

Systematic studies on the reactions of lanthanide trichlorides with Na[1,3-bis(trimethylsilyl)cyclopentadienyl]. Crystal structures of [1,3-(Me₃Si)₂C₅H₃]₃Ln (Ln = La, Nd, Gd, Dy)

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Abstract

Reflux of LnCl₃ with an excess amount of Na[(Me₃Si)₂C₅H₃] in THF and then in toluene gave two kinds of complexes dependent upon the size of the central metal, the tris ligand complexes of the type [(Me₃Si)₂C₅H₃]₃Ln (Ln = La, Nd, Sm, Gd or Dy) and the bis ligand complexes of the general formula [(Me₃Si)₂C₅H₃]₂LnCl₂ (Ln = Gd, Dy, Y, Er or Yb). Neither THF coordinated nor THF ring-opened product was isolated. These compounds were fully characterized by elemental analyses, IR, MS and ¹H NMR (for diamagnetic metals) spectroscopy. The structures of the tris ligand complexes of La, Nd, Gd and Dy have been further confirmed by single-crystal X-ray diffraction analyses. Each of the three (Me₃Si)₂C₅H₃ ligands is η⁵-bonded to the central lanthanide atom to form the trigonal planar geometry with an average (ring centroid)–metal–(ring centroid) bond angle of 120°. The variations in the metal–carbon bond distances are consistent with the phenomenon of lanthanide contraction. © 1997 Elsevier Science S.A.

Keywords: Crystal structure; Cyclopentadienyl; Chloride; Trimethylsilyl; Organolanthanide

1. Introduction

Triscyclopentadienyl lanthanide complexes have very interesting structural features in the solid state [1,2]. Their structural models are dependent upon the combination of the sizes of the central metal and the ligands. Variations in structure can occur from zigzag polymers ((C₅H₅)₃Ln, Ln = La [3], Nd [4], Sm [5,6]) through tetramers ((MeC₅H₄)₃Ln, Ln = La [7], Ce [8], Nd [9]) to monomers ((Me₃Si)₂C₅H₃]₃Ln, Ln = Ce [8], Sm [10]; (C₅Me₄H)₃Ln, Ln = La [11], Tb [12]; (C₅Me₄R)₃Sm, R = Me [13], Et [14,15]; (C₁₁H₁₅)₃Nd [16]; (MeOCH₂CH₂C₅H₄)₃Ln, Ln = La, Pr, Nd, Sm, Gd [17]; (Me₂NCH₂CH₂C₅H₄)₃Ln, Ln = La, Nd [18]. This rich coordination chemistry has drawn much attention and many efforts have been recently devoted to the synthesis of very sterically crowded metallocene complexes of 4f elements [1,2,11,14,15]. In case of C₅Me₅⁻ (Cp[#]) ligand, only Cp₃[#]Sm is known, which was syn-

thesized by the oxidation of corresponding divalent species or the reaction of (Cp₂[#]SmH)₂ with tetramethylfulvalene, rather than via the general metathesis methods [13–15]. Reaction of LnCl₃ with three equivalents of Cp[#]Na in THF afforded only the THF ring-opened product Cp₂[#]LnO(CH₂)₄Cp[#](THF) regardless of the lanthanide metals [19]. Under the similar reaction conditions, treatment of LnCl₃ with C₅Me₄H⁻ (Cp[#]) that is slightly smaller than Cp[#] has led to the successful isolation of Cp₃[#]Ln for Ln = La to Tb, but not for the smaller lanthanide metals [11,12]. The (Me₃Si)₂C₅H₃ (Cp^{''}) ligand that was suggested to be more sterically demanding than Cp[#] [20] has been demonstrated to be very useful in developing early lanthanide chemistry [21–23]. Cp^{''} can form the tris ligand complexes with early lanthanide metals (La, Ce, Nd or Sm) [8,10,24–26]. In the presence of alkali metals, complex Cp₃^{''}Ln can carry out interesting reactions with dimethoxyethane (DME) [25] and benzene [24]. Cp₃^{''}Ln is also good starting materials for the synthesis of organolanthanide fluoride [26]. These recent results encourage us to do

