Preparation of Thionylimide Complexes of Titanium, Zirconium, and Hafnium. Crystal Structure of $[Zr(cp)(\eta\text{-}C_5Me_5)(NSO)_2]$†

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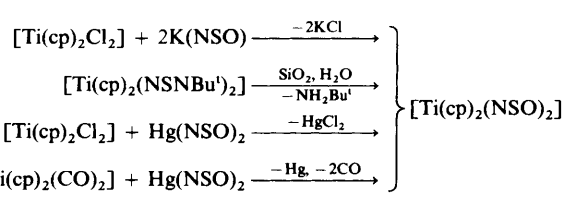
The compounds $[Ti(cp)_2(NSO)_2]$, $[Zr(cp)(\eta\text{-}C_5Me_5)_2(NSO)_2]$, $[Zr(\eta\text{-}C_5Me_5)_2(NSO)_2]$, and $[Hf(cp)(\eta\text{-}C_5Me_5)(NSO)_2]$ (cp = η-C_5H_5) have been prepared from corresponding metal halides and K(NSO). The transition-metal-bonded NSO groups can be transformed into $NSNSiMe_3$ by reaction with $Li[N(SiMe_3)_2]$, giving $[Ti(cp)_2(NSNSiMe_3)_2]$. A compound containing three NSO ligands has been prepared from the reaction of $SnMe_3(NSO)$ and $[Ti(cp)Cl_3]$. The *X*-ray crystal structure of $[Zr(cp)(\eta\text{-}C_5Me_5)(NSO)_2]$ reveals a pseudo-tetrahedral co-ordination of the metal, with two nitrogen-bonded NSO ligands forming a nearly planar $Zr(NSO)_2$ unit.

In a recent communication we reported brief details of the preparation of $[Ti(cp)_2(NSO)_2]$ and $[Ti(cp)_2(NSNSiMe_3)_2]$ (cp = η^5-C_5H_5).[1] The chemistry of transition-metal-bonded sulphur–nitrogen ligands is a rapidly developing area of research. In two recent reviews on this topic[2,3] only a single compound[4] containing transition-metal-bonded NSO was described, but at least eight such compounds are now known (including those reported here).[1,4–7] For $[Ti(cp)_2(NSO)_2]$ four different synthetic routes are now available (Scheme 1).



$$\left.\begin{array}{r} [Ti(cp)_2Cl_2] + 2K(NSO) \xrightarrow{-2KCl} \\ [Ti(cp)_2(NSNBu^t)_2] \xrightarrow[-NH_2Bu^t]{SiO_2,\,H_2O} \\ [Ti(cp)_2Cl_2] + Hg(NSO)_2 \xrightarrow{-HgCl_2} \\ [Ti(cp)_2(CO)_2] + Hg(NSO)_2 \xrightarrow{-Hg,\,-2CO} \end{array}\right\} [Ti(cp)_2(NSO)_2]$$

Scheme 1.

Having synthesized $[Rh(CO)(NSO)(PPh_3)_2]$, the first complex containing the NSO ligand,[4] we were interested in developing a more general route to this type of compounds. Here we describe the synthesis and structural characterization of NSO complexes of titanium, zirconium, and hafnium.

Results and Discussion

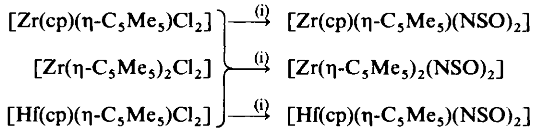
We originally attempted to introduce the thionylimide unit *via* $SiMe_3(NSO)$, but without success. However, the use of K(NSO), another NSO transfer reagent that is easily available from $SiMe_3(NSO)$ and $KOBu^t$, proved to be successful [equation (1)].

$$[Ti(cp)_2Cl_2] + 2K(NSO) \xrightarrow{-2KCl} [Ti(cp)_2(NSO)_2] \quad (1)$$

The course of the reaction can be followed easily by the replacement of the red colour of $[Ti(cp)_2Cl_2]$ by a dirty yellow. Extraction with boiling acetonitrile gives a sufficiently pure product (^1H n.m.r. spectroscopy) that can be recrystallized from MeCN to give yellow crystals of $[Ti(cp)_2(NSO)_2]$ in 80% yield.

