Some Substituted Urea Complexes of Thorium Tetranitrate; Crystal Structure of Tetra(nitrato-*O,O'*)bis(tetramethylurea-*O*)thorium(IV), [Th$(NO_3)_4\{OC(NMe_2)_2\}_2$]†

Abdul Ghany M. Al-Daher and Kenneth W. Bagnall *
Chemistry Department, The University of Manchester, Manchester M13 9PL
Eleonora Forsellini and Franco Benetollo
Istituto di Chimica e Tecnologia dei Radioelementi del C.N.R., Corso Stati Uniti 4, 35100 Padova, Italy
Gabriella Bombieri *
Istituto di Chimica Farmaceutica e Tossicologica, Viale Abruzzi 42, 20131 Milano, Italy

The complexes $Th(NO_3)_4{\cdot}xL$ [$x = 2$, L = $(Me_2N)_2CO$ (tmu), $(MePhN)_2CO$, or $(Bu^i_2N)(Me_2N)CO$; $x = 2.67$, L = tmu or (cyclo-$C_6H_{11}NH)_2CO$] have been prepared and their i.r. and Raman spectra are reported. The crystal structure of [$Th(NO_3)_4(tmu)_2$] has been determined from three-dimensional *X*-ray diffraction data. The compound crystallises in space group $P2_1/a$, with $a = 19.523(2)$, $b = 12.209(1)$, $c = 10.026(1)$ Å, $\beta = 99.4(1)°$, and $Z = 4$. The structure was solved by Patterson and Fourier methods; full-matrix least-squares refinement based on 2 537 reflections gave final *R* values of $R = 0.032$ and $R' = 0.037$. The co-ordination about the thorium is best described as an octahedron with the two tmu molecules *trans* and the four bidentate nitrate groups occupying the equatorial positions.

Although urea complexes with thorium tetranitrate have been reported with a wide range of compositions, from [1] $Th(NO_3)_4{\cdot}2(H_2N)_2CO{\cdot}2H_2O$ to [2] $Th(NO_3)_4{\cdot}11(H_2N)_2CO{\cdot}2.5H_2O$, complexes with substituted ureas do not appear to have been recorded. It was therefore of interest to attempt to prepare a series of complexes with the relatively bulky substituted ureas $(Me_2N)_2CO$ (tmu), $(MePhN)_2CO$ (dmdpu), $(Bu^i_2N)(Me_2N)CO$ (dibdmu), and (cyclo-$C_6H_{11}NH)_2CO$ (dcu) and to obtain structural information on these compounds.

Experimental

The complexes were prepared and handled under dry nitrogen in glove-boxes. Hydrated thorium tetranitrate (B.D.H.) was used as supplied and the substituted ureas were obtained as follows: tmu from B.D.H., dmdpu from K and K Laboratories Inc., dcu from Aldrich Chemical Company Inc., and dibdmu was prepared by the reaction of dimethylcarbamoyl chloride with di-isobutylamine. Spectroscopic measurements and the drying of solvents were carried out as described previously.[3]

Preparations.—(*a*) $Th(NO_3)_4{\cdot}2.67$tmu. A large excess of tmu (0.9 g, 7.8 mmol) in ethanol (5 cm^3) was added to a solution of $Th(NO_3)_4{\cdot}xH_2O$ (0.8 g, 1.4 mmol) in the same solvent. After stirring (1 h) at room temperature, the solution was evaporated to a small volume (*ca.* 4 cm^3) under vacuum, when a colourless oil separated. This oil was left to stand under n-pentane (5 cm^3) overnight. The resulting colourless crystalline solid was ground with n-pentane (2 × 3 cm^3) and the *product* vacuum dried (8 h); yield, *ca.* 70%.

(*b*) $Th(NO_3)_4{\cdot}2.67$dcu. A slight excess of dcu (0.9 g, 4.0 mmol) in ethanol (5 cm^3) was added to a solution of $Th(NO_3)_4{\cdot}xH_2O$ (0.8 g, 1.4 mmol) in the same solvent. After stirring (1 h) at room temperature, the solution was evaporated under vacuum to leave an oil which was washed with n-pentane (5 cm^3) and then dissolved in dichloromethane (5 cm^3). The colourless supernatant was vacuum evaporated to *ca.* 3 cm^3, and n-pentane added dropwise until the solution became cloudy. The solution was cleared by dropwise addition of dichloromethane, and white crystals of the *complex* separated on standing (3 d). The product was washed with n-pentane (2 × 3 cm^3) and vacuum dried (8 h); yield, *ca.* 42%.