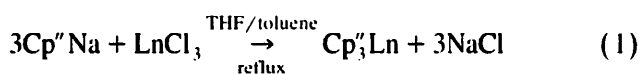
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the systematic studies on the reactions of $\text{Cp}^{\prime\prime}\text{Na}$ with LnCl_3 . It is also interesting to know the steric limits in approaching tris[bis(trimethylsilyl)cyclopentadienyl] lanthanide complexes, and to compare the similarities and the differences between Cp^{\prime} , $\text{Cp}^{\#}$ and $\text{Cp}^{\prime\prime}$ systems.

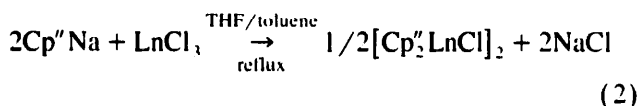
2. Results and discussion

2.1. Synthesis and characterization

The early lanthanocene complexes of the type $\text{Cp}_3^{\prime\prime}\text{Ln}$ ($\text{Ln} = \text{La}$ [24], Ce [8,25], Nd [25], Sm [10,26]) were known and prepared from the reaction of $\text{KCp}^{\prime\prime}$ with LnCl_3 . In this approach, treatment of anhydrous LnCl_3 with excess amounts of $\text{Cp}^{\prime\prime}\text{Na}$ in THF then in toluene at reflux temperature gave the tris ligand complexes $\text{Cp}_3^{\prime\prime}\text{Ln}$ for $\text{Ln} = \text{La}$, Nd or Sm , the bis ligand complexes $[\text{Cp}_2^{\prime\prime}\text{LnCl}]_2$ for $\text{Ln} = \text{Y}$, Er or Yb and a mixture of tris/bis ligand complexes for $\text{Ln} = \text{Gd}$ or Dy according to the Eqs. (1)–(3).

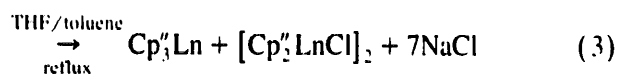


$\text{Ln} = \text{La}$ (**1**), 72%; Nd (**2**), 93%; Sm (**3**), 75%



$\text{Ln} = \text{Y}$ (**8**), 55%; Er (**9**), 56%; Yb (**10**), 55%

$3\text{LnCl}_3 + 7\text{Cp}^{\prime\prime}\text{Na}$



$\text{Ln} = \text{Gd}$ (**4**) (36%) (**6**) (11%)

$\text{Ln} = \text{Dy}$ (**5**) (8%) (**7**) (34%)

The tris ligand complex has more intense color than bis ligand complex does and the solubility of tris ligand complex is much higher than that of bis ligand complex in hexane. Therefore, they can be separated from each other by the fractional crystallization from the hexane solution. It should be pointed out that neither THF coordinated complex $\text{Cp}_3^{\prime\prime}\text{Ln}(\text{THF})$ nor THF ring-opened product $\text{Cp}_2^{\prime\prime}\text{LnO}(\text{CH}_2)_4\text{Cp}^{\prime\prime}(\text{THF})$, was detected in any cases by NMR spectroscopy, and no tris ligand complex was isolated for $\text{Ln} = \text{Y}$, Er or Yb even if reflux of LnCl_3 with a large excess of $\text{Cp}^{\prime\prime}\text{Na}$ in *p*-xylene for 3 days. These results indicate that $\text{Cp}^{\prime\prime}$ plays a similar role to $\text{Cp}^{\#}$ rather than to Cp^{\prime} at least with respect to these metathesis reactions. The formation of tris ligand complexes is getting more difficult from Sm to Dy , which is consistent with the decreasing of the ionic radii of the metals. This variation should be gradual and continuous. The above results suggest that a suitable combination of

the bulky π ligand and the size (and hence oxidation state) of the central metal is the key factor to success in making a monomeric trivalent lanthanide metallocene.

