of O from the plane between the Mn which leads to increased cation–cation repulsions. It is also interesting to note that, in both compounds examined, the O–O distance in the hexagonal layer is short (2·471, $Ba_{0.5}Sr_{0.5}MnO_{2.84}$; 2·506 Å, $Ba_{0.1}Sr_{0.9}MnO_{2.96}$) and comparable with that in $8H$ $BaMnO_3$, 2·507 Å.

The relationships between structures with different stacking sequences and O deficiency in the manganate systems is in marked contrast to that found for other transition metal ions, *e.g.* $BaCoO_{3-x}$ and $BaFeO_{3-x}$. An experiment to investigate the consequences of a different preferred coordination scheme for the reduced ion is at present in progress for $6H$ $BaFeO_{3-x}$.

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References

ANDERSON, P. W. (1952). *Phys. Rev.* **86**, 694–701.

CHAMBERLAND, B. L., SLEIGHT, A. W. & WEIHER, J. F. (1970). *J. Solid State Chem.* **1**, 506–511.

COOPER, M. J. & ROUSE, K. D. (1972). *Z. Kristallogr.* **135**, 316–317.

JACOBSON, A. J. (1973). *Chemical Applications of Thermal Neutron Diffraction*, edited by B. T. M. WILLIS. Oxford Univ. Press.

JACOBSON, A. J., TOFIELD, B. C. & FENDER, B. E. F. (1973). *J. Phys. C*, **6**, 1615–1622.

KATZ, L. & WARD, R. (1964). *Inorg. Chem.* **3**, 205–211.

NEGAS, T. (1973). *J. Solid State Chem.* **6**, 136–150.

NEGAS, T. & ROTH, R. S. (1970). *J. Solid State Chem.* **1**, 409–418.

NEGAS, T. & ROTH, R. S. (1971). *J. Solid State Chem.* **3**, 323–339.

NEUTRON DIFFRACTION COMMISSION (1972). *Acta Cryst.* A**28**, 357–358.

NØRLUND CHRISTENSEN, A. & OLLIVIER, G. (1972). *J. Solid State Chem.* **8**, 131–137.

POTOFF, A. D., CHAMBERLAND, B. L. & KATZ, L. (1973). *J. Solid State Chem.* **8**, 234–237.

RIETVELD, H. M. (1967). *Acta Cryst.* **22**, 151–152.

SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* B**25**, 925–946.

SHIRANE, G. (1959). *Acta Cryst.* **12**, 282–285.

TOFIELD, B. C. & FENDER, B. E. F. (1970). *J. Phys. Chem. Solids*, **31**, 2741–2749.

WATSON, R. E. & FREEMAN, A. J. (1961). *Acta Cryst.* **14**, 27–37.

YAKEL, H., KOEHLER, W. C., BERTAUT, E. F. & FORRAT, F. (1963). *Acta Cryst.* **16**, 957–962.

Acta Cryst. (1976). B**32**, 1008

Tris(tetramethylurea)trinitratoeuropium(III)

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$EuH_{36}C_{15}N_9O_{12}$, monoclinic, $P2_1/c$, $a=9{\cdot}428\ (6)$, $b=16{\cdot}034\ (8)$, $c=18{\cdot}921\ (9)$ Å, $\beta=96{\cdot}0\ (3)^\circ$; $Z=4$; $D_m=1{\cdot}62$ (flotation), $D_x=1{\cdot}60$ g cm^{-3}; μ(Mo $K\alpha$)$=22{\cdot}9$ cm^{-1}. Single crystals were obtained by mixing ethanolic solutions of europium nitrate and of tetramethylurea (TMU) in a mole ratio of about 1:8. Europium has a nominal coordination number of nine with the three nitrates symmetrically coordinated in a bidentate fashion and the three TMU's bonded through their oxygens. The mean Eu–O distances are 2·51 Å for the nitrate oxygens, and 2·33 Å for the oxygens of the TMU's.