The complex $Th(NO_3)_4{\cdot}2$dmdpu (yield, *ca.* 55%) was prepared in the same way.

(*c*) $Th(NO_3)_4{\cdot}2$dibdmu. This was prepared as in (*b*) except that the dichloromethane solution was vacuum evaporated to dryness, leaving an oily residue which almost completely solidified on standing overnight under n-pentane (5 cm^3). This product was ground under n-pentane (2 × 5 cm^3) to yield the white, solid *complex* which was vacuum dried (8 h); yield, *ca.* 81%.

(*d*) $Th(NO_3)_4{\cdot}2$tmu. n-Pentane was added to a solution of $Th(NO_3)_4{\cdot}2.67$tmu (0.6 g, 0.76 mmol) in dichloromethane (5 cm^3) until the solution became cloudy. Dichloromethane was added dropwise until the solution became clear, and large colourless crystals of the *product* separated on standing overnight. These were washed with n-pentane (2 × 3 cm^3) and vacuum dried (8 h); yield, *ca.* 64%.

The analytical results are summarised in Table 1.

X-Ray Measurements and Structure Determination.—[$Th(NO_3)_4(tmu)_2$] crystallises in the form of white, transparent, regular square-bipyramidal prisms. A single crystal (0.28 × 0.28 × 0.40 mm) was lodged in a Lindemann glass capillary

Table 1. Analytical data (%)*

Compound	Th	C	H	N
$Th(NO_3)_4{\cdot}2$tmu	32.8 (32.6)	16.7 (16.9)	3.3 (3.4)	15.1 (15.7)
$Th(NO_3)_4{\cdot}2.67$tmu	30.0 (29.4)	20.4 (20.3)	4.1 (4.1)	16.8 (16.6)
$Th(NO_3)_4{\cdot}2$dmdpu	23.4 (24.1)	37.4 (37.5)	3.3 (3.3)	11.3 (11.7)
$Th(NO_3)_4{\cdot}2$dibdmu	26.4 (26.4)	29.8 (30.0)	5.6 (5.5)	12.3 (12.7)
$Th(NO_3)_4{\cdot}2.67$dcu	21.8 (21.5)	38.3 (38.6)	6.0 (5.9)	11.9 (12.1)

* Calculated values in parentheses.

---

† *Supplementary data available* (No. SUP 56445, 11 pp.): thermal parameters, complete list of bond lengths and angles. See Instructions for Authors *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

and centred on a four-circle Philips PW 1100 automated diffractometer equipped with graphite-monochromated Mo-K_α radiation. The orientation matrix and preliminary unit-cell dimensions were determined from 25 reflections found by mounting the crystal at random, varying the orientation angles φ and χ in the range of 120° each, the detector position varying between $\theta = 6$ and 9°. For the determination of precise lattice parameters 25 strong reflections with $9 \leqslant \theta \leqslant 16°$ were considered.

Crystal data. $C_{10}H_{24}N_8O_{14}Th$, $M = 712.4$, monoclinic, space group $P2_1/a$, $a = 19.523(2)$, $b = 12.209(1)$, $c = 10.026(1)$ Å, $\beta = 99.4(1)°$, $U = 2\,357.7$ Å^3, $D_c = 2.01$ Mg m^{-3}, $Z = 4$, $F(000) = 1\,368$, μ(Mo-K_α) = 61.1 cm^{-1}. Integrated intensities for *hkl* reflections were measured using the $\theta/2\theta$ scan method with a scan speed of 1.80° min^{-1}, scan width 1.20°, and two background counts of 10 s at each end of the scan. 5 161 Reflections ($2\theta_{max.} = 50°$) were measured which when merged gave 2 537 unique reflections with $I \geqslant 3\sigma(I)$. Refinement converged to $R\,[= \Sigma(|F_o| - |F_c|)/\Sigma F_o] = 0.032$ and $R'\,\{= [(\Sigma w|F_o| - |F_c|^2)/\Sigma w|F_o|^2]^{\frac{1}{2}}\} = 0.037$.