In contrast to organic compounds containing NSO,[8] solid $[Ti(cp)_2(NSO)_2]$ is remarkably stable towards air and atmospheric moisture, although solutions exposed to air decompose rapidly.

This synthetic scheme can be applied to a number of related cyclopentadienyl-substituted metal halides (Scheme 2). The analogous reaction of $[Zr(cp)_2Cl_2]$ probably yields $[Zr(cp)_2(NSO)_2]$, but the grey crystals cannot be purified and seem to decompose in solution and in the solid state.



$$\begin{array}{l} [Zr(cp)(\eta\text{-}C_5Me_5)Cl_2] \xrightarrow{(i)} [Zr(cp)(\eta\text{-}C_5Me_5)(NSO)_2] \\ [Zr(\eta\text{-}C_5Me_5)_2Cl_2] \xrightarrow{(i)} [Zr(\eta\text{-}C_5Me_5)_2(NSO)_2] \\ [Hf(cp)(\eta\text{-}C_5Me_5)Cl_2] \xrightarrow{(i)} [Hf(cp)(\eta\text{-}C_5Me_5)(NSO)_2] \end{array}$$

Scheme 2. (*i*) +2K(NSO), MeCN, −2KCl

All these complexes form pale to deep yellow crystals, which are only slightly sensitive to atmospheric moisture. They can be easily characterized by mass spectroscopy, where all give the molecular ion. The ^1H n.m.r. signals are shifted to high field with respect to the starting materials. The i.r. spectra of all these compounds contain three absorptions characteristic of NSO[9] at *ca.* 1 250, 1 080, and 520 cm^{-1}.

We did not succeed in preparing $[Ti(cp)(NSO)_3]$ by the reaction of $[Ti(cp)Cl_3]$ and K(NSO). The Ti–Cl bond is more reactive in $[Ti(cp)Cl_3]$ than in $[Ti(cp)_2Cl_2]$. To retain a high selectivity in the reaction, the NSO transfer reagent should thus be less reactive. Consequently K(NSO) was replaced by $SnMe_3(NSO)$, which is prepared in nearly quantitative yield from K(NSO) and $SnMe_3Cl$ in refluxing tetrahydrofuran (thf) [equation (2)].[10] The resulting yellow material is insoluble in non-co-ordinating solvents, but slightly soluble in acetonitrile. These solutions decompose within a few minutes so that it is neither possible to obtain a reasonable n.m.r. spectrum nor to recrystallize the compound. In the i.r. spectrum absorptions that can be ascribed to NSO are observed. The elemental analysis (Table 1) confirms the composition $[Ti(cp)(NSO)_3]$.

$$[Ti(cp)Cl_3] + 3SnMe_3(NSO) \xrightarrow[-3SnMe_3Cl]{\text{toluene}} [Ti(cp)(NSO)_3] \quad (2)$$

X-Ray Crystal Structure of $[Zr(cp)(\eta\text{-}C_5Me_5)(NSO)_2]$ (**2**).—The structure of $[Zr(cp)(\eta\text{-}C_5Me_5)(NSO)_2]$ (Figure) is comparable to that of $[Ti(cp)_2(NSO)_2]$ with the central metal

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† η-Cyclopentadienyl(η-pentamethylcyclopentadienyl)bis(sulphinylamido-*N*)zirconium.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Analytical data for the new compounds

Compound	Colour	Decomp. (°C)	Analysis^a (%) C	H	S
(**1**) $[Ti(cp)_2(NSO)_2]$	Yellow	>230	38.6 (39.7)	3.2 (3.3)	9.2 (9.3)
(**2**) $[Zr(cp)(\eta-C_5Me_5)(NSO)_2]$	Bright yellow	>215	43.3 (43.3)	4.9 (4.9)	15.3 (15.3)
(**3**) $[Zr(\eta-C_5Me_5)_2(NSO)_2]$	Bright yellow	>220	49.5 (49.4)	6.3 (6.2)	
(**4**) $[Hf(cp)(\eta-C_5Me_5)(NSO)_2]$	Pale yellow	>155	37.2 (35.8)	4.4 (4.0)	11.9 (12.7)
(**5**) $[Ti(cp)(NSO)_3]^b$	Pale yellow	>55	22.7 (20.1)	2.3 (1.7)	32.7 (32.2)
(**6**) $[Ti(cp)_2(NSNSiMe_3)_2]$	Yellow	>180	42.5 (43.2)	6.0 (6.3)	

^{a} Calculated values are given in parentheses. ^{b} N 13.2 (14.0)%.