Introduction

This structure determination is the first of a series to investigate the coordination geometry around lanthanoid atoms in complexes involving *N*-substituted ureas. TMU forms complexes with lanthanoid nitrates and perchlorates with stoichiometries of $Ln(NO_3)_3(TMU)_3$ and $Ln(ClO_4)_3(TMU)_6$ respectively (Burgess, 1970; Giesbrecht & Kawashita, 1970; Vicentini & Najjar, 1970). Inferrential evidence (electrical conductivity and infrared data) indicates differences between the two series of compounds and suggests that they should be formulated as $[Ln(TMU)_3(NO_3)_3]$ and $[Ln(TMU)_6](ClO_4)_3$ respectively (Burgess, 1970). Presumably the coordination number of the lanthanoid in the perchlorate series is 6 but in the nitrate series it could be 6, 7, 8 or 9 depending upon the manner in which the nitrate is bonded. On the basis of previous work it seemed probable that the nitrates would be functioning as bidentate ligands [see for example, Beineke & Delgaudio (1968), Al-Karaghouli & Wood (1968, 1973), Toogood & Chieh (1975)] and hence that the coordination number of the lanthanoid would be 9. With the current interest in the structures of compounds with higher coordination numbers, we report the X-ray study of $Eu[(TMU)_3(NO_3)_3]$.

The fine prismatic crystals are white with a slight pinkish tinge. Elemental analyses for Eu, C and H were consistent with the formula $Eu(TMU)_3(NO_3)_3$. On prolonged exposure to air the crystals are hygroscopic so the crystal chosen for the study was sealed in a capillary tube. The crystal used was approximately a cube of dimension 0·25 mm.

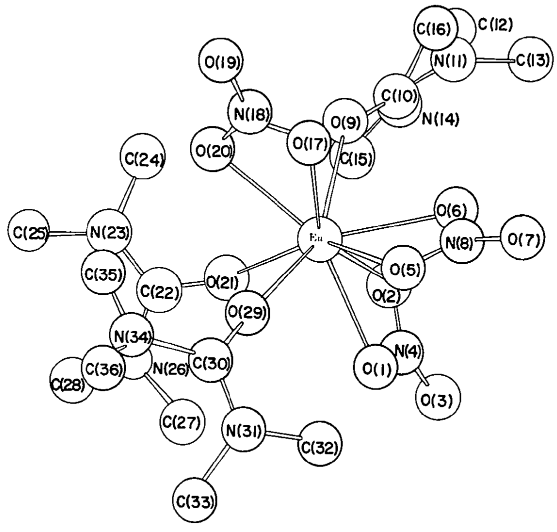

Fig. 1. Numbering of the atoms in the $Eu(TMU)_3(NO_3)_3$ complex.

Preliminary crystal data were taken from a series of Weissenberg and precession photographs. The cell constants were refined by least-squares methods based on the 2θ (Zr-filtered Mo $K\alpha$) values measured on the diffractometer. The crystal was mounted with **b** parallel to the φ axis of the G. E. XRD-6 automatic diffractometer which was equipped with a scintillation counter and pulse-height analyser. Zr-filtered Mo $K\alpha$ radiation was used for intensity measurement. Three standard reflexions were measured every 100 reflexions; the intensities exhibited no significant change throughout the data collection period. Of 4799 reflexions ($2\theta < 50°$) measured by the θ–2θ scan method, 2950 considered observed, had intensities $> 1·5\ \sigma_I$. Scan speed was 2° min^{-1} over a range of $\pm(0·9 + 0·3 \tan \theta)$. The majority of unobserved reflexions were between $2\theta = 40$–$50°$. Absorption corrections were not made ($\mu R = 0·6$) and Lorentz and polarization factors were applied to derive the structure amplitudes.