The intensities of two standard reflections 2 2 3 and 6 2 2 were monitored every 180 min. There was no significant fluctuation in intensities other than those expected from Poisson statistics.

The intensity data were corrected for Lorentz-polarization effects, and for absorption following the method of North *et al.*[4] The structure was solved using three-dimensional Patterson and Fourier syntheses and refined by full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms.

A final difference map failed to reveal the hydrogen-atom positions; they were not included in the refinement. The anomalous dispersion terms[5] for Th were taken into account in the refinement. Atomic scattering factors were from ref. 5. Data processing and computation were carried out using the SHELX 76 program package.[6]

Final positional parameters are presented in Table 2.

Results and Discussion

The solid complexes were obtained by treating a solution of $Th(NO_3)_4 \cdot xH_2O$ in ethanol with the ligand in the same solvent, using a large excess of the latter for $Th(NO_3)_4 \cdot 2.67$tmu, but only a slight excess for $Th(NO_3)_4 \cdot 2.67$dcu, $Th(NO_3)_4 \cdot 2$dibdmu, and $Th(NO_3)_4 \cdot 2$dmdpu. The attempted preparation of complexes of $Th(NO_3)_4$ with $(Et_2N)_2CO$, $(Et_2N)(Me_2N)CO$, and $(Pr^i{}_2N)(Me_2N)CO$ by these procedures yielded oils which could not be induced to solidify. $Th(NO_3)_4 \cdot 2$tmu was obtained by recrystallisation of $Th(NO_3)_4 \cdot 2.67$tmu from a mixture of dichloromethane and n-pentane.

Features of the i.r. and Raman spectra of all the prepared complexes are summarised in Table 3. The nitrate modes are consistent with bidentate NO_3^- groups,[7] and the shifts in ν(CO) of the ureas on co-ordination [Δν(CO)] indicate

Table 2. Fractional atomic co-ordinates (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses for $[Th(NO_3)_4(tmu)_2]$

Atom	*x*	*y*	*z*
Th	−1 050.9(1)	−2 502.6(3)	−2 558.4(2)
O(1)	−133(4)	−2 312(5)	−3 721(7)
C(1)	298(4)	−2 072(8)	−4 512(9)
N(1)	177(5)	−2 454(6)	−5 772(8)
C(3)	−287(5)	−3 396(9)	−6 165(10)
C(4)	384(7)	−1 876(9)	−6 942(10)
N(2)	844(4)	−1 476(6)	−4 067(8)
C(5)	1 527(6)	−1 583(9)	−4 587(13)
C(6)	877(8)	−877(11)	−2 826(13)
O(2)	−2 131(3)	−1 996(5)	−2 138(6)
C(2)	−2 638(4)	−1 625(7)	−1 613(9)
N(3)	−2 806(5)	−2 078(8)	−535(9)
C(7)	−2 484(7)	−3 189(10)	−97(14)
C(8)	−3 139(6)	−1 441(11)	484(12)
N(4)	−2 990(4)	−768(7)	−2 213(8)
C(9)	−3 742(7)	−593(13)	−2 215(13)
C(10)	−2 689(7)	−137(9)	−3 242(13)
O(3)	−884(4)	−3 674(6)	−451(7)
O(4)	44(4)	−2 991(7)	−986(7)
N(5)	−220(5)	−3 556(7)	−155(8)
O(5)	125(4)	−3 970(6)	818(7)
O(6)	−775(3)	−4 408(5)	−3 256(7)
O(7)	−1 798(3)	−4 233(5)	−2 750(7)
N(6)	−1 349(5)	−4 860(6)	−3 168(8)
O(8)	−1 470(5)	−5 804(5)	−3 438(9)
O(9)	−811(4)	−510(5)	−2 093(9)
O(10)	−942(5)	−1 400(7)	−275(7)
N(7)	−834(5)	−494(9)	−814(10)
O(11)	−796(6)	387(7)	−276(10)
O(12)	−1 720(4)	−2 845(6)	−4 903(8)
O(13)	−1 409(4)	−1 166(6)	−4 541(7)
N(8)	−1 685(5)	−1 883(7)	−5 368(9)
O(14)	−1 883(5)	−1 706(9)	−6 531(8)

Table 3. Infrared and Raman spectral data (cm^{-1})[a]