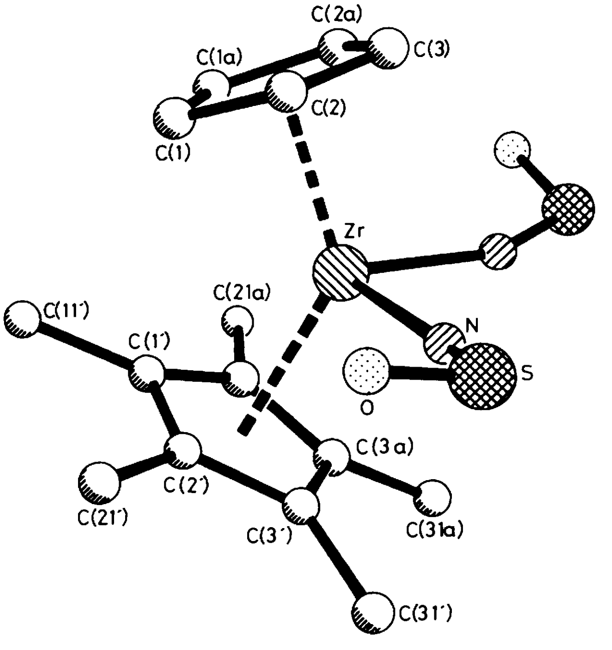


Figure. Molecular structure of $[Zr(cp)(\eta-C_5H_5)(NSO)_2]$ (**2**)

atom in a pseudo-tetrahedral environment. A selection of important bond lengths and angles is given in Table 2. The long Zr–N (Table 2) and the Ti–N bonds in $[Ti(cp)(NSO)_2]$ are comparable to those of related compounds such as $[Ti(cp)_2(NCO)_2]$,[11] $[Zr(cp)_2(NCO)_2]$,[11] $[Ti(cp)_2(N_3)_2]$,[12] and $[Ti(cp)_2(NCS)_2]$[13] and indicate little multiple bonding. The atoms of the $Zr(NSO)_2$ unit are nearly coplanar (± 3 pm).

The known metal complexes with thionylimide ligands allow a comparison of the important bond lengths and angles (Table 3). Except for the S–O bond in the rhodium complex (the structure is partially disordered and hence less reliable), all bond lengths within the NSO ligand are similar. The S–O bond in MeNSO is comparable in length[14] with those of the metal complexes. On the other hand the N–S bond (average 147.4 pm) is significantly shorter (5 pm) than in MeNSO. A bond shortening between nitrogen and carbon was also observed in the analogous isocyanate complexes.[11] If significant p_π–d_π interactions occur in the metal complexes the bonding situation could be described by the resonance extremes, $Ti{-}N{=}S{=}O \longleftrightarrow \bar{T}i{=}\overset{+}{N}{=}S{=}O \longleftrightarrow \bar{T}i{=}N{-}\overset{+}{S}{=}O$, and a lengthening of the N–S bond would result. Just the opposite is observed, indicating higher N–S bond order and a more ionic bonding situation.

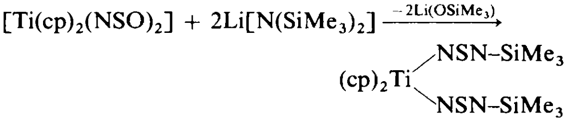
Table 2. Selected bond lengths (pm) and angles (°) for $[Zr(cp)(\eta-C_5Me_5)(NSO)_2]$

Zr–N	212.1(4)	Zr–N–S	159.8(2)
N–S	146.9(4)	O–S–N	120.0(2)
S–O	143.5(4)	N–Zr–N	97.1(2)
Zr–X	221.0(3)	X–Zr–X*	133.2(2)
Zr–X*	220.8(3)		

X and X* are the centroids of the C_5 rings.

