $\mu$ <sub>3</sub>-O)<sub>2</sub>(O<sub>2</sub>CN<sup>*i*</sup>Pr<sub>2</sub>)<sub>12</sub>, **2**.

The cerium(IV) product was recrystallized from heptane, and studied by X-ray diffraction. A schematic drawing of the molecule of **2** is shown in Fig. 2. The structure has the same architecture as U<sub>4</sub>( $\mu$ <sub>3</sub>-O)<sub>2</sub>O<sub>2</sub>CNEt<sub>2</sub>)<sub>12</sub> [33]. The molecule has

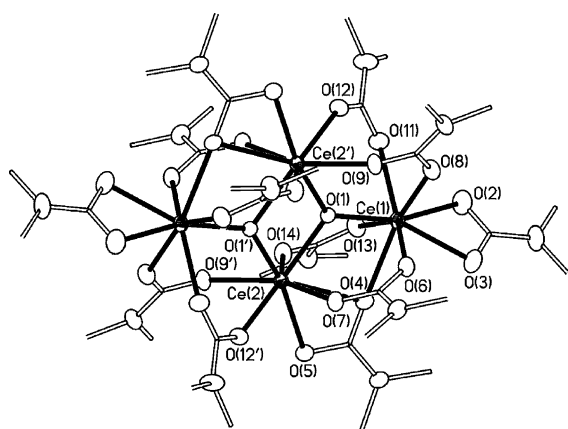


Fig. 2. View of the molecular structure of Ce<sub>4</sub>( $\mu$ <sub>3</sub>-O)<sub>2</sub>(O<sub>2</sub>CN<sup>*i*</sup>Pr<sub>2</sub>)<sub>12</sub>. Methyl groups and carbon atoms have been omitted for clarity. Thermal ellipsoids of Ce, N and O atoms are at 30% probability (see Table 3 for atom labelling).

Table 3

Ce–O bond distances (Å) in the structure of **2**

Ce(1)–O(1)	2.129(2)	Ce(2)–O(1')	2.225(2)
Ce(1)–O(8)	2.314(3)	Ce(2)–O(1)	2.249(2)
Ce(1)–O(13)	2.331(3)	Ce(2)–O(9')	2.308(2)
Ce(1)–O(6)	2.364(3)	Ce(2)–O(7)	2.318(2)
Ce(1)–O(11)	2.364(3)	Ce(2)–O(12')	2.338(2)
Ce(1)–O(3)	2.400(3)	Ce(2)–O(14)	2.341(3)
Ce(1)–O(2)	2.412(3)	Ce(2)–O(5)	2.378(3)
Ce(1)–O(4)	2.465(3)	Ce(2)–O(4)	2.643(3)

Symmetry transformations used to generate equivalent atoms: ' =  $-x + 1, -y + 2, -z$ .

a centre of symmetry so that only two independent cerium atoms are present and the four metal atoms form a perfectly planar lozenge.

Both independent cerium atoms are eight-coordinated, but their coordination geometries are slightly different. While the Ce(2) polyhedron may be considered as a distorted square antiprism, the polyhedron of Ce(1) is hardly compared with a regular or a semiregular eight-corners polyhedron. The Ce–O bond distances, which are listed in Table 3, are slightly shorter (difference  $\leq 0.05$  Å) than those found in the U(IV) compound mentioned above [33].

The oxo groups, as in the uranium compound, are trigonally coordinated with the oxygen slightly removed (0.167 Å) from the coordination plane. The carbamato ligands show only the a, b and c ligation types outlined in Scheme 1.

Inspection of the packing of **1** shows that the metal atoms are not completely embedded by the ligands, as the large tetranuclear molecules in the crystal structure of **1** leave channels and cavities which are not completely obstructed by the disordered lattice heptane, thus allowing dioxygen to permeate the solid. If we consider that the molecule of **2** can be derived from the reaction of **1** with O<sub>2</sub> with moderate rearrangements, we could anticipate that this reaction could proceed also in the solid state (vide infra). Complexes of metals of the first transition series in the oxidation state +II have been reported to react with dioxygen [36,37]. Also the oxygen uptake by *N,N*-dialkylcarbamato complexes of iron(II), R = Et, <sup>*i*</sup>Pr, Cy, has been previously studied [38,39]. On the contrary, reactions of metal complexes in the +III oxidation state with dioxygen are rare [40].

The oxidizing nature of cerium(IV) is normally so high as to limit the existence of metal complexes to

ligands which are not too easily oxidized. Moreover, stabilization of cerium(IV) is influenced by the nature of the ligand, and it has also been shown that the oxidation potential depends on the nature of the counterion in aqueous media [41–43], an alkaline medium tending to stabilize the tetrapositive cerium cation [44,45].  $\beta$ -Diketonato complexes of cerium(III) have been reported to be converted into the corresponding cerium(IV) derivatives [46] upon exposure to dioxygen, the corresponding  $\beta$ -diketonates of cerium(IV) being thus obtained [47–50], in the presence of the required amount of the  $\beta$ -diketone.

Compound **1** is readily affected by carefully pre-dried dioxygen even in the solid state. Crystalline colourless **1** was oxidized to a yellow  $\mu$ -oxo compound without apparent loss of morphology. However, the resulting product was shown to be amorphous. These data suggest that the lattice of **1** is permeable to dioxygen and easily accommodates the newly formed oxide ligands. Dioxygen probably reacts first at the surface of the solid, then diffusing to the interior driven by the gradient of chemical potential. The crystal packing of the cerium(III) precursor **1** is compatible with this possibility. It is interesting to note that an oxidative process of an antimony compound by dioxygen in the solid state has been reported to occur with retention of the crystal habitus and space group [51].

#### 4. Conclusions

Oxygenation of the cerium(III) tetranuclear compound was accompanied by no major structural change: the presence of the oxo ligand has no large influence on the structure. The carbamate group appears to be resistant to oxidation by cerium(IV), being therefore possible to classify it as an appropriate ligand for both low [24,52] and relatively high oxidation states. These complexes appear to be good candidates for their grafting on hydroxylated oxides, according to a technique already acquired in these laboratories [14–16]. Accordingly, experiments are being carried out and will be reported in a forthcoming paper.

#### 5. Supplementary material

Further details of crystal characterisation and structures refinement have been deposited in the form of

the CIF files with the Cambridge Crystallographic Data Centre, deposition references CCDC 195504 and CCDC 195505 for compounds **1** and **2**, respectively. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

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