		Nitrate modes[b]							
Compound		ν_1	ν_4	ν_2	ν_6	ν_3	ν_5	ν(CO)	Δν(CO)
$Th(NO_3)_4 \cdot 2$tmu	I.r.	1 530vs	1 278s	1 023s	809m	742s	703vw	1 584s	53
	Raman	1 468m	1 250vw	1 023vs		740m	704w		
$Th(NO_3)_4 \cdot 2.67$tmu	I.r.	1 508s	1 291s br	1 028s	810m	743s (sh)	707w (sh)	1 568s (sh)	69
	Raman	1 520w 1 468s	1 338w	1 038vs	813vw	753w	710vw		
$Th(NO_3)_4 \cdot 2$dibdmu	I.r.	1 512vs	1 277s	1 017s	804m	736m	718w (sh)	1 545s (sh)	97
	Raman	1 464m (sh) 1 450m	1 280vw	1 024s	814m	746m	705w		
$Th(NO_3)_4 \cdot 2$dmdpu	I.r.	1 521s	1 275s	1 020s	808m	741s	718w (sh)	1 560s (sh)	84
	Raman	1 522m	1 290w	1 023s	831vw	750w	715w		
$Th(NO_3)_4 \cdot 2.67$dcu	I.r.	1 487s (sh)	1 294s br	1 018s	807m	750m (sh)	719w (sh)	1 590s br	33
	Raman	1 448m	1 313w	1 044s	835w	752w	708vw		

[a] s = Strong, m = medium, w = weak, v = very, br = broad, sh = shoulder. [b] Nitrate vibrations assigned on the basis of bidentate nitrate groups.

Table 4. Distances (Å) and principal angles (°) with e.s.d.s in parentheses for [$Th(NO_3)_4(tmu)_2$]

(*a*) Thorium co-ordination polyhedron and environment

Th–O(1)$_{urea}$	2.304(6)	Th–O(7)	2.556(6)	O(1)–Th–O(2)	151.3(2)	O(12)–Th–O(13)	49.8(2)
Th–O(2)$_{urea}$	2.301(5)	Th–O(9)	2.507(6)	O(9)–Th–O(10)	49.9(3)	O(6)–Th–O(7)	50.2(2)
Th–O(3)	2.528(6)	Th–O(10)	2.634(7)	Th–O(2)–C(2)	164.9(5)	Th–O(1)–C(1)	168.6(6)
Th–O(4)	2.511(7)	Th–O(12)	2.531(7)	O(3)–Th–O(4)	50.3(2)		
Th–O(6)	2.513(6)	Th–O(13)	2.579(6)				

Mean Th–O$_{nitrate}$ 2.545(6)

(*b*) tmu ligands

O(1)–C(1)	1.28(1)	O(2)–C(2)	1.28(1)	Th–O(1)–C(1)	168.6(6)	Th–O(2)–C(2)	164.9(6)
C(1)–N(1)	1.33(1)	C(2)–N(3)	1.30(1)	O(1)–C(1)–N(1)	118.3(8)	O(2)–C(2)–N(3)	120.6(8)
N(1)–C(3)	1.48(1)	N(3)–C(7)	1.53(1)	O(1)–C(1)–N(2)	119.8(8)	O(2)–C(2)–N(4)	117.8(8)
N(1)–C(4)	1.48(1)	N(3)–C(8)	1.51(1)	N(1)–C(1)–N(2)	121.8(8)	N(3)–C(2)–N(4)	121.7(8)
C(1)–N(2)	1.31(1)	C(2)–N(4)	1.34(1)	C(1)–N(1)–C(3)	122.2(8)	C(2)–N(3)–C(7)	117.9(8)
N(2)–C(5)	1.52(1)	N(4)–C(9)	1.48(1)	C(1)–N(1)–C(4)	123.8(8)	C(2)–N(3)–C(8)	122.4(9)
N(2)–C(6)	1.44(1)	N(4)–C(10)	1.48(1)	C(3)–N(1)–C(4)	113.2(8)	C(7)–N(3)–C(8)	117.7(9)
				C(1)–N(2)–C(5)	123.3(8)	C(2)–N(4)–C(9)	123.2(9)
				C(1)–N(2)–C(6)	119.9(8)	C(2)–N(4)–C(10)	119.1(8)
				C(5)–N(2)–C(6)	115.2(9)	C(9)–N(4)–C(10)	115.3(9)