Chemical Reactions of Transition-metal-bonded Thionylimide.—The NSO group, being a heterocumulene, is a potential site for a number of reactions. When substituted with electron-withdrawing groups it is a very reactive dienophile[15] or can be condensed (SO_2 abstraction) under mild conditions to yield sulphur di-imides.[16] Appel and co-workers[17] reported the reaction of RNSO (R = Et, Ph, or Bu^t) with $Li[N(SiMe_3)_2]$ to give monosilylated sulphur di-imides.

Because $[Ti(cp)_2(NSO)_2]$ is easily available in 10—20 g quantities, our investigations have concentrated on reactions with this compound. Cycloadditions or base-catalysed condensations were not achieved, but the reaction with $Li[N(SiMe_3)_2]$ was successful [equation (3)]. In order to simplify the workup,



$$[Ti(cp)_2(NSO)_2] + 2Li[N(SiMe_3)_2] \xrightarrow{-2Li(OSiMe_3)} (cp)_2Ti\begin{matrix}\nearrow NSN{-}SiMe_3\\ \searrow NSN{-}SiMe_3\end{matrix} \quad (3)$$

$SiMe_3Cl$ is added [equation (4)] after the reaction. The

$$Li(OSiMe_3) + SiMe_3Cl \longrightarrow Me_3SiOSiMe_3 + LiCl \quad (4)$$

compounds LiCl and $Me_3SiOSiMe_3$ can be separated more easily from the product. Recrystallization from hexane gives thin yellow plates of $[Ti(cp)_2(NSNSiMe_3)_2]$ in 65% yield.

In principle, four isomers (*E,E*, *E,Z*, *Z,E*, *Z,Z*) are possible for each of the two sulphur di-imide groups. Herberhold *et al.*[5] have reported that $[Ti(cp)_2(NSNBu^t)_2]$ gives rise to temperature-dependent n.m.r. spectra. At −60 °C (90 MHz) they distinguished two different isomers, possibly the *E,E*; *E,E* and *E,E*; *E,Z*. In the case of the closely related compound $[Ti(cp)_2(NSNSiMe_3)_2]$ the ^1H n.m.r. spectrum remains unchanged until −80 °C ($[^2H_8]$toluene, 250 MHz), except for

Table 3. Selected bond lengths and angles for compounds containing NSO

	Lengths (pm)		Angles (°)		
	N–S	S–O	At N	NSO	Ref.
$[Rh(CO)(NSO)(PPh_3)_2]$	148.0	150.9	135.1	122.5	4
$[Ti(cp)_2(NSO)_2]$	147.4	145.2	150.8	119.1	1
$[Pt(NSO)_2(PPh_3)_2]$	147.2	145.5	133.3	120.7	6
$[Zr(cp)(\eta\text{-}C_5Me_5)(NSO)_2]$	146.9	143.5	159.8	120.0	This work
MeNSO	152.5	146.6		117	14

Table 4. Atomic co-ordinates ($\times 10^4$) for complex (**2**)

Atom	x	y	z
Zr	3 270(1)	0	1 351(1)
O	4 052(4)	2 729(3)	1 187(6)
S	4 592(1)	1 980(1)	1 785(2)
N	4 194(3)	1 077(3)	1 825(4)
C(1)	2 298(3)	479(4)	−903(5)
C(2)	3 169(4)	763(3)	−1 085(5)
C(3)	3 692(5)	0	−1 175(7)
C(1′)	1 799(4)	0	2 249(7)
C(11′)	883(5)	0	1 371(10)
C(2′)	2 269(3)	776(3)	2 857(5)
C(21′)	1 991(5)	1 761(4)	2 572(7)
C(3′)	3 003(3)	487(3)	3 861(5)
C(31′)	3 613(4)	1 074(5)	4 905(6)
C(11)	−776(12)	0	4 431(15)
C(12)	0	1 389(11)	5 000
C(13)	0	465(17)	5 000
C(14)	−754(12)	950(15)	4 421(16)

decomposition reactions that are relatively fast at room temperature (after 15 min changes are noticeable in the n.m.r. spectrum).