The formation of alkali–metal–halide adducts is a common feature of organolanthanide chemistry involving the cyclopentadienyl ligands [1,2]. Reaction of $\text{Cp}^{\prime\prime}\text{Li}$ with LnCl_3 in a molar ratio of 2:1 gave the adduct of the general formula $[\text{Cp}_2^{\prime\prime}\text{Ln}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2]$, followed by the sublimation at $240\text{--}260^\circ\text{C}/10^{-3}$ torr to yield $[\text{Cp}_2^{\prime\prime}\text{Ln}(\mu\text{-Cl})_2]$ [21,23]. The synthetic route reported here (Eq. (2)) can avoid the possible formation of alkali–metal–chloride adducts and directly produce the target dimeric complex of the type $[\text{Cp}_2^{\prime\prime}\text{Ln}(\mu\text{-Cl})_2]$, which is more economic and convenient than the known procedures. Recrystallization of $[\text{Cp}_2^{\prime\prime}\text{Ln}(\mu\text{-Cl})_2]$ from THF/hexane mixture does not form the monomeric THF coordinated complex $\text{Cp}_2^{\prime\prime}\text{LnCl}(\text{THF})$, indicating that the donor solvent like THF may be involved in the solubilizing process, but this interaction is labile and insufficiently strong to prevail in the solid state.

The synthesized complexes were characterized by various spectroscopies. The molecular structures of compounds **1**, **2**, **4** and **5** have been confirmed by X-ray analyses. It is noteworthy that the melting points of $\text{Cp}_3^{\prime\prime}\text{Ln}$ are lower than those of $[\text{Cp}_2^{\prime\prime}\text{LnCl}]_2$ by $60\text{--}110^\circ\text{C}$, which serves a useful tool in the rapid distinguishing tris ligand from bis ligand complexes.

2.2. Molecular structures of compounds **1**, **2**, **4** and **5**

X-ray crystal structure analyses reveal that compounds **1**, **2**, **4** and **5** are isostructural, and compounds **1** and **2**, **4** and **5** are isomorphous, respectively. Less symmetry is found in the molecular structures of **4** and **5** probably due to the highly crowded environment of smaller metal ions. To our knowledge, there are no structurally characterized examples of nine-coordinate cyclopentadienyl-gadolinium and -dysprosium compounds reported in the literature. Fig. 1 shows the representative structure for the tris ligand complexes. As shown in Fig. 1, each of the three $\text{Cp}^{\prime\prime}$ ligands is η^5 -bonded to the central lanthanide atom to form the trigonal planar geometry (considering the centroid of a cyclopentadienyl ring as occupying one coordination site) with an average (ring centroid)–metal–(ring centroid) bond angle of 120° . Thus, the formal coordination number of the lanthanide atom is nine. The trimethylsilyl groups are evenly located above and below the trigonal plane to form a protecting shell that shields the metal center from intermolecular interactions, which is a key to make unsolvated monomeric compounds.

Table 1 lists the selected bond distances and angles for $\text{Cp}_3^{\prime\prime}\text{Ln}$. The average $\text{La}\text{--C}$ distance in **1** is 2.852 (8) Å as compared to 2.83 (4) Å in $\text{Cp}_3^{\prime\prime}\text{Ce}$ [8], 2.798 (2) Å in **2**, 2.76 (4) Å in **3**, 2.740 (6) Å in **4** and 2.713 (6) Å in **5**. The decreases of the above values in going from