The heavy atom was located by a Patterson synthesis

Table 1. *Atomic coordinates* (*fractional* × 10^4) *and anisotropic thermal parameters* (Å^2) *in the form* $exp\,[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})\times 10^{-4}]$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Eu(× 10^5)	7940 (7)	25857 (4)	86434 (4)	679 (8)	276 (3)	202 (2)	−44 (5)	85 (3)	−24 (3)
O(1)	2285 (13)	2519 (9)	9817 (6)	160 (16)	75 (7)	34 (4)	28 (10)	−2 (6)	−13 (5)
O(2)	2931 (14)	1669 (8)	9028 (7)	161 (19)	71 (7)	36 (5)	26 (9)	−3 (8)	−1 (5)
O(3)	4086 (15)	1716 (11)	10088 (8)	149 (20)	113 (10)	51 (6)	25 (12)	−26 (9)	3 (6)
N(4)	3122 (15)	1961 (10)	9661 (8)	104 (19)	61 (8)	29 (5)	−10 (10)	12 (8)	11 (5)
O(5)	1627 (15)	4072 (8)	8899 (8)	166 (20)	54 (6)	59 (6)	−13 (9)	25 (9)	−7 (5)
O(6)	2956 (12)	3305 (8)	8346 (6)	130 (16)	62 (7)	37 (4)	−28 (8)	7 (7)	−9 (4)
O(7)	3581 (15)	4596 (9)	8568 (8)	193 (22)	60 (7)	68 (7)	−60 (10)	10 (10)	−1 (5)
N(8)	2736 (16)	4008 (9)	8605 (8)	128 (22)	45 (7)	39 (6)	−17 (10)	−13 (9)	1 (5)
O(9)	1405 (11)	1904 (7)	7624 (6)	127 (15)	55 (5)	25 (3)	12 (7)	20 (6)	−4 (3)
C(10)	2453 (19)	1729 (13)	7277 (10)	112 (24)	79 (11)	29 (6)	19 (1)	−2 (10)	−27 (7)
N(11)	3110 (16)	2324 (12)	6905 (9)	121 (20)	87 (10)	43 (6)	10 (13)	25 (9)	4 (7)
C(12)	2326 (28)	3102 (16)	6709 (10)	292 (46)	102 (15)	23 (6)	24 (21)	41 (14)	24 (8)
C(13)	4628 (22)	2409 (24)	6892 (14)	110 (25)	207 (31)	64 (10)	−4 (26)	31 (13)	44 (16)
N(14)	2917 (19)	911 (13)	7303 (10)	191 (28)	88 (12)	43 (7)	53 (15)	−18 (11)	−35 (7)
C(15)	2430 (32)	312 (16)	7808 (17)	304 (54)	63 (12)	89 (15)	−3 (21)	8 (23)	34 (11)
C(16)	3674 (32)	615 (22)	6658 (15)	289 (53)	166 (25)	55 (11)	120 (30)	17 (20)	−40 (14)
O(17)	276 (13)	3568 (8)	7714 (7)	130 (17)	54 (6)	50 (5)	−4 (8)	−10 (8)	6 (4)
N(18)	−1354 (15)	3111 (9)	7506 (7)	133 (21)	47 (7)	22 (4)	17 (10)	18 (8)	4 (4)
O(19)	−2202 (17)	3300 (10)	7004 (8)	227 (26)	81 (8)	53 (6)	18 (12)	−32 (11)	11 (6)
O(20)	−1484 (11)	2415 (7)	7835 (6)	133 (14)	51 (5)	37 (4)	4 (8)	5 (6)	2 (4)
O(21)	−199 (12)	1347 (7)	9038 (6)	108 (14)	54 (5)	33 (4)	−20 (7)	20 (6)	0 (4)
C(22)	−1301 (16)	951 (9)	9194 (8)	104 (20)	41 (7)	24 (5)	12 (9)	9 (8)	5 (5)
N(23)	−2190 (17)	591 (10)	8657 (9)	158 (25)	76 (9)	34 (6)	−47 (12)	−25 (10)	5 (6)
C(24)	−1658 (35)	478 (15)	7970 (11)	497 (73)	76 (13)	27 (7)	−110 (26)	10 (18)	−15 (8)
C(25)	−3758 (24)	583 (20)	8690 (15)	111 (29)	123 (19)	90 (15)	−33 (19)	−37 (17)	−11 (13)
N(26)	−1583 (16)	880 (10)	9866 (9)	144 (23)	53 (8)	46 (7)	−12 (10)	24 (10)	0 (6)
C(27)	−660 (32)	1380 (14)	10412 (12)	346 (56)	64 (11)	37 (8)	−1 (20)	−4 (17)	−1 (8)
C(28)	−2401 (27)	213 (16)	10138 (13)	240 (43)	99 (15)	56 (10)	−20 (20)	42 (17)	38 (10)
O(29)	−772 (11)	3186 (8)	9346 (6)	82 (13)	78 (7)	26 (4)	5 (7)	16 (6)	−10 (4)
C(30)	−1542 (19)	3415 (11)	9797 (9)	139 (26)	51 (8)	23 (5)	4 (11)	12 (9)	8 (5)
N(31)	−1018 (20)	3737 (10)	10450 (8)	225 (31)	56 (8)	23 (6)	33 (12)	15 (10)	3 (5)
C(32)	485 (23)	4013 (15)	10552 (10)	145 (31)	104 (14)	26 (6)	23 (17)	−18 (11)	−8 (8)
C(33)	−1711 (33)	3571 (19)	11107 (13)	361 (60)	120 (18)	38 (8)	80 (27)	61 (18)	12 (10)
N(34)	−2990 (15)	3398 (10)	9650 (8)	106 (20)	73 (9)	38 (6)	19 (11)	29 (9)	9 (6)
C(35)	−3628 (20)	2958 (15)	9001 (13)	93 (24)	94 (14)	58 (10)	−34 (14)	0 (12)	−15 (9)
C(36)	−4014 (26)	3946 (18)	9952 (13)	214 (39)	123 (18)	47 (9)	68 (22)	33 (15)	−26 (10)