We expected $[Ti(cp)_2(NSNSiMe_3)_2]$ to be an ideal precursor for novel eight-membered metallacycles, because it contains two reactive N–Si bonds. However, reactions with halogen-active species such as SCl_2, $SiMe_2Cl_2$, or $TiCl_4$ did not result in ring formation but rather in cleavage of the Ti–N bond. The only isolable product is $[Ti(cp)_2Cl_2]$. These observations are very much consistent with related results presented in a recent publication by Rauchfuss and co-workers,[18] who tried to insert halogen-active species into a four-membered $[Ti(cp)_2(S_2SiMe_2)]$ ring, but also obtained $[Ti(cp)_2Cl_2]$. It was concluded that the Ti–S bond is substantially more labile than the Si–S bond. Thus we conclude that in $[Ti(cp)_2(NSNSiMe_3)_2]$ the Ti–N bond is much more reactive than the N–Si bond.

Experimental

Microanalyses were performed by the analytical laboratory of our Institute. Spectrometers: i.r., Perkin-Elmer 180 and 325 (spectra in Nujol mulls; w = weak, m = medium, s = strong, v = very, and sh = shoulder); n.m.r., Bruker WP 80 SY and AM 250 (data relative to $SiMe_4$); mass spectra, electron impact, Finnigan MAT 8230 (70 eV, *ca.* 1.12×10^{-17} J).

All manipulations were made under nitrogen or *in vacuo*. Solvents were dried by standard methods. The starting materials $[Zr(cp)(\eta\text{-}C_5Me_5)Cl_2]$,[19] $[Zr(\eta\text{-}C_5Me_5)_2Cl_2]$,[20] $[Hf(cp)(\eta\text{-}C_5Me_5)Cl_2]$,[21] $[Ti(cp)Cl_3]$,[22] $SnMe_3(NSO)$,[10] K(NSO),[10] C_5Me_5H,[23] and $Li[N(SiMe_3)_2]$ [24] were prepared as described in the literature or were commercially available. For the synthesis of K(NSO) it was found necessary to sublime commercially available $K(OBu^t)$ prior to use.

$[Ti(cp)_2(NSO)_2]$ (**1**).—To a mixture of $[Ti(cp)_2Cl_2]$ (12.45 g, 50 mmol) and K(NSO) (10.6 g, 105 mmol) at −40 °C, MeCN (200 cm^3) cooled to −40 °C was added with stirring. The reaction mixture was allowed to warm to room temperature overnight, then filtered, and the solid residue extracted in a reflux of the filtrate. The volume was reduced to *ca.* 50 cm^3 and after cooling to 0 °C, the crystalline, yellow product was filtered off, washed with MeCN (10 cm^3), and dried *in vacuo*. Yield: 12.1 g (80%). I.r.: 3 110w, 1 235vs, 1 075s, 1 010m, 835s, 525m, 430w, and 400w cm^{-1}. ^1H N.m.r. ($CDCl_3$): δ 6.38 (cp).

$[Zr(cp)(\eta\text{-}C_5Me_5)(NSO)_2]$ (**2**), $[Zr(\eta\text{-}C_5Me_5)_2(NSO)_2]$ (**3**), and $[Hf(cp)(\eta\text{-}C_5Me_5)(NSO)_2]$ (**4**).—To a mixture of $[Zr(cp)(\eta\text{-}C_5Me_5)Cl_2]$ (1.09 g, 3 mmol), $[Zr(\eta\text{-}C_5Me_5)_2Cl_2]$ (1.30 g, 3 mmol), or $[Hf(cp)(\eta\text{-}C_5Me_5)Cl_2]$ (1.35 g, 3 mmol) and K(NSO) (6.36 g, 6.3 mmol) at −40 °C, MeCN (25 cm^3) was added slowly with stirring. The reaction mixture was allowed to warm to room temperature overnight. Having removed the solvent *in vacuo*, the solid residue was recrystallized from toluene–hexane. $[Zr(cp)(\eta\text{-}C_5Me_5)(NSO)_2]$: yield 0.70 g (56%); i.r. 3 100w, 1 280s, 1 210vs, 1 090m, 1 080m, 1 030m, 1 010m, 840m, 825s, 730m, 515m, and 380s cm^{-1}; m/z 414 (M^+); ^1H n.m.r. ($CDCl_3$) δ 2.03 (s, $\eta\text{-}C_5Me_5$) and 6.22 (s, cp). $[Zr(\eta\text{-}C_5Me_5)_2(NSO)_2]$: yield 0.6 g (43%); i.r. 1 290(sh), 1 260vs, 1 090s, 1 035m, 735m, and 525w cm^{-1}; m/z 484 (M^+); ^1H n.m.r. ($CDCl_3$) δ 1.95 ($\eta\text{-}C_5Me_5$). $[Hf(cp)(\eta\text{-}C_5Me_5)(NSO)_2]$; yield 0.6 g (40%); i.r. 3 100w, 1 290(sh), 1 260s, 1 090s, 1 085(sh), 1 020m, 835s, 730m, and 520m cm^{-1}; m/z 504 (M^+); ^1H n.m.r. ($CDCl_3$) δ 2.06 (s, $\eta\text{-}C_5Me_5$) and 6.14 (s, cp).