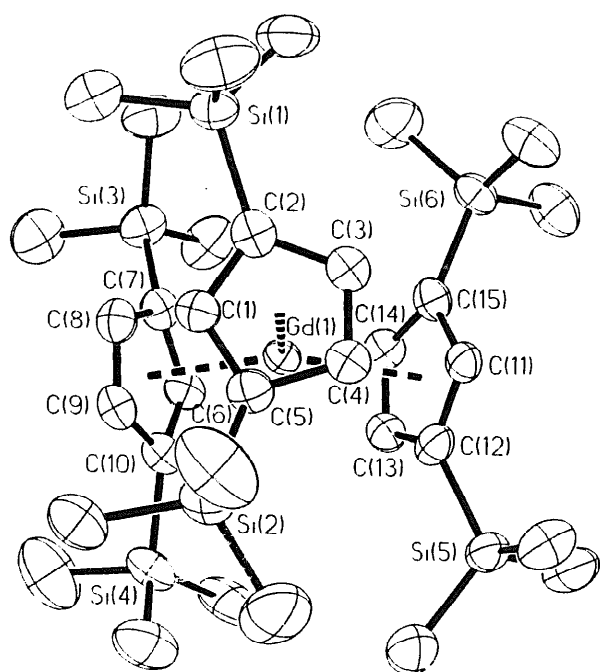


Fig. 1. Perspective view of the molecular structure of **4**. All hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at the 35% probability level.

La to Dy are those expected from the decreases in the nine-coordinate metals' ionic radii [27]. For instance, a change of lanthanum for cerium makes the average metal–C distance shorter by 0.022 Å, which is consistent with the 0.02 Å difference in the ionic radii of lanthanum and cerium [27]. By using Raymond and Eigenbrot's method [28], the effective ionic radius of the Cp^{''} in Cp₃Ln was found to be 1.632 ± 0.004 Å. This value is rather close to the one suggested for the cyclopentadienyl ligand, 1.64 ± 0.04 Å [28], and 1.64 Å for Cp^{*} ligand [29], implying that these ligands are participating in the same type of bonding interaction with the lanthanide metals, namely ionic. The average La–C distance (2.852 (8) Å) in the present nine-coordinate complex is similar to the 2.840 (6) Å in (C₅Me₄H)₃La [11], which is indistinguishable from those in ten- or eleven-coordinate trivalent lanthanum complexes in the range of 2.82–2.86 Å [17,18]. The average Nd–C, Gd–C and Dy–C distances fall in the

range normally observed for the cyclopentadienyl-based organolanthanide compounds [9,16,30]. It should be noted that unlike those observed in the Ce [8], Sm [10] and complex **5**, there is no regular pattern of long distances associated with the sterically crowded positions in compounds **1**, **2**, and **4**.

3. Conclusion

This ligand compounds of the type Cp₃Ln can be prepared for Ln = La to Dy, but not for the smaller metals. This study suggests that Cp^{''} should be less sterically demanding than Cp^{*} [20] and be comparable to Cp[#]. It is notable that although organolanthanide analogues are often isostructural and isomorphous, exceptional cases can be found in very sterically crowded compounds such as Cp₃Ln. In addition, the synthetic route to [Cp₂LnCl]₂ is also informative.

4. Experimental section

4.1. General procedure

All experiments were performed under an atmosphere of dry dinitrogen using standard Schlenk or cannula techniques, or in a glovebox. All solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. Anhydrous lanthanide chlorides were prepared from the hydrates by standard procedures [31]. Cp^{''}Na was prepared by the literature methods [32]. All other chemicals were purchased from Aldrich Chemical and used as received unless otherwise noted. Infrared spectra were obtained on a Perkin–Elmer 1600 Fourier transform spectrometer. Mass spectra were recorded on a HP5989A spectrometer. ¹H NMR spectra were recorded on a Bruker WM-250 spectrometer. All melting points are uncorrected and were taken under nitrogen in the sealed capillaries.

4.2. Preparation of Cp₃La (**1**)

In a carefully dried Schlenk flask, Cp^{''}Na (19.5 ml of a 0.57 M solution in THF, 11.11 mmol) was added to a

Table 1
Selected bond distances (Å) and angles (°) for Cp₃Ln

Ln	La	Ce	Nd	Sm	Gd	Dy
Ionic radius ^a (Å)	1.216	1.196	1.163	1.132	1.107	1.083
Average Ln–C	2.852 (8)	2.83 (4)	2.789 (2)	2.76 (4)	2.740 (6)	2.713 (6)
Average Ln–Cent ^b	2.600	2.57	2.525	2.486	2.463	2.432
Average Cent–Ln–Cent	120	120	120	120	120	120
Reference	This work	[8]	This work	[10]	This work	This work

^aSee Ref. [27].