(*c*) Nitrate ligands

N(5)–O(3)	1.29(1)	N(7)–O(9)	1.29(1)	O(3)–N(5)–O(5)	123.3(9)	O(9)–N(7)–O(11)	116.7(11)
N(5)–O(4)	1.26(1)	N(7)–O(10)	1.26(1)	O(4)–N(5)–O(5)	122.2(9)	O(10)–N(7)–O(11)	126.5(10)
N(5)–O(5)	1.20(1)	N(7)–O(11)	1.20(1)	O(3)–N(5)–O(4)	114.5(8)	O(9)–N(7)–O(10)	116.6(9)
N(6)–O(6)	1.27(1)	N(8)–O(12)	1.27(1)	O(6)–N(6)–O(8)	123.2(9)	O(12)–N(8)–O(14)	120.1(9)
N(6)–O(7)	1.28(1)	N(8)–O(13)	1.26(1)	O(7)–N(6)–O(8)	121.9(9)	O(13)–N(8)–O(14)	123.6(9)
N(6)–O(8)	1.20(1)	N(8)–O(14)	1.19(1)	O(6)–N(6)–O(7)	114.9(7)	O(12)–N(8)–O(13)	116.3(8)

Mean N–O$_{co-ord.}$ = 1.27(1)
Mean N–O$_{terminal}$ = 1.20(1)

bonding to the metal through the carbonyl oxygen atom only, as shown by the structure determination of [$Th(NO_3)_4(tmu)_2$].

The formation of the complexes $Th(NO_3)_4{\cdot}2.67L$ (L = tmu or dcu) presumably results from disproportionation of the tris complexes, $Th(NO_3)_4{\cdot}3L$, which, on the cone-packing model,[8] would be somewhat overcrowded [Σc.a.f. = 0.86; c.a.f. = cone angle factor]. Such non-stoicheiometric species are known to be of the form [$Th(NO_3)_3L_4$]$_2$[$Th(NO_3)_6$] for L = PMe_3O[9] or $P(NMe_2)_3O$,[10] and if the tmu and dcu complexes are of this type, the values of Σc.a.f. would be 0.82 and 0.84 for the complex cation and anion respectively, both of which are within the 'stable' region for complexes of known structures (see ref. 8). In the case of the bis complexes, $Th(NO_3)_4{\cdot}2L$, the value of Σc.a.f. is *ca.* 0.76, which is at the lower limit of the 'stable' region, so that it is not surprising that $Th(NO_3)_4{\cdot}2.67$tmu is easily degraded to the bis complex because of the relatively high second-order crowding (see ref. 8) provided by the bulky ligand. Similarly, the formation of only the bis complexes with the very bulky ligands dibdmu and dmdpu is not unexpected.

The crystal structure of the bis tmu complex consists of discrete [$Th(NO_3)_4(tmu)_2$] molecules and a view of the molecule down *b* is shown in the Figure together with the atom-numbering scheme. Important interatomic distances and angles are listed in Table 4. The thorium has a co-ordination number of ten involving eight oxygen atoms from four bidentate nitrate groups and two oxygen atoms from the two *trans* tmu ligands.

The co-ordination geometry is similar to that found for [$Th(NO_3)_4(PPh_3O)_2$];[11] however, the Th–O(nitrate) bond distances vary from 2.507(6) to 2.634(7) Å. This significant variation, which is higher than that found in [$Th(NO_3)_4$-($PPh_3O)_2$],[11] in which the Th–O(nitrate) bond distances lie in the range 2.52(2)—2.58(2) Å, could be related to a higher degree of hindering of the two *trans* tetramethylurea ligands as compared with the PPh_3O groups.