$[Ti(cp)(NSO)_3]$ (**5**).—To a stirred solution of $[Ti(cp)Cl_3]$ (1.4 g, 6.4 mmol) in toluene (20 cm^3) at 0 °C, $SnMe_3(NSO)$ (4.4 g, 19.5 mmol) in toluene (5 cm^3) was added dropwise with stirring. After 6 h at this temperature the yellow solid was filtered off, washed with toluene (10 cm^3), and dried *in vacuo*. Yield: 1.3 g (80%). I.r.: 3 075m, 1 260s, 1 220vs, 1 090m, 1 035m, 845s, 740m, 620m, and 540w cm^{-1}.

$[Ti(cp)_2(NSNSiMe_3)_2]$ (**6**).—To $[Ti(cp)_2(NSO)_2]$ (1.5 g, 5 mmol) in diethyl ether (20 cm^3) was added dropwise with stirring $Li[N(SiMe_3)_2]$ (1.7 g, 10 mmol) dissolved in diethyl ether (10 cm^3). After 1 h, $SiMe_3Cl$ (2 cm^3) was added. One hour later the volatiles were removed *in vacuo* and the solid residue was recrystallized from n-hexane. Yield: 1.4 g (64%). I.r.: 3 070m, 1 255s, 1 200vs, 1 125s, 1 025m, 860s, 845s, 825s, 765m, 735m, 700m, and 520m cm^{-1}. ^1H N.m.r. ([$^2H_8$]toluene; 297 K, 250 MHz): δ 0.34 (s, $SiMe_3$) and 5.83 (s, cp).

Crystal Structure Determination of $[Zr(cp)(\eta\text{-}C_5Me_5)(NSO)_2]$ (**2**).—Complex (**2**) crystallizes from a toluene–n-hexane mixture with half a molecule of toluene.

Crystal data. $M = 461.8$, monoclinic, space group $C2/m$, $a = 1\,518.5(8)$, $b = 1\,476.8(7)$, $c = 931.2(5)$ pm, $\beta = 98.58(2)°$, $U = 2.065$ nm^3, $Z = 4$, $D_c = 1.483$ Mg m^{-3}, $F(000) = 948$, $\lambda(\text{Mo-}K_\alpha) = 71.069$ pm, $\mu(\text{Mo-}K_\alpha) = 0.73$ mm^{-1}, crystal dimensions $0.3 \times 0.4 \times 0.5$ mm.

2 470 Data were collected for $2\theta < 45°$ on a Stoe–Siemens four-circle diffractometer and Lorentz, polarization but no absorption correction applied. Equivalent data were merged to yield 1 405 unique reflections, of which 1 348 with $F > 3\sigma(F)$ were used in the refinement. Structure solution was performed with the Patterson section of SHELX 86 [25] and refinement with SHELX 76.[26] The complex lies on mirror plane $y = 0$. In a Fourier difference synthesis a disordered solvent molecule at 0 0 0.5, site symmetry $2/m$, was evident. Atomic positions C(11)—C(14) represent half a molecule of toluene. Because of high thermal motion in cp and C_5Me_5 and disorder of toluene, no attempt was made to include hydrogen atoms. Refinement

converged to $R = \Sigma\Delta F/\Sigma F_o = 0.036$, $R' = (\Sigma w\Delta F^2/\Sigma wF_o^2)^{\frac{1}{2}} = 0.06$ with weight $w = [\sigma^2(F_o) + 0.0004F_o^2]^{-1}$. A final difference map showed peaks near Zr of maximum density 0.6×10^6 and minimum -0.3×10^6 e pm^{-3}. Final atomic co-ordinates are given in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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