^bCent: centroid of the cyclopentadienyl ring.

stirring suspension of LaCl_3 (0.887 g, 3.62 mmol) in 20 ml of THF. The reaction mixture was then refluxed under stirring for 24 h. After removal of the solvent, sublimation of the residue solid at 200–250°C/10⁻² torr gave **1** as colorless crystals (2.0 g, 72%), m.p. 157–159°C. Anal. Calcd. for $\text{C}_{33}\text{H}_{63}\text{LaSi}_6$: C, 51.65; H, 8.29; La, 18.10. Found: C, 51.43; H, 8.18; La, 18.30. ¹H NMR (C_6D_6): δ 6.68 (s, 2H), 6.49 (s, 1H), -0.08 (s, 18H). MS (EI): m/z (%) = 751 (2) [$M\text{-Me}$]⁺, 693 (2) [$M\text{-SiMe}_3$]⁺, 557 (100) [$M\text{-Cp}''$]⁺, 73 (81) [SiMe_3]⁺. IR (KBr, cm^{-1}): 3076w, 3053w, 2951s, 2898s, 1436s, 1404m, 1319m, 1244s, 1210m, 1079s, 940s, 865vs, 750vs, 700s, 630s.

4.3. Preparation of $\text{Cp}''_3\text{Nd}$ (**2**)

A THF solution of $\text{Cp}''\text{Na}$ (15.0 ml, 7.87 mmol) was added to the stirring suspension of NdCl_3 (0.57 g, 2.25 mmol) in 10 ml of THF at room temperature. The mixture was stirred at room temperature overnight. After removal of the THF and addition of dry toluene (25 ml), the reaction mixture was then refluxed for 3 days. Toluene was removed and the green residue was extracted with *n*-hexane (3 × 30 ml). Concentration of the hexane solution gave **2** as green crystals (1.58 g, 93%), m.p. 192–194°C. Complexometric anal. Calcd. for $\text{C}_{33}\text{H}_{63}\text{NdSi}_6$: Nd, 18.67. Found: Nd, 18.62. MS (EI): m/z (%) = 739 (2) [$M\text{-2Me}$]⁺, 560 (12) [$M\text{-Cp}''$]⁺, 351 (3) [$\text{Cp}''\text{Nd}$]⁺, 73 (100) [SiMe_3]⁺. IR (KBr, cm^{-1}): 3080w, 3056w, 2956s, 2897s, 1437s, 1403m, 1319m, 1247s, 1206m, 1079s, 921s, 834vs, 777s, 750s, 689m, 639m.

4.4. Preparation of $\text{Cp}''_3\text{Sm}$ (**3**)

This compound was prepared in an analogous manner to **2** and isolated as orange crystals in 75% yield, m.p. 182–184°C. All other analytical data including the unit cell parameters are identical with the known one [10].

4.5. Preparation of $\text{Cp}''_3\text{Gd}$ (**4**) and $[\text{Cp}''_2\text{GdCl}]_2$ (**6**)

A THF solution of $\text{Cp}''\text{Na}$ (14.3 ml, 4.87 mmol) was added to the stirring suspension of GdCl_3 (0.37 g, 1.40 mmol) in 15 ml of THF at room temperature. The mixture was refluxed overnight. After removal of the THF and addition of dry toluene (30 ml), the reaction mixture was then refluxed for 2 days. Toluene was removed and the pale-yellow residue was extracted with *n*-hexane (3 × 30 ml). Removal of two thirds of the hexane solution at room temperature gave colorless crystals which were identified to be $[\text{Cp}''_2\text{GdCl}]_2$ [**23**] (0.090 g, 11% based on GdCl_3), m.p. 295–297°C. The