and the non-hydrogen atoms from successive Fourier maps. The structure was refined by the full-matrix least-squares method, initially with isotropic temperature factors. In the final stages anisotropic thermal parameters were introduced together with a dispersion correction for Eu. The atomic scattering curves were taken from *International Tables for X-ray Crystallography*. The function minimized is $\sum w(F_o-F_c)^2$ with $w=(50\cdot0-F_o+0\cdot01F_o^2)^{-1}$. All 36 H atoms are in the methyl groups of the TMU's and the difference Fourier map did not give prominent positions for them; therefore, they were not included in the structure factor calculations. The refinement stopped at the point where the shifts in parameters were small compared to the standard deviations. The final R is 0·067 and weighted R, 0·085. The atomic parameters are listed in Table 1.* The numbering of the atoms is shown in Fig. 1.

Discussion

The structure consists of nine-coordinated Eu complexes. The Eu ion is attached to three symmetrically bidentate nitrates and three monodentate TMU's coordinated *via* their O atoms. The polyhedron of the Eu coordination sphere conforms to neither of the common geometries for a nine-coordinate configuration, *viz*. tricapped trigonal prismatic or monocapped square antiprismatic (Muetterties & Wright, 1967). Presumably the small 'bite' of the nitrates is primarily responsible for this feature. In this particular case the structure is best described in terms of a pseudo six-coordinate species in which each of the nitrates is considered as occupying a single coordination position (Bergman & Cotton, 1966). The geometry of this coordination polyhedron, consisting of the three urea O atoms and the three nitrate N atoms, is approximately octahedral. A stereo pair of the complex is shown

Table 2. *Bond lengths and angles*

Coordination around Eu (e.s.d.'s are 0·01 Å and 0·4°)

Eu–O(nitrate)	
–O(1)	2·50
–O(2)	2·54
–O(5)	2·54
–O(6)	2·46
–O(17)	2·50
–O(20)	2·52
Average	2·51
Eu–O(TMU's)	
–O(9)	2·34
–O(21)	2·35
–O(29)	2·30
Average	2·33

Angles centred on Eu	
Both oxygens from the same nitrate	
O(1)—Eu–O(2)	51
O(5)— –O(6)	50
O(17)– –O(20)	52
Oxygens of the TMU's	
O(9)—Eu–O(21)	90
O(21)– –O(29)	83
O(9)— –O(29)	154
O(TMU)–Eu–N(nitrate)	
O(9)—Eu–N(4)	99
O(21)– –N(4)	78
O(29)– –N(4)	104
O(9)— –N(8)	98
O(29)– –N(8)	97
O(21)– –N(8)	159
O(9)— –N(18)	75
O(21)– –N(18)	102
O(29)– –N(18)	82
N(nitrate)–Eu–N(nitrate)	
N(4)—Eu–N(8)	82
N(8)— –N(18)	98
N(4)— –N(18)	173