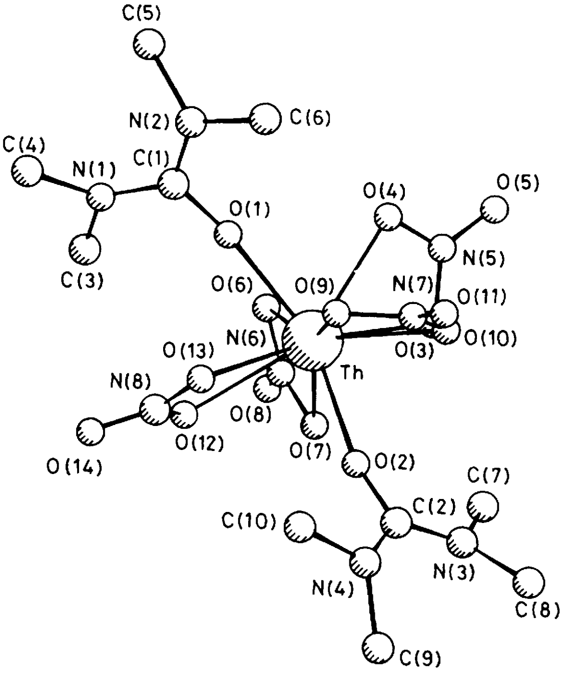

Figure. Molecule of [$Th(NO_3)_4(tmu)_2$] viewed down *b*

The Th–O(tmu) bonds are equal [Th–O(1) 2.304(6) and Th–O(2) 2.301(5) Å] and, as expected, are significantly shorter than the Th–O(PPh_3) bond distances in [$Th(NO_3)_4(PPh_3O)_2$].[11] The O(1)–Th–O(2) bond angle deviates significantly from linearity, being 151.3(2)° and this bending is again related to the crowding around the thorium atom. In fact the O(1)–Th–O(2) moiety bends towards the nitrates containing N(7) and N(8) which have more room between them than the other bidentate ligands. [The angle N(7) ··· Th ··· N(8) is 109.9(4)° while N(7) ··· Th ··· N(5) is 82.8(2)°, N(5) ··· Th ··· N(6) 79.1(2)°, and N(6) ··· Th ··· N(8) 90.8(2)°.] The Th–O(9) and Th–O(10) distances of the N(7) nitrato group are more unsymmetrical, being 2.507(6) and 2.634(7) Å respectively, as an effect of this steric congestion. The nitrate groups are, as expected, planar and the terminal (N–O) bonds are significantly shorter compared with the (N–O)–Th bonds [averages 1.20(1) and 1.27(1) Å respectively]. The two tmu ligands have the same conformation, with the C(1)–O(1)–N(1)–N(2) and C(2)–O(2)–N(3)–N(4) fragments being planar and the methyl groups tilted out above and below these planes [the methyl carbon atom deviations range from −0.64(1) to +0.64(1) Å].

The C–O and C–N bond lengths have partial double-bond character [C–O av. 1.28(1) and C–N 1.32(1) Å] indicating a mesomeric system extended to the planar part of the fragment; the N–Me distances have the usual N–C bond values. The Th–O–C bonds are not collinear; Th–O(1)–C(1) is 168.6(6) and Th–O(2)–C(2) is 164.9(5)°.

Acknowledgements

We thank Mr. M. A. Hart for the microanalyses, and the Government of Iraq for support (to A. G. M. Al-Daher).

References

1 P. S. Gentile, L. S. Campisi, and P. Carfagno, *J. Inorg. Nucl. Chem.*, 1966, **28**, 1143.
2 K. I. Petrov, A. K. Molodkin, O. M. Ivanova, and O. D. Saralidze, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1969, **14**, 215.
3 K. W. Bagnall, J. G. H. du Preez, J. Bajorek, L. Bonner, H. Cooper, and G. Segal, *J. Chem. Soc., Dalton Trans.*, 1973, 2682.
4 A. C. T. North, D. C. Philips, and F. Matheus, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
5 'International Tables for *X*-Ray Crystallography,' 2nd edn., Kynoch Press, Birmingham, 1974, vol. 4, p. 101.
6 SHELX 76, G. M. Sheldrick, University of Cambridge, 1976.
7 C. C. Addison, M. Logan, S. C. Wallwork, and C. D. Garner, *Q. Rev. Chem. Soc.*, 1971, **25**, 289.
8 K. W. Bagnall and Li Xing-fu, *J. Chem. Soc., Dalton Trans.*, 1982, 1365.
9 N. W. Alcock, S. Esperas, K. W. Bagnall, and Wang Hsian-yun, *J. Chem. Soc., Dalton Trans.*, 1978, 638.
10 R. P. English, J. G. H. du Preez, L. R. Nassimbeni, and C. P. J. van Vuuren, *S. Afr. J. Chem.*, 1979, **32**, 119.
11 K. M. A. Malik and J. W. Jeffery, *Acta Crystallogr., Sect. B*, 1973, **29**, 2687.

Received 10*th April* 1985; *Paper* 5/599