filtrate was then cooled down to -20°C to yield **4** as pale-yellow crystals (0.40 g, 36% based on GdCl_3), m.p. 192–194°C. Anal. Calcd. for $\text{C}_{33}\text{H}_{63}\text{GdSi}_6$: C, 50.44; H, 8.08; Gd, 20.02. Found: C, 50.22; H, 7.46; Gd, 19.97. MS (EI): m/z (%) = 770 (1) [$M\text{-Me}$]⁺, 712 (1) [$M\text{-SiMe}_3$]⁺, 576 (29) [$M\text{-Cp}''$]⁺, 73 (100) [SiMe_3]⁺. IR (KBr, cm^{-1}): 3087w, 3058w, 2954s, 2899m, 1437m, 1247s, 1078s, 923s, 832vs, 781s, 751s.

4.6. Preparation of $\text{Cp}''_3\text{Dy}$ (**5**) and $[\text{Cp}''_2\text{DyCl}]_2$ (**7**)

The procedures are the same as those described in Section 4.5. using DyCl_3 (0.22 g, 0.83 mmol). The fractional crystallization at room temperature gave pale-yellow crystals which were characterized to be **7** [**23**] (0.17 g, 34% based on DyCl_3), m.p. 310–312°C, and afforded **5** as yellow crystals at -20°C (0.05 g, 8% based on DyCl_3), m.p. 198–200°C. Anal. Calcd. for $\text{C}_{33}\text{H}_{63}\text{DySi}_6$: C, 50.11; H, 8.03. Found: C, 49.82; H, 7.98. MS (EI): m/z (%) = 776 (5) [$M\text{-Me}$]⁺, 582 (6) [$M\text{-Cp}''$]⁺, 373 (2) [$M\text{-2Cp}''$]⁺, 73 (100) [SiMe_3]⁺. IR (KBr, cm^{-1}): 3089w, 3059w, 2954s, 2898m, 1438m, 1247s, 1079s, 923s, 831vs, 783s, 751s.

4.7. Preparation of $[\text{Cp}''_2\text{YCl}]_2$ (**8**)

The method as for **2** using YCl_3 (0.43 g, 2.20 mmol). The product formed colorless crystalline from hexane. Recrystallization from THF/hexane gave colorless crystals (0.66 g, 55%), m.p. 324–326°C. Anal. Calcd. for $\text{C}_{44}\text{H}_{84}\text{Cl}_2\text{Si}_8\text{Y}_2$: C, 48.55; H, 7.78; Y, 16.36. Found: C, 48.04; H, 8.12; Y, 16.61. ¹H NMR (C_6D_6): δ 6.75–6.60 (m, 3H), 0.04 (s, 18H). MS (EI): m/z (%) = 542 (7) [$1/2 M$]⁺, 527 (74) [$1/2 M\text{-Me}$]⁺, 507 (16) [$1/2 M\text{-Cl}$]⁺, 73 (100) [SiMe_3]⁺. IR (KBr, cm^{-1}): 3086w, 3063w, 2954s, 2896m, 1437m, 1251s, 1078s, 834vs, 752s.

4.8. Preparation of $[\text{Cp}''_2\text{ErCl}]_2$ (**9**)

This compound was prepared in an analogous manner to **2** and isolated as pink crystals in 56% yield. Anal. Calcd. for $\text{C}_{44}\text{H}_{84}\text{Cl}_2\text{Si}_8\text{Er}_2$: C, 42.50; H, 6.82. Found: C, 42.07; H, 6.74. MS (EI): m/z (%) = 621 (5) [$1/2 M$]⁺, 606 (56) [$1/2 M\text{-Me}$]⁺, 586 (9) [$1/2 M\text{-Cl}$]⁺, 73 (100) [SiMe_3]⁺. IR (KBr, cm^{-1}): 3090w, 3060w, 2955s, 2896m, 1438m, 1251s, 1079s, 920s, 834vs, 793m, 753s.