N–O bonds in nitrates (e.s.d.=0·02 Å)	
N(4)—O(1)	1·25
–O(2)	1·28
–O(3)$^{n.c.}$	1·22
N(8)—O(5)	1·24
–O(6)	1·25
–O(7)$^{n.c.}$	1·24
N(18)–O(17)	1·28
–O(19)$^{n.c.}$	1·21
–O(20)	1·29

O–N–O angles (e.s.d.=0·8°)	
O(1)—N–O(2)^{c}	117
O(2)— –O(3)	122
O(3)— –O(1)	122
O(5)— –O(6)^{c}	116
O(6)— –O(7)	122
O(7)— –O(5)	123
O(17)– –O(19)	122
O(19)– –O(20)	120
O(20)– –O(17)^{c}	117

n.c. = non-coordinated bond; c = angle facing Eu.

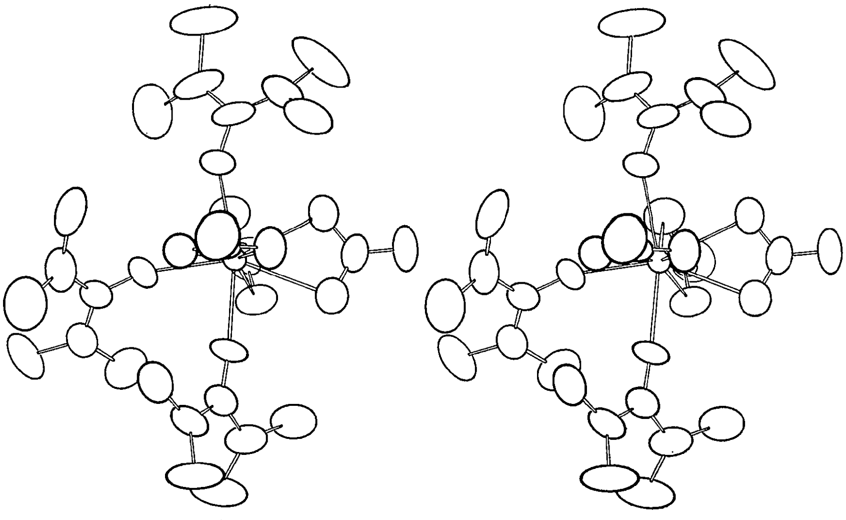

Fig. 2. A stereo pair of structure of $Eu(TMU)_3(NO_3)_3$.

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* The structure factors and a table of the interatomic distances of the TMU's have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31269 (12 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

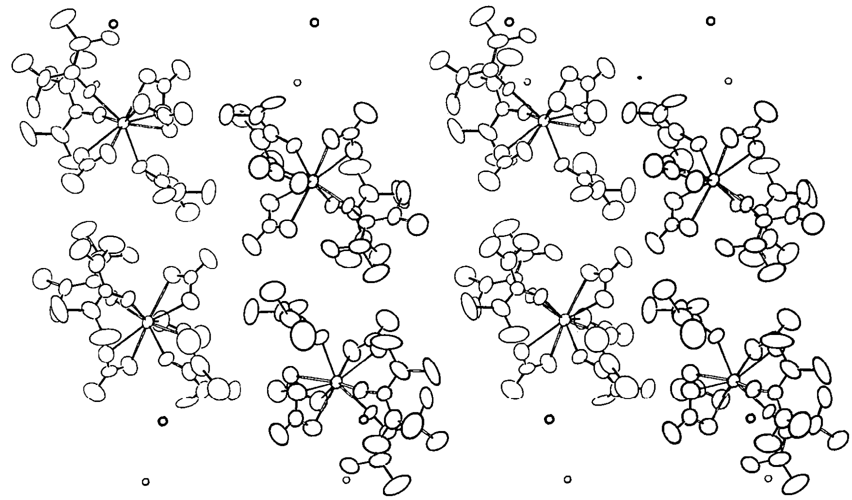

Fig. 3. Packing of the $Eu(TMU)_3(NO_3)_3$ molecules in the monoclinic cell, a stereo pair.