4.9. Preparation of $[\text{Cp}''_2\text{YbCl}]_2$ (**10**)

This compound was prepared in an analogous manner to **2** and isolated as red crystals in 55% yield. The

Table 2
Crystal data and details of data collection and structure refinement for **1**, **2**, **4** and **5**

Compound	Cp [*] ₃ La (1)	Cp [*] ₃ Nd (2)	Cp [*] ₃ Gd (4)	Cp [*] ₃ Dy (5)
Empirical formula	C ₃₃ H ₆₃ LaSi ₆	C ₃₃ H ₆₃ NdSi ₆	C ₃₃ H ₆₃ GdSi ₆	C ₃₃ H ₆₃ DySi ₆
Crystal size (mm)	0.2 × 0.2 × 0.3	0.5 × 0.6 × 0.7	0.3 × 0.4 × 0.5	0.3 × 0.4 × 0.5
<i>M</i>	767.3	772.6	785.6	790.9
Crystal class	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>Cc</i>	<i>Cc</i>	<i>P2₁/c</i>	<i>P2₁/c</i>
<i>a</i> (Å)	24.567 (1)	24.631 (1)	17.950 (1)	17.845 (4)
<i>b</i> (Å)	11.413 (1)	11.324 (1)	13.711 (1)	13.681 (3)
<i>c</i> (Å)	17.367 (1)	17.411 (1)	19.324 (1)	19.290 (4)
β (°)	117.80 (1)	117.21 (1)	112.82 (1)	112.83 (3)
<i>U</i> (Å ³)	4307.4 (14)	4319 (2)	4384 (2)	4341 (2)
<i>Z</i>	4	4	4	4
<i>D_c</i> (g cm ⁻³)	1.183	1.188	1.190	1.210
2 θ range (°)	3.0 to 55.0	3.0 to 55.0	3.0 to 55.0	4.0 to 50.0
μ (mm ⁻¹)	1.177	1.390	1.695	1.906
<i>F</i> (000)	1608	1620	1636	1644
No. of indep reflns	7721	3784	7668	5591
No. of obsd reflns ($ F > n\sigma F $)	7714 (<i>n</i> = 4)	3654 (<i>n</i> = 6)	6926 (<i>n</i> = 6)	5385 (<i>n</i> = 4)
No. of params refnd	390	415	362	379
Data-to-params ratio	19.8:1	8.8:1	19.1:1	14.2:1
Goodness of fit	1.05	1.99	2.37	1.03
<i>R_F</i>	0.054	0.058	0.052	0.032
<i>R_w</i>	0.057	0.076	0.076	0.076
$\Delta\rho_{\max}, \Delta\rho_{\min}/e \text{ \AA}^{-3}$	0.58, -1.09	0.69, -1.07	1.49, -1.89	0.69, -0.72

unit cell parameters are identical to the reported one [21].

4.10. X-ray structure determination

Single crystals suitable for X-ray studies were grown from a hexane solution at room temperature. All single crystals were sealed under N₂ and immersed in Paratone-N oil in a thin-walled glass capillary. All data were collected on a MSC/Rigaku RAXIS-IIC imaging plate using Mo-*K* α radiation from a Rigaku rotating-anode X-ray generator operating at 50 kV and 90 mA. Absorption correction was applied by correlation of symmetry-equivalent reflections using the ABSCOR program [33]. All four structures were solved by direct methods and subsequent Fourier difference techniques, and refined anisotropically for all non-hydrogen atoms by full-matrix least squares, on *F* using the Siemens SHELXTL PLUS program package (PC version) [34] or on *F*² using the SHELXL-93 [35]. All hydrogen atoms were geometrically fixed using the riding model. The crystal data and details of data collection and structure refinement for all four compounds are given in Table 2.

Tables of further details of the X-ray crystal structure determinations, complete atomic coordinates, thermal parameters, bond lengths and angles and atom-number-

ing schemes for four compounds. Ordering information is given on any current masthead page.

Acknowledgements

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