in Fig. 2. One can see that two nitrates occupy the apices of the octahedron and three TMU's and the other nitrate form a tetrahedrally distorted equatorial plane. The structures of several nitrato complexes of lanthanoids are known. Among these, the pentanitrato complexes of Ce^{III} (Al-Karaghouli & Wood, 1973) and Ho^{III} ions (Toogood & Chieh, 1975) can be described as trigonal bipyramidal. In the title compound three monodentate TMU's have taken the place of two nitrates of the pentanitrato complexes to give rise to a distorted octahedral arrangement of the ligands. The hexanitratocerate(IV), $Ce(NO_3)_6{}^-$, is octahedral with approximate symmetry T_h, (Beineke & Delgaudio, 1968). Owing to the nonequivalence of the ligands, the complex $Eu(TMU)_3(NO_3)_3$ is rather distorted from the 'ideal' geometrical configuration. The metal to coordinated oxygen distances fall into two categories. The nitrate O atoms lie between 2·46 and 2·54 Å (average 2·51 Å) from Eu, whereas the urea O atoms are significantly closer (average 2·33 Å). The bond lengths and angles are listed in Table 2.

Bidentate nitrate groups have been considered as symmetrically bonded within each $\mathrm{M}\overset{\mathrm{O}}{\underset{\mathrm{O}}{<\,>}}\mathrm{N{-}O}$ grouping if the M–O distances differ by less than 0·2 Å (Addison, Logan, Wallwork & Garner, 1971); in the present study the largest difference is 0·08 Å. Within the $\mathrm{M}\overset{\mathrm{O}}{\underset{\mathrm{O}}{<\,>}}\mathrm{N{-}O}$ groupings, the variance of the N–O(bonded) distances is less than 0·03 Å. The N–O (nonbonded) distance in each grouping is slightly smaller than the average of the other two. Bond angles within the $\mathrm{M}\overset{\mathrm{O}}{\underset{\mathrm{O}}{<\,>}}\mathrm{N{-}O}$ groupings are similar to those in the pentanitratolanthanates (Al-Karaghouli & Wood 1973; Toogood & Chieh, 1975) and compare favourably with other symmetrically bidentate nitrato compounds (Addison *et al.*, 1971).

The manner in which the TMU's are bonded is similar to that found in hexakis(urea)titanium(III) iodide (Davis & Wood, 1970). No crystallographic data for TMU or its complexes are available in the literature, and so a detailed comparison of the bond angles and lengths of the TMU's of the present work seems inappropriate. However, these values seem normal although the angles C–N–C of the dimethylamine groups are closer to 120° than tetrahedral. A stereo pair of the packing diagram is shown in Fig. 3. It is a typical molecular structure with no significant intermolecular interactions.

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References

Addison, C. C., Logan, N., Wallwork, S. C. & Garner, C. D. (1971). *Quart. Rev.* **25**, 289–322.

Al-Karaghouli, A. R. & Wood, J. S. (1968). *J. Amer. Chem. Soc.* **90**, 6548–6549.

Al-Karaghouli, A. R. & Wood, J. S. (1973). *J. Chem. Soc. Dalton*, pp. 2318–2321.

Beineke, T. A. & Delgaudio, J. (1968). *Inorg. Chem.* **7**, 715–721.

Bergman, J. A. & Cotton, F. A. (1966). *Inorg. Chem.* **5**, 1208–1213.

Burgess, C. M. (1970). Ph. D. Thesis, Univ. of Waterloo, Waterloo, Ontario, Canada.

Davis, P. H. & Wood, J. S. (1970). *Inorg. Chem.* **9**, 1111–1116.

Giesbrecht, E. & Kawashita, M. (1970). *J. Inorg. Nucl. Chem.* **32**, 2461–2464.

Muetterties, E. L. & Wright, C. M. (1967). *Quart. Rev.* **21**, 109–194.

Toogood, G. E. & Chieh, C. (1975). *Canad. J. Chem.* **53**, 831–835.

Vicentini, G. & Najjar, R. (1970). *Inorg. Nucl. Chem. Lett.* **6**, 571–577.